Deep Ocean Methane Clathrates: An Important New Source for Energy?

by

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Abstract

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Abstract

Methane clathrates, commonly called methane hydrates, are formed when a methane molecule is trapped inside of a water cage-like structure. The hydrate structure is not thermodynamically stable without a guest, such as methane. Methane clathrate formation can occur in cold shallow permafrost regions (< 250 m) or in deep ocean water sediment (>250 m). The conditions necessary for formation are low temperatures (<27 ºC), high pressure (> 0.6 MPa), sedimentation greater than 1 cm/kr, and organic content of approximately 1%. Methane, produced by anaerobic bacteria, travels up through sediment and enters into the hydrate structure producing three hydrate structures. Of the three hydrate structures (I, II, & H), structure I proves to be the most naturally occurring. Methane located in clathrate hydrates provides a rich source of methane useful for energy consumption of industrialized nations. Investigations have been made by scientists in recent years to understand their potential use in energy production. Deep ocean wells have already been drilled in Canada and Japan to harness the energy potential. This paper provides a review of the chemical and physical properties of methane clathrates and their potential as an energy resource.

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Introduction

Deep beneath the oceans' surface exists a vast natural resource full of potential. Methane clathrates, also known as methane hydrates or methane ice, are structures composed of a solid form of water and a large amount of methane within its crystal structure, a clathrate hydrate. A clathrate, from the Latin clatraus, meaning bars or a lattice, contains one type of molecule trapping a second type of molecule. A specific type of clathrate is called a clathrate hydrate, which contains water. Methane clathrates are structures believed to form from migration of gas along geological faults or organic sediment, which hits cold sea water and crystallizes from the depths. First discovered in 1778, by Joseph Priestley, gas hydrates are typically associated with Michael Faraday's boss, Sir Humphrey Davy.[1] In 1810, Davy discovered that a solid could be formed when an aqueous solution of chlorine was cooled below 9.0 ℃ to form clathrate hydrates.[2]

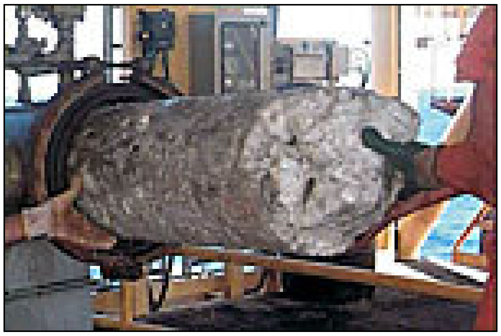


Figure 1: A gas-hydrate plug that is being removed from a gas production line.[1]

In 1934, the Michigan oil and gas industry noticed that transportation pipes were being clogged by the formation of clathrate hydrates (Figure 1) of natural gas under cold conditions.[1] These cage-like structures of water surrounded by methane proved to be problematic. Once a hydrate plug has formed, it can take weeks or even months to dissociate it safely. Ever since 1934, clathrate hydrates, specifically, methane clathrates, have gained attention in the scientific community. Methane clathrates can occur within 2000 m of the earth surface and typically form along the gas-liquid interface. They can consist of a variety of gases within the cage-like structure of ice including ethane, propane, nitrogen, among others. Temperature and pressure limit their stability, thus, they are found in the cold earth's permafrost (eg North Slope of Alaska) or along continental shelves in the deep oceans (eg the Middle America Trench off Costa Rica; Japan Sea; Gulf of Mexico; Crimea, Ukraine, Black Sea in Russia; Mackenzie Delta in Canada).[1]

Chemical and petroleum engineers, chemists, and earth/space environmental scientists have been studying methane clathrates not only because it is a fuel source, but because of the potential of a large scale release of methane. Methane is a known greenhouse gas, with the potential to cause warming of the atmosphere.[3] Studying the physical properties is essential because of the possible utilization of man-made clathrate hydrates for natural gas storage and transportation, cool energy storage, hydrogen storage, carbon dioxide sequestration, fuel/flue gas separation, and seawater desalination.[4] Many positive benefits and potential dangers have yet to be discovered. Many ask the question; are the methane clathrates safe energy?

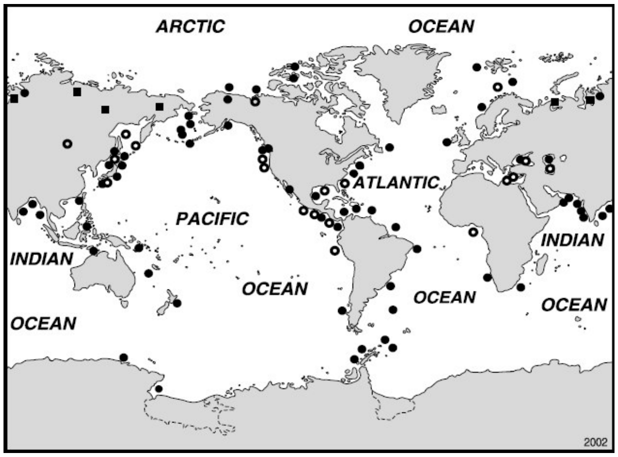


Figure 2: Worldwide Locations of Methane Clathrates in 2002 (Source 4)

Because of their instability, changes in temperature or pressure have released the methane into the atmosphere, causing widespread concern. Methane was first detected in the atmosphere in 1948. The first survey in 1971 (The Study of Man's Impact on Climate in Stockholm) on human modification on climate stated that "Methane has no direct effects on the climate or the biosphere [and] it is considered to be of no importance".[5] However, Wei-Chyung Wang at NASA GISS (Goddard Institute for Space Studies), first indicated (through the use of infrared spectroscopy) that methane was a significant greenhouse gas.[5] Over the last 200 years, methane concentration in the atmosphere have more than doubled (from 320 ppb to 620 ppb).[7, 8] Leaks from mining and natural gas pipelines, landfills, increased irrigation (wetlands), and increased livestock have led to the increase. A new contributor, methane clathrates, has been discovered and has been a cause for concern. Estimates of the quantity of methane clathrates globally (see Figure 2 and 3) range from 5,000 to 12,000 Gigatons of carbon.[9] This amount is double current estimates of existing fossil fuel sources. Therefore, the U.S., Canada, Russia, India, and Japan have been highly interested in harnessing this fuel source.[9] As of 2001, geophysical and geochemical methods indicate that there are 77 locations where methane clathrates are found.

This paper will describe and review the properties of methane clathrates, their use as an energy source, and their possible role in climate change. The chemistry behind the formation and dissociation will be given as well as a structural study of the most thermodynamically favorable methane clathrate structures. Past and present retrieval processes will be analyzed as well as the environmental concerns with methane's reactions in the atmosphere.

Methane Overview

A cursory overview of methane oxidation is helpful to understanding methane clathrate hydrates. Methane is a green house gas, and its primary oxidative product is carbon dioxide (CO_2). Methane is the main component of "natural gas", which contains between 70 and 95% methane, often over 90%.[10] Natural gas originates in the same way as crude oil, by the anaerobic decomposition of microscopic sea animals under the pressure of layers of silt and mud over a period of millions of years.[10] The combustion of methane is a very exothermic reaction ($\Delta H = -891$ kJ/mol). Therefore, methane is widely used as a fuel, not least because the volatile and non-toxic products make it "clean", though one product, carbon dioxide, is a "greenhouse gas".[10] The reaction shows this combustion below:

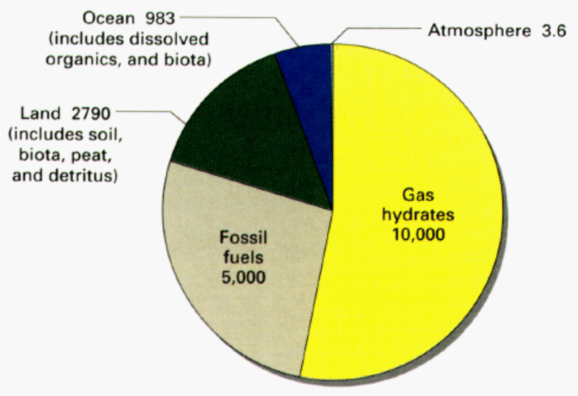


Figure 3: Organic Carbon on Earth (excluding dispersed carbon in rocks and sediment)
(Source USGS http://marine.usgs.gov/fact-sheets/gas-hydrates/gas-hydrates-3.gif)

$$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g) \qquad \textbf{(1)}$$

Incomplete combustion of methane yields carbon (soot) or toxic carbon monoxide. Its reaction with steam in the presence of a hot nickel catalyst (below) affords the mixture of CO and H_2 known as "synthesis gas", which is widely used to make chemicals such as hydrogen, methanol and acetic acid (see equation 2).

$$CH_4\,(g) + H_2O\,(g) \xrightarrow{Ni} CO\,(g) + 3H_2\,(g) \qquad \textbf{(2)}$$

Methane can be made in the laboratory by a variety of reactions, including the action of water and aluminum carbide (see equation 3).

$$Al_4C_3\,(s) + 12H_2O\,(l) \longrightarrow 3CH_4\,(g) + 4Al(OH)_3\,(s) \qquad \textbf{(3)}$$

Methane can also be made by heating a mixture of solid sodium hydroxide with sodium acetate (see equation 4).

$$CH_3COONa\,(s) + NaOH\,(s) \rightarrow CH_4\,(g) + Na_2CO_3\,(s) \qquad \textbf{(4)}$$

Formation

Methane clathrate formation is considered in terms of water depth, temperature, and O_2 concentration.[11] There are three places to find methane clathrates: oceanic sediment of continental slopes and rises greater than 300 m (ocean pressure is approximately 0.3 MPa) , deep-water sediment of inland lakes and seas greater than 300 m (where the pressure is approximately 0.3 MPa, and polar sediment of both continents and continental shelves.[6] When the pressure is high (greater than 0.6 MPa) and temperature is low (less than 300 K), water can freeze and incorporate a fraction of produced methane.[12] (1 MPa = 1×10^6 Pascals, 0.6 MPa is approximately equal to six times greater than the atmospheric pressure). Therefore, depending on the conditions (See Figure 4), clathrate hydrates can exist at temperatures below or above the normal freezing point of water. In shallow waters, clathrates most likely do not form below 600 m due to warm sea temperatures. However, in the Arctic Ocean, clathrates form in only 250 m because of cold sea temperatures. In deeper waters, methane clathrates are commonly found in depths of 1000 to 3000 m.[11] At these depths, these clathrates are located in the top few hundred meters of marine sediment.

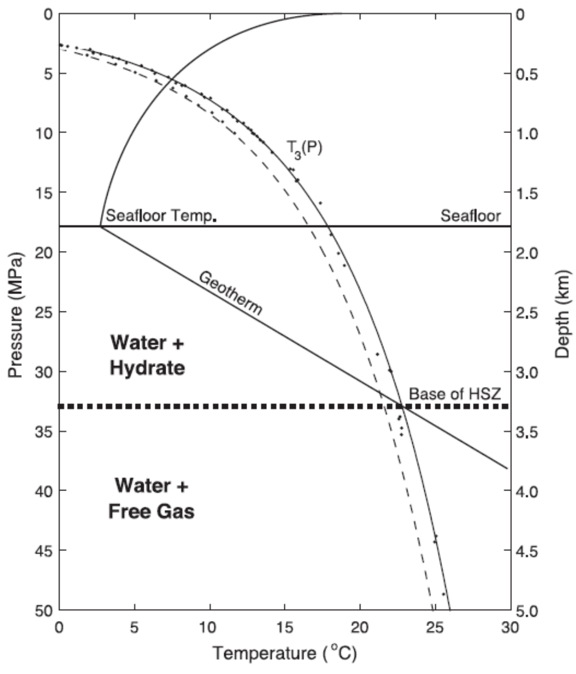


Figure 4: Stability Graph of Methane Clathrates (T_3P) versus Temperature, Pressure, and Depth.[13]

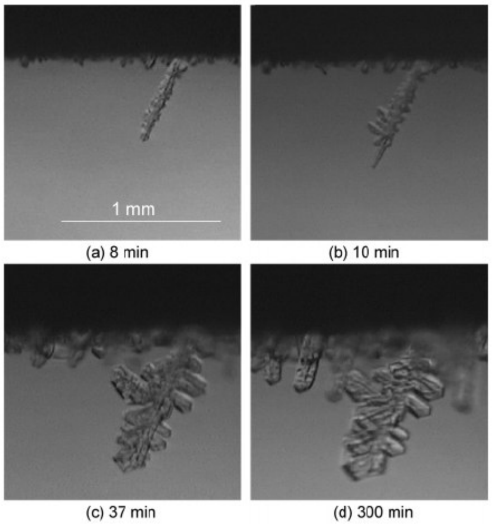
A basic understanding of methane clathrate formation reveals that organic matter falls from the surface to the bottom of the ocean and is often called 'carbon rain'. Necessary for methane production, this organic matter is typically located off the coast of continents. This convenient location allows researchers to study and extract samples from the clathrates. After the carbon rain (organic matter) is buried below the sulfate-reducing zone, methanogens (several varieties of anaerobic bacteria) convert a fraction of this carbon to methane.[11]

Anaerobic decomposition converts cellulose ($C_nH_20_m$) into methane and carbon dioxide (see equation 5).

$$2\ C_nH_20_m\ (s) \rightarrow \ldots \rightarrow CH_4\ (g) + CO_2\ (g) \qquad \textbf{(5)}$$

After the methanogenic bacteria in a pH of 6-8 convert organic matter to methane, the methane saturates the pore waters. Despite decades of research, methane clathrate formation is still not very clear.[7, 11] Pictures from methane clathrate laboratory formation reveal hydrate crystals growing at the methane gas-water interface (See Figure 5 and 6).

Measuring the formation of clathrates can be difficult because of the many factors that are involved. Formation is typically slow because of the limited supply of the methanogenic bacteria which breaks down the organic matter.[14] The formation also depends on the concentration and distribution of methane gas dissolved in the water that fills the pores between sediment grains.[1, 15] Gering (2003), used a growth profile simulation covering 20 million years for methane hydrates and methane free gas, recorded in a vertical sediment column. He found that there are fairly specific conditions for the formation of clathrates. Lab results and field tests of existing clathrates in the oceans have confirmed that sedimentation must be high (>1cm/kyr) (1 kyr = 1,000 years), organic content (>1%) must be present, and aerobic bacterial activity must not be able to oxidize all of the organic carbon matter (buried within the mineral sediments) needed for the formation of methane clathrates.[17]



(a) 8 min (b) 10 min (c) 37 min (d) 300 min

Figure 5: Videographs of the growth of methane hydrate crystals, along the methane-water interface, at a Pressure = 8.2 MPa and Temperature = 273.7 K. Time is indicated for the conditions listed.[16]

Gering (2003) further described these conditions, noting that the amount of hydrate formation is directly related to compaction/sedimentation rates, liquid advection rates, seafloor depth, and the geothermal gradient.[18] The formation rate; however, can be also difficult to measure because of the fluctuation in the carbon-conversion efficiency of methanogens.[14] In addition, despite anaerobic oxidation of methane being a widespread and geochemically well known process, the specific microbes are not known because they are difficult to isolate in cultures. Nonetheless, Orphan found that microbes critically impact global geochemical cycles.[19]

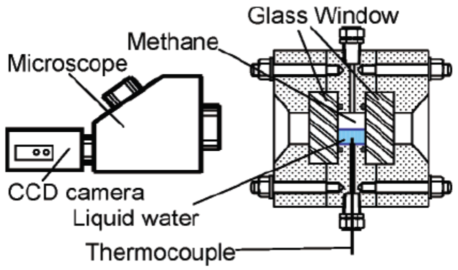


Figure 6: Experimental apparatus to produce methane clathrates in the laboratory.[16]

Dissociation

Methane clathrates, as part of the global carbon cycle, can change with varying environmental conditions. Methane can dissociate and leave the clathrates in sediment in two possible forms: dissolved gas and bubbles. Dissociation which occurs through a change in temperature and pressure are usually considered the largest threats to methane clathrate stability. Methane clathrates dissociates rapidly under laboratory conditions because the temperature and pressure needed to maintain their stability is not found under standard conditions. In their natural environment, methane clathrates also dissociate, but at a slower rate. Buffett and Archer (2004) indicate that changes in sea level have very little effect on the overall inventory of methane clathrates but a change in ocean temperature or oxidation could have a great effect on the dissociation of methane clathrates.

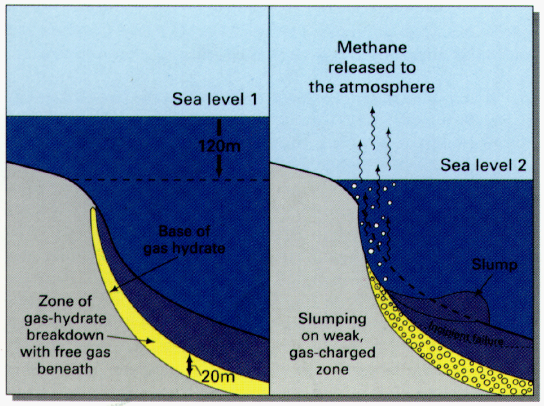


Figure 7: Changes in Sea Level Affecting Deep Ocean Methane Clathrates
(Source USGS-http://marine.usgs.gov/fact-sheets/gas-hydrates/gas-hydrates-6.gif)

A change in ocean levels due to natural environmental changes could have two effects: If the ocean level drops (See Figure 7), methane clathrates near the surface of the water would experience a greater temperature, thus decreasing their stability and potentially causing their dissociation. If the ocean levels increase (See Figure 8), methane clathrates trapped under cold permafrost would slowly be covered by warm ocean water, releasing methane into the atmosphere. Kvenvolden estimated that the average thickness of the stability zone was around 400 m.[11] However, the sea level has only a small effect on clathrate inventory. A 1 m drop in sea level reduces the thickness of the methane clathrate stability zone by less than 0.1 m in most locations.

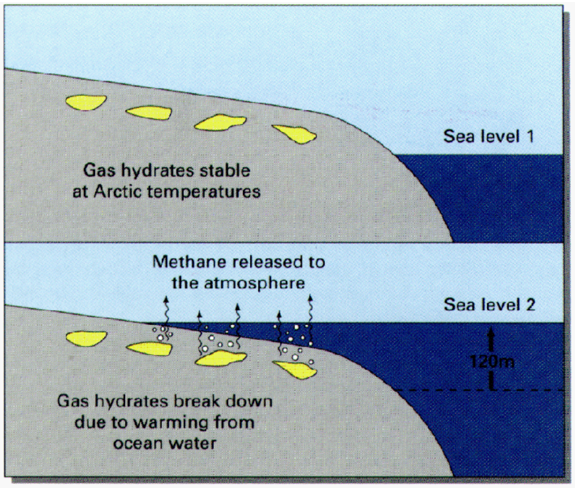


Figure 8: Changes in Temperature from Varying Sea Levels Affecting Shallow Permafrost Methane Clathrates
(Source USGS-http://marine.usgs.gov/fact-sheets/gas-hydrates/gas-hydrates-5.gif)

An increase in ocean temperatures could cause methane clathrate in the ocean to dissociate as well. Buffett and Archer (2004) predicted through a theoretical model that methane inventory will decrease 85% in response to 3 ºC of ocean warming (See Figure 9). This 3 ºC change in deep ocean water temperatures would not occur in normal environmental conditions. However, evidence to suggest two to three degree changes (in Celsius) in deep ocean water and changes in large atmospheric temperatures have occurred during interglacial periods.[20]

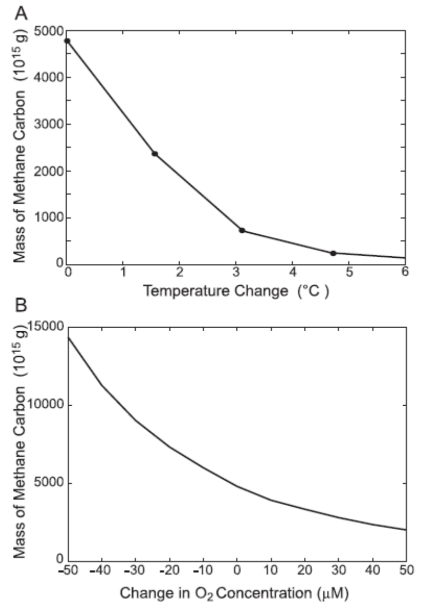


Figure 9: A: The mass of methane carbon is inversely proportional to the temperature change of the ocean.
B: The mass of methane carbon is inversely proportional to the oxygen concentration. (Source 3)

The most common form of methane clathrate dissociation is from methane oxidation, which varies widely with the environmental conditions in the sea.[21] In the ocean depths, methane gas is typically unsaturated (the concentration of methane is not maximized in the ocean) in the water because of the ongoing oxidation process.[21] Methane oxidation is tied directly to the oxygen concentration, which is most likely regulated by the burial of organic matter.[14] The lower the oxygen concentration and the greater the burial of organic matter, the greater the formation of methane clathrates. In addition, changes in oxygen concentrations can strongly affect the preservation of carbon in sediment (See Figure 9). As a result, Buffett (2004) notes that a “modest” 40 microMolar decrease in the oxygen concentration can increase methane clathrate inventories by a factor of two (because of the lack of methane oxidation).[11]

Microbial anaerobic bacteria also limit the production of methane due to oxidation in the surface sediment.[6] It is estimated that microorganisms living in anoxic marine sediments consume more than 80% of the methane produced in the world’s oceans.[19]. This consumption limits the amount of methane that enters the water column above the methane clathrates. The methane, typically in the form of bubbles, remains trapped in the sediments as the clathrate dissociates. Methane oxidation continues when some of the methane dissolves into the surrounding pore water and is transported toward the seafloor by diffusion and fluid flow. Then, the methane escapes into the water column and is oxidized by aerobic microbial bacteria reacting with sulfate, followed by sulfide precipitation. Methane carbon, in the form of HCO_3- causes precipitation of $CaCO_3$, which remains stable in the sediment column or is released in the form of dissolved CO_2.[13] More will be discussed concerning the methane that is released into Earth’s atmosphere.

WHEW! GAS PRODUCING BACTERIA USED FOR GOBAR GAS

Carbon ‘rains’ down into the deep oceans from coastal sources of organic material. Eventually, as the material falls to the depths of the oceans, it accumulates to produce hundreds of meters of thick rich sediment, which provides an ample source of food for the bacteria in the production of methane clathrates. The bacteria, called methanogens (Figure 10), have been discovered at the bottom of a three kilometer ice core in Greenland and in soil samples in seemingly dry deserts.

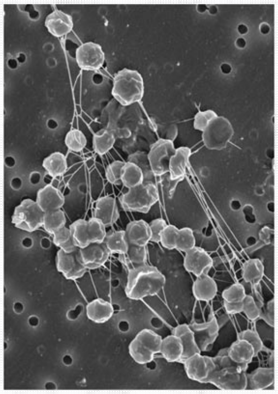


Figure 10: Methanogens Under a High Powered Microscope (Source NASA)

There are many metabolically interdependent bacteria found (more than 50 species) in rich sediment. The carbon dioxide and hydrogen in the sediment provides a source of energy for the bacteria. Methanogens, use some of the carbon dioxide to react with hydrogen, producing methane. Methanogens cannot live in the presence of oxygen, thus, they are commonly called anaerobes. They can be found in wetlands, in the gut of animals and humans, and in deep water ocean sediment.

Methanogens not only produce methane involved in clathrates but also in production of fuel, commonly called bio-gas. Energy is extracted out of the gas produced from the anaerobic digestion in many substances including; trash, animal feces, and sludge from sewage treatment plants. Bio-gas is made up of 60-70 percent methane, 30-40 percent carbon dioxide, and many other trace gases such as ammonia and hydrogen sulfide. The bacteria rely upon a constant temperature, pH, and a source of organic matter to produce the bio-gas.


Figure 11: Gobar gas plant
(Source www.motherearth.org)

Harvesting bio-gas as an energy source can be done in an enclosed container, called a digester. After the breakdown the organic matter by acid-forming bacteria, the methanogens break down the organic matter even further producing methane. This can be a valuable source of energy, specifically for third world countries. Gobar gas, a type of bio-gas produced from the dung of cow manure is being used all over the world. Gobar, hindi for ‘cow dung’, is collected and stored in an enclosed container. This method was first introduced in 1939 by the Indian Agricultural Research Institute.[22] A cattle dung digester was designed and built and the process was subsequently studied.

The Gobar Gas Research Station in India has been producing methane gas from cow manure since 1960 (Figure 11). An airtight tank, called the digester tank, is filled with a slurry of organic matter. Bacteria break down the material in a two part process. The bio gas generated is used to cook food, light homes, and heat homes in India. Other benefits include time/labor saving in cooking and fuel collection, a free organic fertilizer, and better health/sanitation through the removal of cattle dung from open spaces. The use of methanogens, in naturally occurring cow dung has proven to be effective for rural inhabitants of India.[22]

Case study of Methane Clathrate Formation/Dissociation

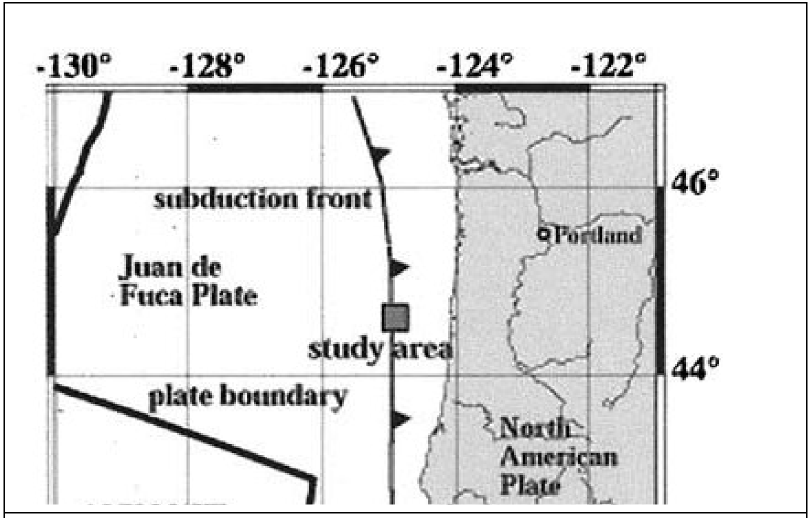


Figure 12: The study area of the "hydrate ridge" off the coast of Oregon.[23]

For the past decade, the hydrate ridge (See Figure 12) study area off the coast of Oregon has undergone research with regard to methane clathrates. The Jan de Fuca continental plate is subducted beneath the continental North American Plate. The focus of the Ocean Drilling Project has been gas hydrate research.[23] Core drilling over the last decade revealed a lateral piece of gas hydrate approximately 10 cm thick. The depth of the drilling was around 750m below the sea surface.

Similar to research completed by Hyndman and Davis (1993), chlorinity levels of the pore fluid samples above the methane clathrates were used to determine the rate of methane clathrate formation. Methane bubbles rise in sediment and enter into the solid hydrate structure. The hydrate 'cage-like' structure is thermodynamically unstable without a molecule.[26] The non-polar methane molecule provides the stability necessary for the clathrate hydrate to exist (the polar chloride ion would not provide stability in the hydrate structure). While methane rises in the sediment, chloride ions (See Figure 13) (which already dwell in the water) are displaced by the methane clathrate formation.[23] The chlorinity of the pore fluid above the clathrate provides an approximate measure of the amount of hydrate that was present before methane clathrate sample recovery.[24] Hyndman and Davis' (1993) research found that the methane hydrate formation was not a continuous process. They estimated that the rate of methane hydrate formation, based on the concentration of the methane bubbles, should be 30-40 cm in depth within 4-10 weeks. However, the layer discovered was only 10 cm thick. Haeckel (2004), concluded that methane hydrate deposits are constantly being formed and dissociated where they meet the seafloor due to microorganisms, which use seawater sulfate and oxygen to oxidize dissolved methane. This process of formation and dissociation is ongoing.

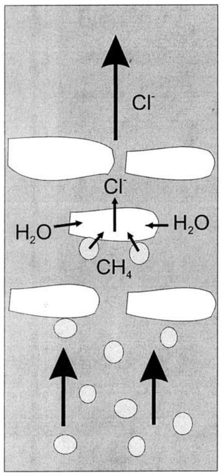


Figure 13: Conceptual model of methane clathrate formation as methane bubbles rise from ocean sediment, replacing chloride ions in water hydrates.[23]

Structural Study of Methane Hydrate

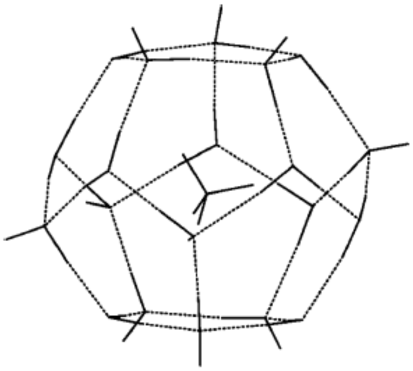


Figure 14: The optimized structure of a methane ‘guest’ inside of a hydrate ‘host’.[26]

A structural study of methane hydrates reveals much information about the microscopic interactions that keeps methane clathrates together. Methane clathrates are typically mixed with soil in the arctic permafrost or with marine sediment; therefore the properties of methane clathrates are difficult to obtain.[25] Methane clathrates are considered to be inclusion compounds, which consist of a host molecule and a guest (See Figure 14). Methane clathrates are composed of many water molecules (the host) that surround the methane molecule (the guest). The ‘host’ water cavity cage-like structure is between 780 and 920 pm in diameter (1 pm = 1×10^{12} m). As a ‘guest’ molecule, methane has a diameter of 436 pm.[7, 26] The host water lattice traps the guest methane molecule within the ice cages in a 1:5.75 ratio (moles of methane to moles of water). This ratio can be determined from the combination of methane clathrate ice cages (called Structure I), which contains 46 water molecules with up to 8 molecules of methane. Methane is free to rotate within the ice cages. Other molecules can be trapped, but methane is the most abundant form of natural clathrate hydrate. The ice cages are not large enough to fit large alkane molecules but can contain trace amounts of ethane and carbon dioxide among the methane clathrate.[6]

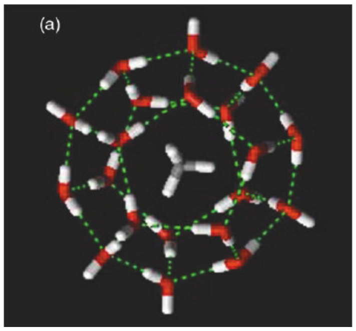


Figure 15: A pentagon dodecahedron hydrate with methane in the middle and 20 water molecules forming the cage-like structure.[27]

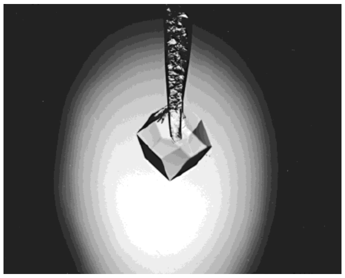


Figure 16: Single crystal hydrate grown from the melt.[12]

Due to the non-polar nature of methane, there is no bond chemically to the water, but only weak van der Waals forces.[1] In contrast, the lattice of water molecules is held together due to the hydrogen bonds of water and is further stabilized by intermolecular forces with the trapped solutes. As a result, methane clathrates are 20 times stronger than pure water at the same conditions of temperature and strain rate.[25] English and Macelroy (2003) discovered through simulations that the empty lattices of clathrate hydrates are thermodynamically unstable. In nature, typically 90% of the cage-like structures are occupied by methane to provide the stabilization necessary.[26] Methane clathrate decomposition was observed in laboratory conditions when less than 40% of the ice cages were unoccupied.[4] Given the wide values of density of methane clathrates (between 0.8-1.2 g/cm^3), an average liter of methane clathrate solid under high pressure would contain 168 liters of methane gas at standard temperature and pressure (STP). In comparison, approximately one liter of methane solid would contain approximately 1000 liters of methane gas at STP.

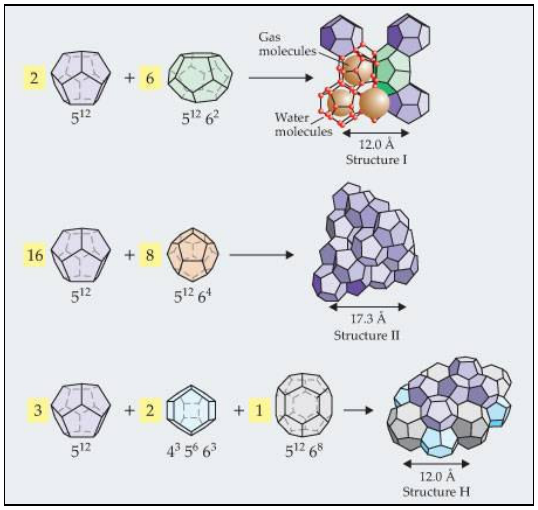


Figure 17: Complex structures of methane clathrates forming from their simple clathrate structure.[1]

There are three types of structures that methane clathrates form; sI, sII, and H. Structure I clathrate hydrates contain guests (methane, xenon, argon, krypton, nitrogen, and carbon dioxide) with a diameter of 400-550 pm, structure II contain guests (propane, isobutene) with a diameter of 600-700 pm, and structure H with larger guests (methane + neohexane, methane + cycloheptane) with a diameter larger than700 pm.[7] X-ray diffraction reveals that the most naturally occurring methane clathrates are sI structures because of methane's diameter of 436 pm.[7, 26] sI structures are called the 5^{12} cage. The 5^{12} cage is a pentagonal dodecahedron (See Figure 13). This is a polygon consisting of twelve pentagonal faces, which can fit one guest molecule.[2] The pentagonal dodecahedrons are typically bonded by their faces to create a larger series of linked cages. If 6 of the 5^{12} cages are linked together, a structure I takes form.

Methane Clathrate Structure Information

Hydrate Crystal Structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$	5^{12}	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
# Cavities / unit cell	2	6	16	8	3	2	1
Average cavity radius (pm)	395	433	391	473	391	406	571
Coordination number*	20	24	20	28	20	20	36
# waters / unit cell	46		136		34		

**Number of oxygens at the periphery of each cavity*
$5^{12}6^{4}$ – indicates 12 pentagonal and four hexagonal sides to a structure.

Figure 18: Methane Clathrate Structure Information for the Hydrate Crystal Structures I, II, and H. (Adapted from Sloan, 2003)

Structure I, II, and H characteristics are drawn and listed in the Figures 17 and 18.[7] Each cage-like structure can transform into different orientations according to the pressure on the clathrate.[1] As noted before, the pressure and temperature greatly affect the clathrate stability and percent occupancy of the methane.[11] Full methane occupancies in both small and medium clathrates cages are preferred at higher pressures.[4] In all three structures (I,II, & III), there is usually only one guest molecule in a cage. At high pressure and temperature conditions, there can be more than one molecule in a cage.

Global Carbon Cycle

Carbon fluxes from marine sediment have varied greatly in the geological record (See Figure 19). Many models are used to estimate the amount of carbon in fossil fuels and in methane clathrates. Geochemical and geophysical methods, such as sonic waves, are used to detect ocean hydrate deposits, but quantifying these deposits can be inaccurate.[12] The most common method to determine the amount of methane clathrates is through deep-ocean drilling or Bottom Simulating Reflector (BSR). BSR is a seismic reflection survey that marks a transition in the velocity of reflected sound waves as they pass though icy gas hydrates to sediments below that contain “free” gas. The methane reserves are in the form of clathrates and bubbles. The present day model of Archer and Buffett (2005) predicts 3,000 Gt of carbon in clathrates and another 2,000 Gt trapped as methane bubbles in underlying sediment. As a whole, literature sources indicates that the methane clathrate inventory in the arctic permafrost and oceans is between 3,000 and 15,000 Giga tons (1 Gt = 10^9 t).[11, 28, 29] No estimate has been made in the Antarctic permafrost yet. With an average estimate of 10,000 Gt, the total amount of methane is twice the amount of current fossil fuel reserves (oil, coal, and natural gas consist of a reserve of approximately 5,000 Gt) .[6, 29] Other mechanistic models can provide the distribution of methane clathrate in marine sediments.[11]

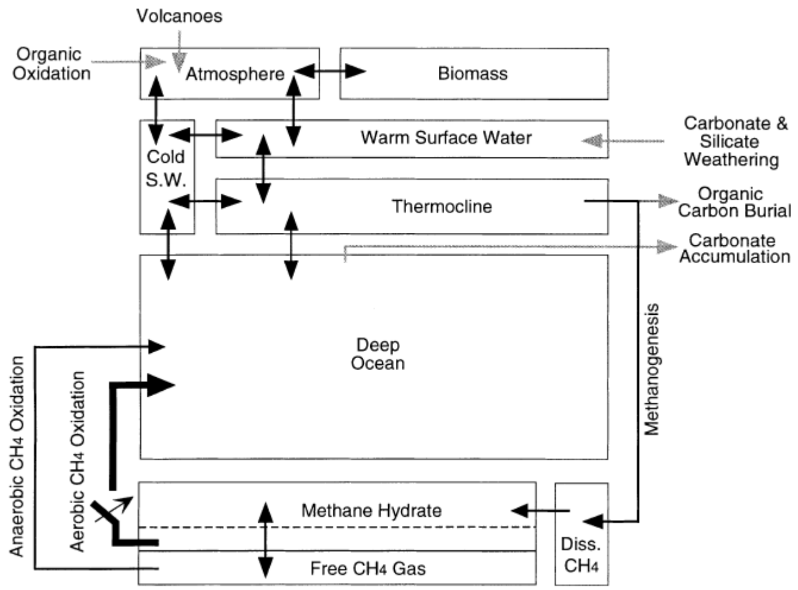


Figure 19: Global Carbon Cycle.[6]

Used as a Energy Source

Methane clathrates have been highly studied recently because of three main issues surrounding them; their use as a potential energy resource, their possible contribution to global climate change, and their potential danger in causing submarine geohazards. First, their potential development as an energy resource is not likely in the near future because of "various geological constraints and difficult technological problems".[30] These problems are still being investigated; specifically the rates of gas hydrate dissociation and the rates of release and destruction. Currently research is primarily being driven by the high fuel costs and because many methane clathrates exist in shallow waters. Existing natural gas reserves exist and are readily available. Therefore, free market factors will likely determine whether collecting methane from clathrates is economically wise

Recovery of methane from clathrates as an energy source can be traced back several decades. The USSR tried to recover gas hydrates, although unsuccessful, from permafrost reservoirs in the 1960's and 1970's.[9] The Messoyakha field in Siberia (located 300-700 m below the earth's surface) was explored in the 1970's and the Mallik well was drilled in Canada in 2002.[1] As a result of the many past successes and discoveries of methane clathrates, Japan, India, and the United States have launched national projects to examine the potential of gas hydrates.[31] In the United States, projects like the "Ocean Drilling Program" on Blake Ridge off the coast of Charleston, N.C., has provided valuable opportunities for research.[32] One day methane hydrates could produce gas that could burn cleanly, cause fewer pollution problems, and produce less carbon dioxide. Figure 20 shows the combustion general reactions of methane and gasoline and the amount of carbon dioxide byproducts. For every one mole of carbon dioxide produced in methane, 890.4 kJ/mol of energy are produced (see equation 6). For every one mole of carbon dioxide produced in gasoline, 634.25 kJ/mol of energy are produced (see equation 7).

Combustion of Methane:

$$CH_4(g) + 2\,O_2(g) \xrightarrow{\Delta} CO_2(g) + 2\,H_2O(l), \quad \Delta H = -\,890.4\ \text{kJ/mol} \qquad \textbf{(6)}$$

Combustion of Gasoline:

$$C_8H_{18}(l) + 12.5O_2(g) \xrightarrow{\Delta} 8CO_2(g) + 9H_2O(l), \quad \Delta H = -\,5074\ \text{kJ/mol} \qquad \textbf{(7)}$$

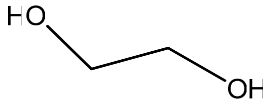
Figure 20 : Combustion reactions of methane and gasoline.[33]

Methane composes 4% by volume of a clathrate, but when multiplied by the total inventory worldwide, Sloan (2003) estimates that the entire hydrate reserves would be sufficient to supply the USA for 600 years at the current energy usage. However, many recovery problems still exist.

Currently there are many problems in recovering methane for energy. It is estimated that approximately 70% of the total gas reserve is either too far from existing pipelines or not in a large enough quantity to economically collect the methane gas.[7] Methane clathrates would contain a large volume of water and sediment that would make it difficult to move to collection stations. In addition, an infrastructure for collection and transportation would have to be built. Once collected, the flammable gas would have to be safely transported without further clathrate formation (in colder climates). The storing of methane clathrates at standard conditions can be difficult as well. Given the challenges, it is likely that gas production from permafrost regions will likely begin in the next decade, with Japan and American programs formally beginning by 2015.[7] It seems likely that methane from clathrates will become a fuel source in the near future.

Retrieval Ideas and Consequences

There have been many ideas concerning the retrieval of methane from clathrates. The primary principle is to reduce the pressure below the stability, add enough energy to disrupt the water hydrogen bonds, or add a strong hydrogen bonding chemical like alcohol (-OH) or ethylene glycol (Figure 21). The addition of a chemical is called 'solvent injection'. This process has shown promise, but the technique is difficult to apply uniformly throughout a formation, and may not be used for deep formations.[34] Other methods include thermal stimulation and decompression. In 2002, the Mallik well drilled in Canada used hot water and dissociation methods to melt the clathrates. Other ideas have been suggested including pumping hot $CaCl_2$ solution down into methane clathrates, using acidic catalysts to speed up the reaction of decomposition, and using hot water from neighboring aquifers to melt the clathrates.[35] One unique suggestion uses carbon dioxide to liberate the methane through the use of "hydrates exchange reaction". In this process, gaseous carbon dioxide is injected into subterraneous methane hydrate fields. The carbon dioxide frees the methane through an exchange, leaving the carbon dioxide clathrate and retrieving the methane gas.



Ethylene Glycol

Figure 21: Polar molecules disrupt the hydrogen bonding of methane clathrates; ethylene glycols

Instead of using the slow, and potentially leaky process of "hydrate exchange", Cheng (2008), suggests in a recent patent that methane can be recovered through the use of buckets attached to a series of rotating chains. After the methane mud mixture is brought up, the decomposed methane can be brought to the surface and collected into a methane dome and processed into liquefied natural gas or synthetic liquid fuels. Besides Cheng's patented invention, Bell (2008) describes a method where two electrodes would be placed in the formation of the methane clathrates on the ocean floor. The conductive pathway across the surface of the methane clathrate would create resistance in the formation. This would generate heat energy sufficient to thermally react with the methane, thereby releasing methane gas from the formation. The gas is then formed at elevated pressure, which drives the gas into an extraction well. The methane gas can be recovered and stored on an ocean vessel and can be transported to land for use as energy.

The traditional method of mining gas involves drilling through sediment to reach the gas layer. Outgassing is a concern for these conditions. If methane clathrates were drilled, there is a possibility that the gas hydrate layer, which can act as a cap for a free gas layer beneath, can release a huge gas bubble traveling up through the water column. This dangerous scenario has scientists developing remote methane clathrate recovery systems where an anchored drilling apparatus brings up the entire methane clathrate. This would not allow the clathrate to turn into a gas and expand. Current technology is no where near representing these ideas.

Previous Methane Release

There are natural consequences from the retrieval ideas listed above. Environmentalists are opposed to injecting chemicals into water and scientists are critical about supplying the heat necessary to 'melt' the clathrates. There is much debate over what recovery methods would work successfully. If the methane could not be successfully recovered from methane clathrates brought to the surface there is a potential of the methane reaching the atmosphere and causing climate change.

Climate change has happened due to natural means, beyond the scope of any human intervention. Scientists at the University of California, Riverside and Columbia University found evidence that an "enormous quantity" of methane gas as ice sheets possibly melted at the end of a global ice age, about 600 million years ago, during the end of the Neoproterozoic era.[36] The evidence was based on a chemical fingerprint of methane gas found on rocks in southern China, indicating that the heavier isotope of carbon, carbon-13 (^{13}C), was deposited from carbonate rocks as the temperatures rose. Methane clathrates, when destabilized, are typically oxidized at the sediment-ocean interface, producing excess calcium carbonate ($CaCO_3^{2-}$) in surrounding sedimentary structures, called cap carbonates. Furthermore, the methane seeps in the ocean sediment typically produce variation in the isotopic record (as compared to the carbon-13 content of existing limestone structures) The amount of carbon-13 in cap carbonates above methane seeps (~25% ^{13}C)can be compared to other underwater structures that reveal highly variable carbon-13 values. A large loss of carbon-13 from the surrounding area would indicate a negative isotopic value. Jiang (2003) and his colleagues found large negative values for isotopes of carbon-13 in ocean sediment (around -41% in carbonate carbon) possibly indicating a large methane release.

Other scientists have found similar evidence to suggest that there was a large carbon emission in the Paleocene-Eocene Era, 55 million years ago, which disrupted the climate of the globe.[5, 17, 30]. Carbon-13 decreased 2.5% (in ocean sediments, in fossil tooth enamel, and in carbonates and organic sediments) during the Paleocene era, while measurements from the same era on land (from plant tissues) increased 5%. This possibly indicates that there was a large release of methane from the oceans and eventually reached the atmosphere.[6, 7,9] In the early 1990's, Kennett, of Scripps Institute of Oceanography, first noticed this "short amount of time at the transition between the Paleocene and Eocene epochs." He documented that around this time, ice core samples (although lagging in time) revealed an extreme warming of the globe (around 2-3 degrees Celsius) .[5] He called his theory the "clathrate gun hypothesis", which says that methane builds up during periods of global cool periods and then, when the globe warms, methane is explosively released. This larger release of methane is thought to cause the massive species extinction during the same Paleocene-Eocene period.[17]

Atmospheric Changes due to Methane Clathrate Release

Climate change, created by naturally dissociated methane clathrates, would likely take decades rather than years to happen.[30]. Currently, studies in the Beaufort Sea continental shelf of Alaska already indicate that there is a seasonal source of methane to the atmosphere in a small amount.[30] However, disturbing the stability of methane clathrates is critical for many reasons, notably because of the effect methane has on the earth's atmosphere. If additional methane is released due to human activity, the methane could persist in the Earth's atmosphere, increasing atmospheric temperatures. As a result of higher atmospheric temperatures, higher anaerobic biomass decay would result and increase temperatures even more.[37]

There are six different sources of atmospheric methane: natural wetlands, fossil fuels, landfills, ruminant animals, agricultural paddies, and biomass burning (See Figure 22).[37] Ice core sample data, which extends back to nearly 160,000 years from Lake Vostok, Antarctica, indicates that methane in the atmosphere has more than doubled in concentration (from 320 ppb to 620 ppb) in the last 200 years.[8] Methane is a greenhouse gas and can be oxidized by hydroxyl radicals in the atmosphere. Although the role of gas hydrates in global climate change is not entirely understood, methane released from the ocean in large quantities could cause significant atmospheric changes. If there is a destabilization of methane clathrates due to natural or anthropogenic means, it is uncertain whether hydroxyl radicals would be able to oxidize the large amount of methane released into the atmosphere.

Methane released into the atmosphere depends on several factors: hydrate dissociation, gas migration and trapping in sediments, gas venting into the water column, and methane oxidation resulting in carbon dioxide formation. At present, methane is in very low abundance in the Earth's present atmosphere, approximately 0.0002%. 43% of the methane in the atmosphere is natural (methanogenic bacteria, termites, forests) and 57% anthropogenic (fossil fuel leaks, flatulence of domestic ruminants).[17] The primary problem with this low percentage of methane in the earth's atmosphere, is in terms of methane's persistence. The persistence time of one molecule of methane in the atmosphere, at present conditions, is around 8-10 years before it is oxidized.[5, 13]

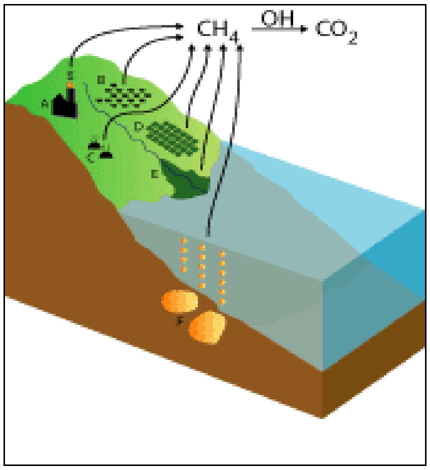


Figure 22: Sources of Methane: A-fossil fuels, B-ruminant animals, C-landfills, D-agricultural paddies, E-natural wetlands, F-gas hydrates (Source NASA GISS)

The Earth has a variety of sources and sinks for atmospheric methane. 90% of methane loss, a sink, is through atmospheric oxidation in Earth's troposphere (below 10-12 km). Two other sinks are the reaction with soil and destruction (through chemical reactions) in the stratosphere (15-50 km above the Earth's surface) .[37] In earth's troposphere, below 10-12 km, 85% of atmospheric methane is oxidized by OH radicals and reduced to water and oxygen through a series of chemical reactions.[5, 37] In earth's stratosphere, the remaining methane is either destroyed by OH radicals, reacts with Cl radicals, and escapes into space as hydrogen.[8] Despite the destruction of methane in the atmosphere, a positive feedback occurs with methane in the atmosphere. The more methane there is in the earth's atmosphere, there more OH is "used up" and the longer methane can persist.

CONCLUSIONS ON ATMOSPHERIC METHANE

A recent study in Atlantic Ocean by Rehder concluded that "the oxidation rate of methane in the water column is one of the unknown parameters in the climate scenario of methane emissions from gas hydrates to the atmosphere as the cause for past global warming".[32] The main question is whether or not methane, from dissociated clathrates, ever really has a large effect on the earth's atmosphere. Mau and his colleagues found that only one percent of this dissolved methane from the ocean floor enters the atmosphere under normal dissociation of methane clathrates.[38] What happens to the rest of the methane? Either the methane enters the atmosphere farther away from research testing site, becomes oxidized by microbes in shallow water, or mixes deeper into the water column where is it is subsequently oxidized.[38]

Valentine et al, researched how much methane from decomposing hydrates actually reaches the atmosphere and discovered where the methane was going. They wanted to quantify microbial methane oxidation by measuring the water column from isotopic carbon-13 and oxidation rates. Eight sites were chosen in the Eel River Basin off the coast of northern California for their active release of methane from the ocean sediment.[39] When methane is released from the ocean sediment or from existing hydrates, it travels to the water column above as a dissolved gas or through advection of pore water. The dissolved gas may become saturated in the water, in which case, methane bubbles form and rise to the surface. Valentine et al found that oxidation concentrations were high (20-300 nM) in depths greater than 370 m and low (3-10 nM) near the surface of the water column. This research confirmed that the oxidative process for methane was occurring to a great extent in the ocean depths and is the primary reason why methane does not reach Earth's atmosphere upon its release from ocean sediment or deep hydrate structures.

Where was the oxidation occurring though? It was discovered that methanotrophy in sediments and water is the primary control on the release of hydrate derived methane to the atmosphere.[39] Aerobic methanotrophs oxidize methane that escapes into the water column. This process has been observed around existing hydrate structures. Many wonder what the maximum amount of methane the methanotrophs can oxidize upon a release. Gradual releases are able to be controlled by the oxidative process. This is why large methane releases from clathrates can be dangerous because of the possibility the gas can reach the atmosphere. If methane reaches the atmosphere in large quantities, several ideas have been proposed: Obtaining a catalyst to react with methane from ground facilities and turn the methane in to carbon dioxide and water, speeding up the natural destruction of methane by oxygen rich radicals (eg. OH^-) by injecting water into the high altitudes from aircraft, and enhancing the oxygen efficiency of micro-organisms (no details were given as to how this would be done).[17]

Other Environmental Concerns

Many other environmental concerns exist for methane clathrates besides the sudden release of methane to the atmosphere. With approximately 90% of global methane clathrates occurring at depths of less than 1000 m, their stability is highly sensitive.[11] A large concern is related to the sediment sections around and near the methane clathrates. These large unstable volumes of sediment, methane, and water have resulted in huge slides off the Norwegian coastline.[9] The movement of marine sediment (from the dissociation of methane clathrates or other physical changes) causes slumping, which can quickly release methane from the sediment (called outgasing). As a result of the displaced water from the slumping, tsunamis could develop.[9] One of the Norwegian gas-hydrate linked slides produced a tsunami which deposited sediment up to four meters above the high water line in Scotland.[9] In addition, the quick release of methane is a big deal because methane has a very low water solubility (22 mg/L @ 298K).

Thus, the methane would not be dissolved or oxidized in the water column when released, but would reach Earth's atmosphere. Zonenshayn et all in 1987, indicated that a "large pulsating gas plume" in the Sea of Okhotsk (located on the northwestern edge of the Pacific Ocean) was due to volcanic heating of overlying gas hydrates.[2] Gas-driven eruptions are commonly known for lakes but are also possible for oceans.

Sudden releases of methane due to slumping or dissociation can not only cause atmospheric problems but also the cause of geohazards such as landslides, earthquakes, and tsunamis.[4] The petroleum industry is seeking to search deeper for energy reserves, which produces a strain on the fragile depths of the ocean methane clathrates.[30] Kvenvolden in 2000 notes of the "superficial slides and slumps on the continental slop and rise of West Africa; slumps and collapse features on the U.S. Atlantic continental slope; large submarine slides on the Norwegian continental margin; sediment blocks on the sea floor in fjords of British Columbia; and massive bedding-plane slides and rotational slumps on the Alaskan Beaufort Sea continental margin".[30] Archer and Buffett (2005), found that an increase of methane in the sediment column from the bubbles could cause a series of oceanic landslides over a period of thousands of years. The dissociation of methane clathrates can also be caused by heat transfer during petroleum production and can cause collapse of engineering structures, such as platforms and pipelines.[12, 30] There is no doubt that many geohazards can be environmental dangers.

LAKE NYOS-A TRAGIC OUTGASSING DISASTER

In August, 1986, a severe and violent eruption of toxic gas was emitted from Lake Nyos, a very small lake in Cameroon, West Africa. 1700 people died as a result of carbon dioxide (CO_2) flowing down from the elevated lake into a nearby valley. How could this tragedy occur? Moreover, what can be learned about the outgassing of carbon dioxide? Can the knowledge be applied to the outgassing of methane from the depths of the oceans?

Centered on top of a volcanic crater, Lake Nyos is one of three lakes in the world known to be saturated with CO_2. An active volcano below the lake was slowly pouring CO_2 into the cold deep waters. This CO_2 is soluble in water, especially cold water. Because the lake contained layered waters of cold and warm water, there was a difference in the amount of CO_2 that was soluble in the various layers. Under normal conditions, this layered water is stirred and mixed to create a uniform concentration of soluble gas. However, the water at Lake Nyos was in physical and chemical equilibrium for a very long time. As a result, the cold water in the depths of the lake contained high saturated concentrations of CO_2, while the warm water at the top of the lake contained very low, unsaturated concentrations of CO_2.

Figure 23: Lake Nyos under normal conditions (above) and after the eruption in 1986 (below).[40]

Either the deep water became overly saturated or an underwater land mass movement (land slip, earthquake, or volcanic eruption) caused the fragile equilibrium to be disrupted. After the earth's movement, the layered waters mixed, causing the saturated CO_2 waters to become unstable. A large release of CO_2 came out of the lake in the form of a bubble. Upon reaching the surface of the lake, the CO_2, which is denser than air, traveled down the side of the mountain suffocating the villagers who lived nearby. Trees were knocked down by the gas and the level of the water dropped by approximately one foot. After the outgassing, the blue water from the lake turned a deep red due to iron-rich water that was oxidized near the surface of the lake (See Figure 23).

To prevent the disaster in the future, a degassing tube (See Figure 24) was placed in the center of the lake to pump up saturated CO_2 water. This will allow the gas-saturated water to leak safely to the surface, preventing future disasters.

The outgassing at Lake Nyos has encouraged scientists to look into the causes of outgassing and apply the knowledge to other environmental situations such as methane gas hydrates. The potential of violent gas-driven eruptions caused Zhang and Kling (2006) to review experimental simulations of CO_2-driven water eruptions. Although no one has observed or witnessed ocean eruptions of gas yet, there has been evidence to suggest that methane gas has been released in large quantities in the past.[11] If the stability of methane clathrates in deep oceans is compromised, large amounts of methane can occur in the form of an ocean gas-driven eruption. The methane gas plume would rise quickly to the top of the ocean. Unlike the denser CO_2, the methane would rise into the atmosphere and be hazardous to boats and planes above the gas plume release. It is uncertain what exactly would happen to the vessels. If the methane was in concentrations great enough, the methane could ignite.[40]

Figure 24: Degassing tube place in Lake Nyos in 2001.[40]

Conclusion

The vast potential of methane clathrates has given rise to an intense study of hydrate structures. This paper specifically describes and reviews the properties of methane clathrates and their potential use in energy production. Determining the physical properties of methane clathrates has allowed scientists to discover how methane clathrates form; in cold permafrost regions or in deep ocean sediment. An appropriate amount of organic sediment, a decreased level of oxygen concentration, and a source of methane production is necessary for this formation. Methane clathrate hydrates provide the necessary structure to trap methane produced by anaerobic bacteria in deep ocean sediment. Weak van der Waals forces contain the freely rotating methane molecule inside of the hydrate. In nature, 90% of the hydrate cages are filled. The basic pentagon dodecahedron hydrate, held together by hydrogen bonds, can be repeated to form a larger structure (known as Structure I). This structure is the most naturally occurring. Depending on the size of the guest which occupies the cage-like hydrate structure, larger structures, such as II and H can form. Without the methane guest molecule, the hydrate is thermodynamically unstable.

Many wonder whether or not methane clathrates can be used as a fuel source. Given the recent success of the Mallik well drilled in Canada, and the commitments of countries such as Japan, the United States, and India for further research, harvesting methane clathrates for fuel possibly could occur within the next 10 years or so. The potential rich carbon source has the opportunity to provide tremendous amounts of energy. However, technological, economic, recovery, and environmental problems could prevent the full scale production of methane from clathrates in the near future. Future methane clathrate research is ongoing. Determining better methods to find methane clathrates, the likely scale of recoverable methane clathrates, and specific production technologies are just some of the future endeavors that could be undertaken by researchers. With approximately 10,000 Gt of methane clathrates around the world, twice that of existing fossil fuel resources, the scientific community should continue in this vital research.

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Target Course/Grade Level: General Chemistry Class, 11/12th grade

School: Mastery Charter High School

Title: The Global Carbon Cycle / Methanogenic Bacteria

Date: 8-14-07

Student Background Knowledge:

Students will have taken a general science course and have a basic understanding of elements and their relationship to the world. Students will have the prerequisite knowledge of the periodic table as well.

Day 1: POGIL based on the carbon cycle.
Day 2: Methanogens production of methane webquest
Day 3: Methanogens use of enzymes to produce methane POGIL

PA Department of Education Academic Standards or Science and Technology	Objectives and Related Standards Students will be able to:
3.1 Unifying Themes **3.1.12.A**-Apply concepts of systems, subsystems feedback and control to solve complex technological problems. **3.1.12.B**-Apply concepts of models as a method to predict and understand science and technology. **3.2** Inquiry and Design **3.2.10.A**-Apply knowledge and understanding about the nature of scientific and technological knowledge. **3.2.10.C**-Apply the elements of scientific inquiry to solve problems. **3.3** Biological Sciences **3.3.12.A**-Explain the relationship between structure and function at all levels of organization. **3.4** Physical Sciences, Chemistry & Physics **3.4.12.A**-Apply concepts about the structure and properties of matter. **3.4.10.B**-Analyze energy sources and transfers of heat.	1. Identify the main parts of the carbon cycle and how they affect each other. (**3.1.12.A**) 2. Give examples of where carbon is produced and consumed within the carbon cycle. (**3.1.12.B**) 3. Identify the function of methanogens and their role in biological systems. (**3.2.10.A**) 4. Describe the physical and chemical properties of methane and its relationship to the global carbon cycle. (**3.2.10.C**), (**3.4.12.A**) 5. Discuss how methane produced from bacteria could help solve our current energy crisis. (**3.2.10.C**), (**3.4.10.B**) 6. Describe what an enzyme is and its benefit within a chemical reaction. (**3.2.10.A**) 7. List the basic types of structures within proteins. (**3.3.12.A**) 8. Describe how methane is produce from the enzymatic reaction within bacteria. (**3.3.12.A**)

Day 1: POGIL based on the carbon cycle

OBJECTIVES:

- Identify the main parts of the carbon cycle and how they affect each other. (3.1.12.A)
- Give examples of where carbon is produced and consumed within the carbon cycle. (3.1.12.B)

Do Now / Pre-assessment:

1. Students will answer the following questions after they enter the room:
    - Define the carbon cycle and give an example of where carbon can come from.
    - When burning a hydrocarbon, what are the products and reactants of the reaction?
    - From earlier discussions, how have scientists contributed to the production of energy sources such as oil, gasoline, and natural gas?

Demonstration:

1. Students will use candle, test tube, lighter to determine the products and reactants of a combustion reaction.
    - Students will make observations of the candle and test tube before the demonstration in their notebook.
    - Question: What will you see on the surface of the test tube.
    - Teacher will have students burn a candle at their desk (in groups of 4).
    - Students will invert a test tube over the candle for 5-10 seconds to ‘capture’ any gases that may be produced and observe any ‘staining’ that may occur as a result of the reaction.
    - Students will copy down observations and record what they think the reactants and products are in word form or in chemical symbols in their notebook.
    - CAUTION: STUDENTS COULD BURN THEMSELVES NEAR FLAME OR IF TEST TUBE IS HELD LONGER THAN 10 SECONDS.
    - Question: What is the black residue that occurred on the test tube.
    - Question: Where did the moisture come from on the inside of the tube? Why did it ‘disappear’ after a few seconds or so?

Direct Instruction:

1. Teacher will review the element of carbon; its properties, location on the periodic table, and where it is specifically found in nature.
2. Teacher will pass around a sample of carbon in a sealed vial for students to look at.
3. Teacher will introduce POGIL-The carbon cycle (separate document attached)

   a. Think/Pair/Share: Where do you think carbon is located in the world around us?
   b. Roles for the POGIL will be distributed to the group of 4 students (Task Master, Calculator, Timer, and Presenter). Each member of the group has a role during the POGIL to stay on task.

Guided Practice:

1. Each group will start POGIL for the first few questions along with the teacher. Teacher will model what it looks like to use the Carbon cycle image at the beginning of the POGIL to answer the questions.
2. Teacher will stress that each student in the group must stay on the same question and have the same answer.

Independent Practice:

1. Teacher will put on board the starting and ending point for the sections of POGIL questions.
2. Students will work together in groups of 4 to complete POGIL questions. Teacher will monitor answers, circling the room, checking student answers for correctness.

Reflection/Exit Ticket:

1. Teacher will have the Present for each group to be ready to answer questions posed by the teacher.
2. Teacher will ask each group to compose a main idea from a particular POGIL section to engage more of a class reflection. Groups will get 2-3 minutes to give a main idea from the POGIL.
3. Exit Ticket: Teacher will distribute the following questions to the class as an assessment of their learning. Student will complete the questions on their own.
   - Explain what the carbon cycle is?
   - In the U.S., what source of carbon is used the most? What source of carbon is produced the most?

Homework:

Finish POGIL questions and exercises if they were not completed in class.

Write a 2 paragraph essay reflecting on the following prompt/questions (related to the carbon cycle). This may require some research on the internet.

High energy costs in our society have caused many to question where additional energy will come from. Where does our oil and gasoline come from and how does it relate to the carbon cycle? Burning these fossil fuels does not eliminate the carbon associated with these energy sources. In what form is the carbon produced?

Day 2: Methanogens production of methane webquest

OBJECTIVES:

- Identify the function of methanogens and their role in biological systems. (3.2.10.A)
- Describe the physical and chemical properties of methane and its relationship to the global carbon cycle. (3.2.10.C), (3.4.12.A)
- Discuss how methane produced from bacteria could help solve our current energy crisis. (3.2.10.C), (3.4.10.B)

Teach students "Control F" function to find information.

Do Now / Pre-assessment:

1. Students will answer the following questions after they enter the room:
   - Describe the carbon cycle and its relationship to the environment.
   - Where is the primary depletion of the carbon cycle occurring at? What is the problem with removing these resources?

Demonstrations:

1. Methane Gas Bubble Explosion-Teacher will use tubing from natural gas to produce methane gas bubbles and then ignite them in mid air.
   - Students will write down observations (chemical and physical) of methane.
   - Teacher will ask questions during discussion:
     1. Why does natural gas smell?
     2. What are some of the physical can chemical properties of methane gas?
     3. Where does methane gas come from? List 3 sources.

Direct Instruction:

1. Continuation of Demonstration above…
2. Teacher will describe the objectives and how the objectives will be achieved; through a webquest.

Guided Practice:

1. Teacher will show you tube video, "Jacob Joseph Methane Gas Story". Discussion questions:
   - What was the main intention of the landfill?
   - How was the methane gas collected?
   - What was the intended use for the methane?
   - Where was the methane coming from? (seeking a deeper answer than just trash)
2. Teacher will show students that when searching on webpages, the student can use the "ctrl f" keys to find text within a PDF file, webpage, or word document.

Teacher will demonstrate through the use of the video projector. Students will follow along at computers to find text within a webpage.

Independent Practice:

1. Webquest: Students will be paired up in twos and complete a webquest on methanogen bacteria. Teacher will monitor students answers and collect assignment at the end of the period.

Reflection/Exit Ticket:

1. Discussion in groups:
    - After completion of the webquest: In groups, discuss how methanogens could be used to help solve our current energy crisis. What are the advantages of using methanogens? The disadvantages? Potential problems?
    - Students will write down their brainstorming thoughts on the production of energy from methanogens in light of the webquest and global carbon cycle studied earlier.
    - After 5-10 minutes teacher will lead discussion with class examining arguments.
    - Student recorder will post advantages and disadvantages on the board for the use of methanogens as an energy source.
2. Exit Ticket: Teacher will distribute the following questions to the class as an assessment of their learning. Student will complete the questions on their own:
    - Describe the physical and chemical properties of methane and its relationship to the global carbon cycle.
    - Identify the function of methanogens and their role in biological systems.

Homework:

1. Students will complete any remaining questions from the webquest that were not completed in class.
2. Students will write a persuasive essay on the use of methanogens to generate energy. The student will write 2-3 paragraphs clearly describing their plan based on class discussions. The student will cover the following items:
    a. What is the problem with current use fuels?
    b. How can methanogens be used to generate energy?
    c. How does this process work?
    d. What are the advantages of your plan?
    e. What are the disadvantages of your plan?

Day 3: Methanogens use of enzymes to produce methane-POGIL

OBJECTIVES:

- Describe what an enzyme is and its benefit within a chemical reaction. (3.2.10.A)
- List the basic types of structures within proteins. (3.3.12.A)
- Describe how methane is produce from the enzymatic reaction within bacteria. (3.3.12.A)

Do Now / Pre-assessment:

Students will answer the following questions after they enter the room:

1. What are methanogens and what is their biological function within the environment?
2. What are catalysts and what are their benefits within a chemical system?

Demonstration:

1. Teacher will have two chemical reactions, one with heat applied as a catalyst and one without. Teacher will show how the addition of a catalyst merely speeds up the reaction, but does not change the outcome of the products.
2. Teacher will show 6 min video clip "Beakman explains catalysts" from you tube.com

Direct Instruction:

1. Teacher will handout POGIL on the enzyme that catalyzes methane and read the introduction with students.
2. Teacher will explain the relationship of methanogens (from the previous class) with this lesson.
3.

Guided Practice:

1. Teacher will briefly go through the mechanism asking the questions related to MODEL 1.

    According to Model 1 above, answer the following questions

    1. List the reactants in the reaction from Model 1.

    Methyl-coenzyme M, Coenzyme B

    2. List the products in the reaction from Model 1.

    Methane and CoM-S-S-CoB

    3. Circle the enzyme used in the reaction from Model 1.
    4. What type of linkage is created in the products?

    A disulfide linkage.

2. Students will answer questions posed by teacher in order to be familiar with POGIL.

Independent Practice:

1. Students will work in groups of four completing questions and staying together on each POGIL question. The teacher will post checkpoints (times on the board) and stop class every 15 minutes to make sure students are on task. Teacher will redirect and refocus where needed.
    a. Roles for the POGIL will be distributed to the group of 4 students (Task Master, Calculator, Timer, and Presenter). Each member of the group has a role during the POGIL to stay on task.
2. Teacher will asses student understanding by monitoring answers while circulation class. Each group will have to have teacher's initials on the group leaders paper to receive class credit for the day.
3. If students finish early, they may begin creating the concept map in the exercises section of the POGIL.

Reflection/Exit Ticket:

1. Class Discussion: After students have completed POGIL, teacher will review the POGIL with the class by asking the recorders in each group the following questions (from the class work).
    - What is a cofactor and why is it necessary?
        - A cofactor is a coenzyme or metal ion that works by changing the shape of an enzyme or participating enzymatic reaction.
    - Describe using your own words how methane (CH_4) is being produced.
        - Methane is produced through the reduction of the Ni cofactor.
    - What are the 4 basic types of structures within proteins?
        - Primary, secondary, tertiary, and quaternary.
    - Identify the 6 subunits for the quaternary structure.
        - Alpha, alpha prime, beta, beta prime, gamma, gamma prime
    - Why would a greater temperature favor the enzyme and hence the production of methane?
        - A great temperature would reduce the activation energy for the reaction and help in the production of methane.
2. Exit Ticket: Teacher will distribute the following questions to the class as an assessment of their learning. Student will complete the questions on their own
    - What is the benefit of enzymes within a chemical reaction? (be specific)
    - Explain the process of how methane is produced from bacteria. Use steps if needed. Include words such as enzyme, substrate, cofactor, reactant, product, etc.
    - List and Describe **one** of the four types of structures within a protein.

Homework:

1. Students will complete any remaining questions from POGIL that were not completed in class.
2. Students will complete two exercises at the end of the POGIL.
    - Hydrophobicity Plot
    - Concept map of POGIL

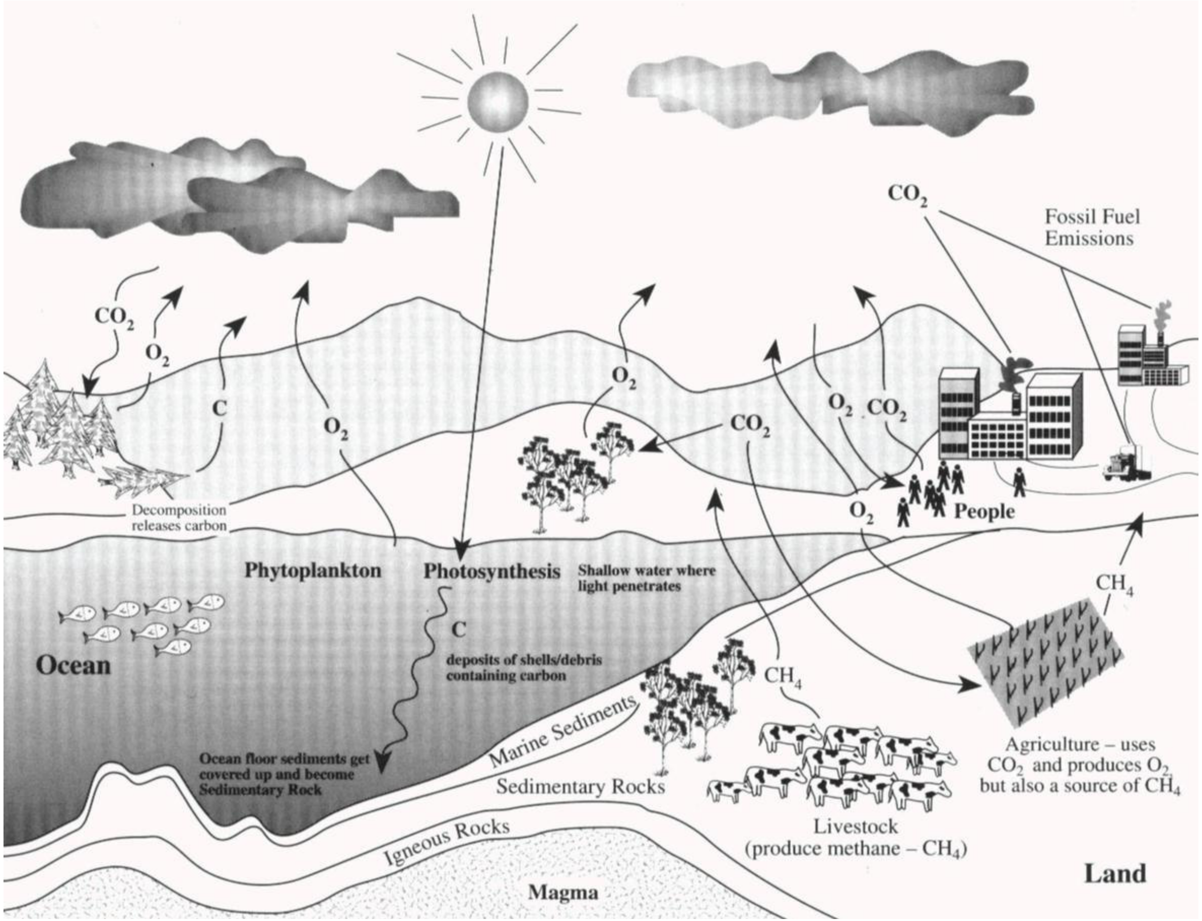
Carbon Cycle POGIL

Name:_____________________________ Date:_______________________

INTRODUCTION:

Carbon is an important source of food that sustains and shelters many human populations. Carbon is the primary energy source that fuels economies and is a major contributor to atmospheric greenhouses that reach the atmosphere. The carbon cycle contains many sources and sinks. Sinks are places where carbon settles and can remain in a stable condition. The carbon cycle contains varying sources of carbon that is used for plants, mammals, and humans. Some forms of carbon are renewable while others are not. Use the following image of the carbon cycle below to answer the questions. Pay careful attention the ways in which carbon is used and produced. A key aspect of the diagram is that marine sediments can provide the necessary fuel for microorganisms to produce methane gas. Take note of other areas where methane can be produce.

MODEL 1 – The Carbon Cycle



Use the diagram in MODEL 1 to answer the following questions:

General:

1. What is the chemical formula represents carbon dioxide?
2. What chemical formula represents methane?
3. List the different sources of carbon are there in the diagram?
4. Who/what uses the carbon sources in the diagram?

Plants:

5. Specifically what living organisms are taking carbon out of the atmosphere? Give two examples.
6. Trees and crops use what source of carbon?
7. Trees and crops give off what gas?
8. When trees decompose, what occurs?

Oceans:

9. Can carbon get into the oceans?
10. What source of carbon can fall into the ocean? What happens to the carbon after reaching the bottom of the ocean?
11. What is necessary for photosynthesis to occur in the oceans? On land?

Land:

12. Where do fossil fuels come from?
13. List three fossil fuels that you know of.

14. How are fossil fuels used?

15. Why do industry and homes combust fossil fuels?

16. What is the result of combustion of fossil fuels?

Other:

17. When trees decompose, what is the name of the source of carbon that is being released?

18. List three sources that produce methane.

19. Where does the methane from livestock come from?

20. Where does the methane from agriculture come from?

21. If much of the carbon ultimately reaches the bottom of the ocean, what do you think happens to the carbon? Can any living organism use the carbon as a source of food?

22. If carbon is ingested by livestock, how do you think the carbon is converted in to methane? What do you think is causing this conversion?

EXERCIESES:

23. A common fossil fuel is natural gas, which is mainly made up of methane gas. Where does this methane gas come from? How is it useful to humans?

24. Agricultural fields, such as wet rice paddies produce a tremendous amounts of methane gas. Where is this methane gas coming from? (plants, water, microorganisms, etc.)

25. Compose a concept map of the carbon cycle above. Connect each main idea with arrows to show their relationship to each other.

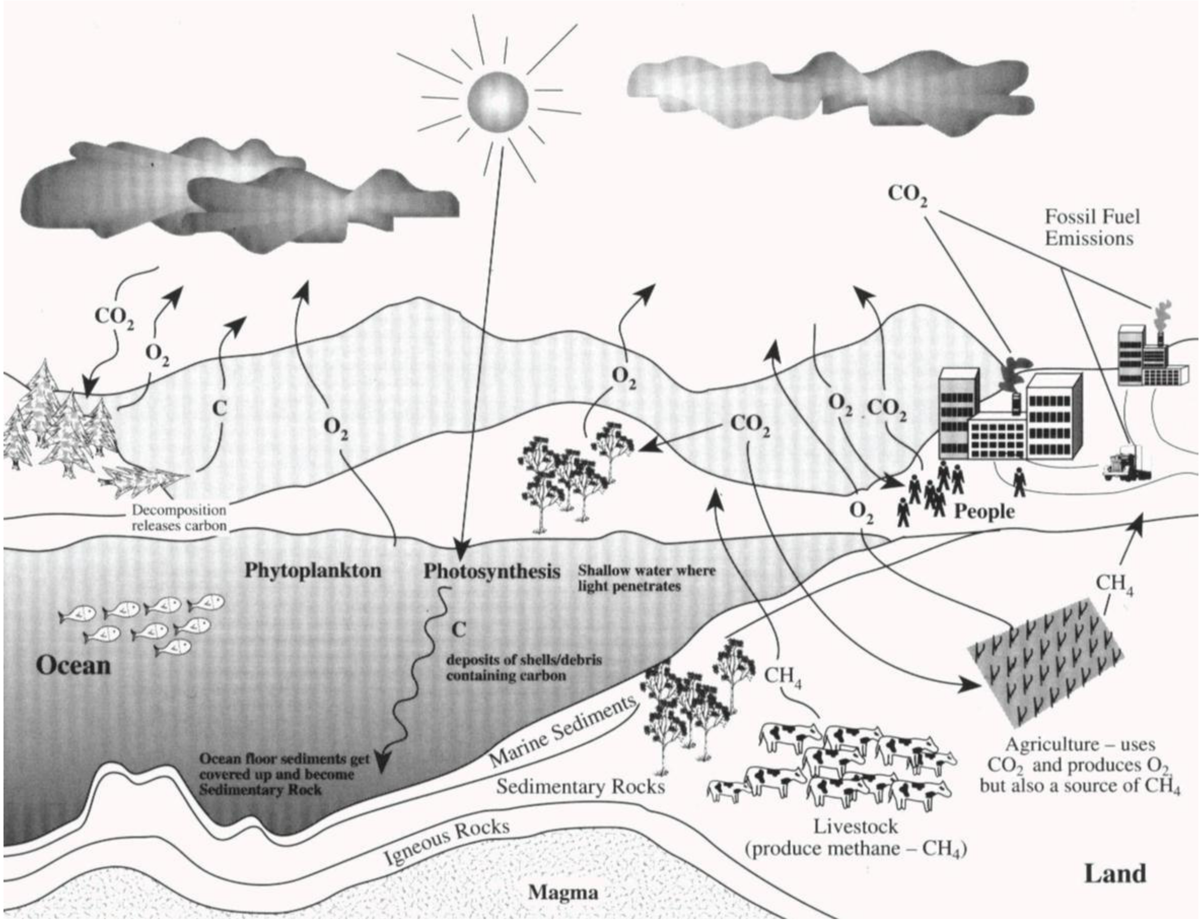
Carbon Cycle POGIL-TEACHER'S COPY

Name:_____________________________ Date:_______________________

INTRODUCTION:

Carbon is an important source of food that sustains and shelters many human populations. Carbon is the primary energy source that fuels economies and is a major contributor to atmospheric greenhouses that reach the atmosphere. The carbon cycle contains many sources and sinks. Sinks are places where carbon settles and can remain in a stable condition. The carbon cycle contains varying sources of carbon that is used for plants, mammals, and humans. Some forms of carbon are renewable while others are not. Use the following image of the carbon cycle below to answer the questions. Pay careful attention the ways in which carbon is used and produced. A key aspect of the diagram is that marine sediments can provide the necessary fuel for microorganisms to produce methane gas. Take note of other areas where methane can be produce.

MODEL 1 – The Carbon Cycle



Use the diagram in MODEL 1 to answer the following questions:

General:

1. What is the chemical formula represents carbon dioxide?

$CO2$

2. What chemical formula represents methane?

$CH4$

3. List the different sources of carbon are there in the diagram?

Carbon dioxide, methane, plants, fossil fuels

4. Who/what uses the carbon sources in the diagram?

People use the carbon from plants, Trees/agriculture use carbon from carbon dioxide.

Plants:

5. Specifically what living organisms are taking carbon out of the atmosphere? Give two examples.

Trees/Plants are taking carbon ($CO2$) are taking carbon out of the atmosphere.

6. Trees and crops use what source of carbon?

Carbon dioxide.

7. Trees and crops give off what gas?

oxygen

8. When trees decompose, what occurs?

Carbon is released in the form of carbon dioxide and methane gas.

Oceans:

9. Can carbon get into the oceans?

Yes.

10. What source of carbon can fall into the ocean? What happens to the carbon after reaching the bottom of the ocean?

Carbon can fall down from existing plants and animals. The carbon can eventually produce sedimentaryrocks.

11. What is necessary for photosynthesis to occur in the oceans? On land?

The sun needs to provide the initial energy.

Land:

12. Where do fossil fuels come from?

Fossil Fuels come from many years of decomposed organic sources that were under heat and pressure.

13. List three fossil fuels that you know of.

Coal, natural gas, and oil.

14. How are fossil fuels used?

Fossil fuels are used as a source energy.

15. Why do industry and homes combust fossil fuels?

To produce energy.

16. What is the result of combustion of fossil fuels?

The release of carbon into the atmosphere.

Other:

17. When trees decompose, what is the name of the source of carbon that is being released?

Methane and carbon dioxide.

18. List three sources that produce methane.

Animals, agricultural, and plants.

19. Where does the methane from livestock come from?

From bacteria that decompose the carbon in the stomach.

20. Where does the methane from agriculture come from?

From bacteria in the organic sediment.

21. If much of the carbon ultimately reaches the bottom of the ocean, what do you think happens to the carbon? Can any living organism use the carbon as a source of food?

The carbon is used as a source of energy for bacteria. Yes.

22. If carbon is ingested by livestock, how do you think the carbon is converted in to methane? What do you think is causing this conversion?

By bateria in the stomach.

EXERCIESES:

23. A common fossil fuel is natural gas, which is mainly made up of methane gas. Where does this methane gas come from? How is it useful to humans?

Methane gas can come from the decomposition of organic material. Bacteria. Source of energy.

24. Agricultural fields, such as wet rice paddies produce a tremendous amounts of methane gas. Where is this methane gas coming from? (plants, water, microorganisms, etc.)

Bacteria.

25. Compose a concept map of the carbon cycle above. Connect each main idea with arrows to show their relationship to each other.

Answers may vary.

Name:________________________________ Date:________________________

Methanogen Webquest

Directions: Use the following links below to answer the questions concerning methane produced from anaerobic bacteria (methanogens). Use complete sentences when possible.

http://scifun.chem.wisc.edu/chemweek/METHANE/Methane.html

http://www.daviddarling.info/encyclopedia/M/methanogen.html

http://www.bookrags.com/research/methane-oxidizing-and-producing-bac-wmi/

http://library.thinkquest.org/11226/main/c17txt.htm

http://marine.usgs.gov/fact-sheets/gas-hydrates/title.html

Methane Overview:

1. What is the formula for methane?
2. Many U.S. households use natural gas for heating and cooking. What percent of methane is in natural gas?
3. Describe the physical **and** chemical properties of methane (boiling point, color, odor, etc.)
4. List two places where methane naturally comes from.
5. How is methane used in the laboratory?
6. What is the principle use of methane in our society? What is the benefit of collecting methane?
7. Write a basic chemical reaction for the combustion of methane.

Bacteria/Methanogens:

8. How does bacteria relate to methane?

9. Methane is a byproduct of what type of function within the bacteria?

10. What is a methanogen? How many species are there?

Use of Methanogens:

11. How are methanogens of 'economic importance'?

12. Describe how methanogen bacteria are important in the carbon cycle (use 2-3 sentences).

13. What is a methane hydrate and where are they located?

14. What are the potential uses for methane hydrates?

15. Where does the methane come from in the production of methane hydrates.

Name:___________________________________ Date:__________________________

Methanogen Webquest
TEACHER'S COPY

Directions: Use the following links below to answer the questions concerning methane produced from anaerobic bacteria (methanogens). Use complete sentences when possible.

http://scifun.chem.wisc.edu/chemweek/METHANE/Methane.html

http://www.daviddarling.info/encyclopedia/M/methanogen.html

http://www.bookrags.com/research/methane-oxidizing-and-producing-bac-wmi/

http://library.thinkquest.org/11226/main/c17txt.htm

http://marine.usgs.gov/fact-sheets/gas-hydrates/title.html

Methane Overview:

1. What is the formula for methane?

CH4

2. Many U.S. households use natural gas for heating and cooking. What percent of methane is in natural gas?

75-90%

3. Describe the physical **and** chemical properties of methane (boiling point, color, odor, etc.)

Methane is colorless and has a low b.p. Methane has no recognizable odor, but in most cases, an additive is added for safety reasons. It melts at –183°C and boils at –164°C. It is not very soluble in water.

4. List two places where methane naturally comes from.

Methane comes from ruminant animals and from the decomposition of biomass.

5. How is methane used in the laboratory?

In the chemical industry, methane is a raw material for the manufacture of methanol (CH_3OH), formaldehyde (CH_2O), nitromethane (CH_3NO_2), chloroform (CH_3Cl), carbon tetrachloride (CCl_4), and some freons (compounds containing carbon and fluorine, and perhaps chlorine and hydrogen).

6. What is the principle use of methane in our society? What is the benefit of collecting methane?

As a fuel source. The benefit of collecting methane is for the economic advantages it provides.

7. Write a basic chemical reaction for the combustion of methane.

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(l)$$

Bacteria/Methanogens:

8. How does bacteria relate to methane?

Bacteria can produce methane through a series of chemical reactions.

9. Methane is a byproduct of what type of function within the bacteria?

metabolism

10. What is a methanogen? How many species are there?

A bacteria who produces methane. There are over 50 species.

Use of Methanogens:

11. How are methanogens of 'economic importance'?

Methanogens could produce methane to use as an energy source, which is of valuable economic importance.

12. Describe how methanogen bacteria are important in the carbon cycle (use 2-3 sentences).

Answers may vary. Answer should include how carbon is used by methanogens and how methane is produced by the methanogens (another carbon source).

13. What is a methane hydrate and where are they located?

A methane hydrate is a solid ice structure that encapsulates methane. They are located in the permafrost regions or deep in the ocean.

14. What are the potential uses for methane hydrates?

Methane hydrates can be used for an additional energy source.

15. Where does the methane come from in the production of methane hydrates.

The methane is trapped inside of the solid hydrate.

Methanogen Bacteria POGIL

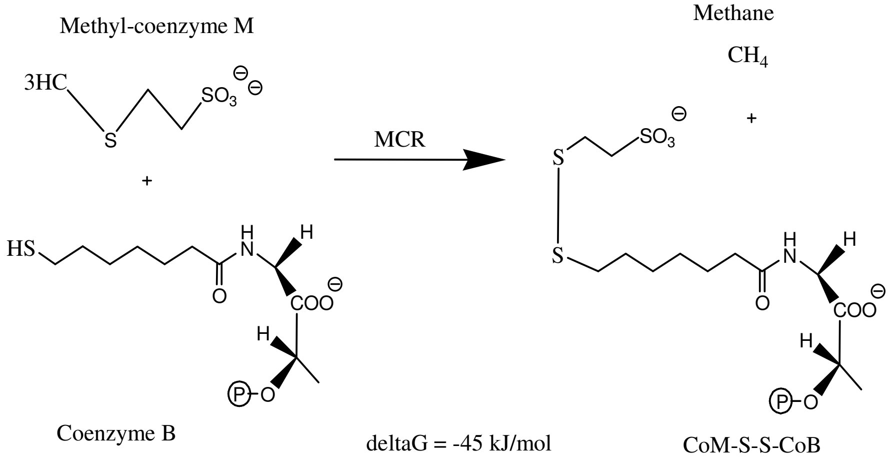
Name:___________________ Date:____________

INFORMATION:
In the past we have discussed about the carbon cycle and how carbon is transferred through various biological systems. We have also discussed what methanogens are and what they produce; methane gas. Methane gas produced by bacteria is actually a bit more complicated.

Enzymes are chemical substances which speed up a chemical reaction. Enzymes are necessary to lower the energy needed for a reaction to proceed, called activation energy. The reactants within enzyme-catalyzed reactions are called substrates. Enzymes bind one or more of the substrates to produce new products.

One such enzyme within the methanogen bacteria is called methyl coenzyme M reductase (MCR). MCR catalyzes the final reaction of the "energy conserving pathway" of methanogenic bacteria. Methyl-coenzyme M (coM) and coenzyme B (coB) are converted to methane and CoM-S-S-CoB.

MODEL 1: Proposed Reaction Catalyzed by MCR



According to Model 1 above, answer the following questions

1. List the reactants in the reaction from Model 1.

2. List the products in the reaction from Model 1.

3. Circle the enzyme used in the reaction from Model 1.

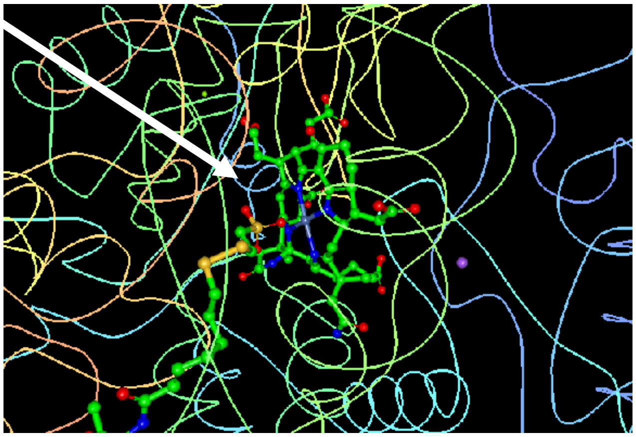
4. What type of linkage is created in the products?

INFORMATION:
Many enzymes can only function under certain conditions. One such condition is the existence of a cofactor. A cofactor, which can be a coenzyme or metal ion work by changing the shape of an enzyme or by actually participating in the enzymatic reaction. MCR uses nickel porphinoid (F_{430}) as the cofactor. Other cofactors associated with MCR include chloride ion, glycerol, magnesium ion, sodium ion, zinc ion.

(Of the 19 magnesium ions, half are coordinated to protein atoms. Of the 11 sodium ions, all are coordinated to the oxygens of the protein located in MCR. A single zinc ion was found along the symmetry axis of MCR. Two chloride ions are also found attached to the beta subunits.)

The most notable cofactor present is the nickel porphinoid F_{430}. Here is an image of the cofactor located within the methyl-coenzyme M reductase (shown in blue and green with arrow pointing towards it).

MODEL 2: Cofactor F_{430}



According to Model 2 and the information above, answer the following questions

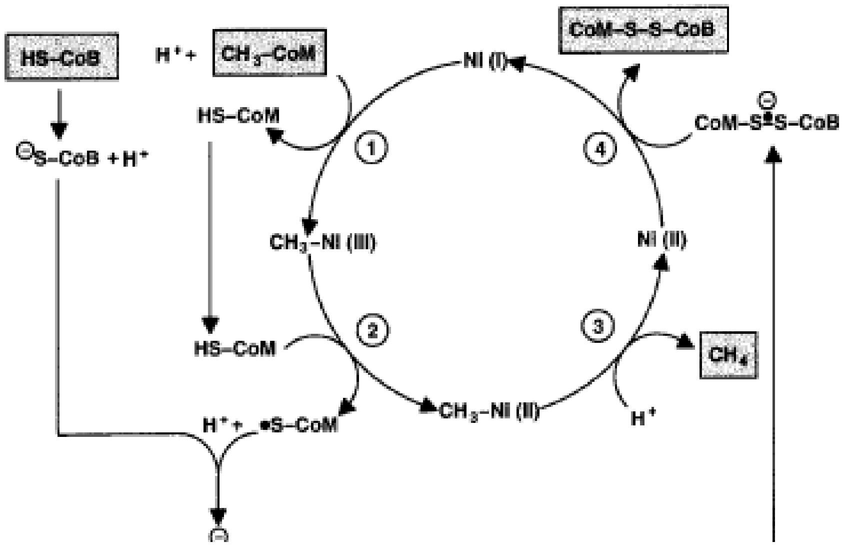
5. What is a cofactor and why is it necessary?

6. Describe F_{430} and its function.

INFORMATION:

A more detailed mechanism is found in the literature for how methane is produced in methanogenic bacteria (according to the reaction in model 3 below). The substrates (coM and coB) bind to the cofactor (F_{430}), methyl-Ni (III) in step one. F_{430}, is bound to histadine gamma-156. In step two, methyl-Ni (III) is reduced to methyl-Ni (II). Upon further reduction, methane gas is formed. This reaction above occurs in anaerobic conditions, such as deep ocean sediment. Upon methane production in deep ocean sediment, methane clathrate hydrates can form.

MODEL 3: Hypothetical catalytic reaction mechanism of methyl-coenzyme M.



According to Model 3 and the information above, answer the following questions.

7. How many main steps are there in this proposed reaction mechanism?

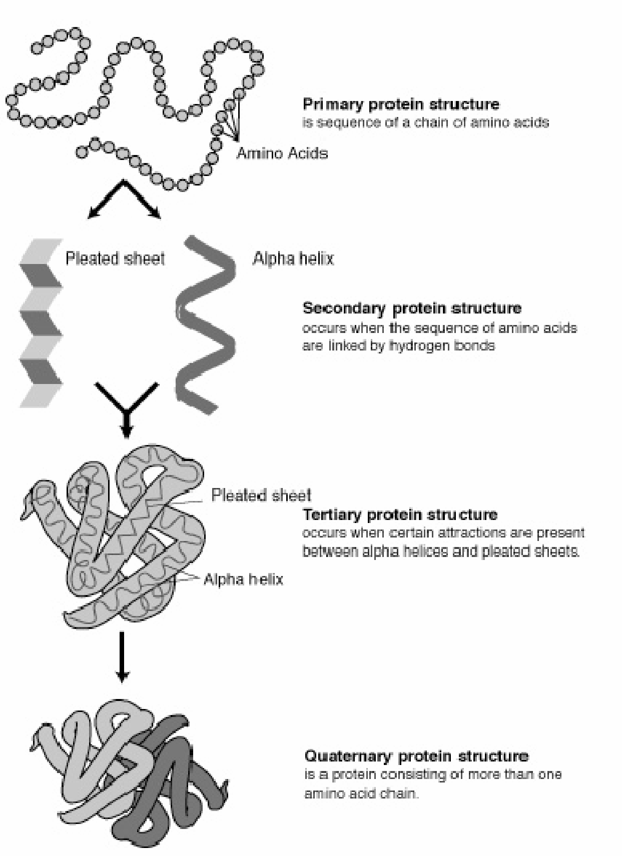
8. What transition metal (the cofactor) is used to bind to the methyl (CH_3) group in step 1?

9. What is the charge on the nickel between each of the 4 steps? Is the nickel being oxidized or reduced?

10. Describe using your own words how methane (CH_4) is being produced.

INFORMATION:
Enzymes, such as MCR act upon proteins within methanogen bacteria. Protein structure is classified into four different levels.

MODEL 4: Four different structures of proteins.



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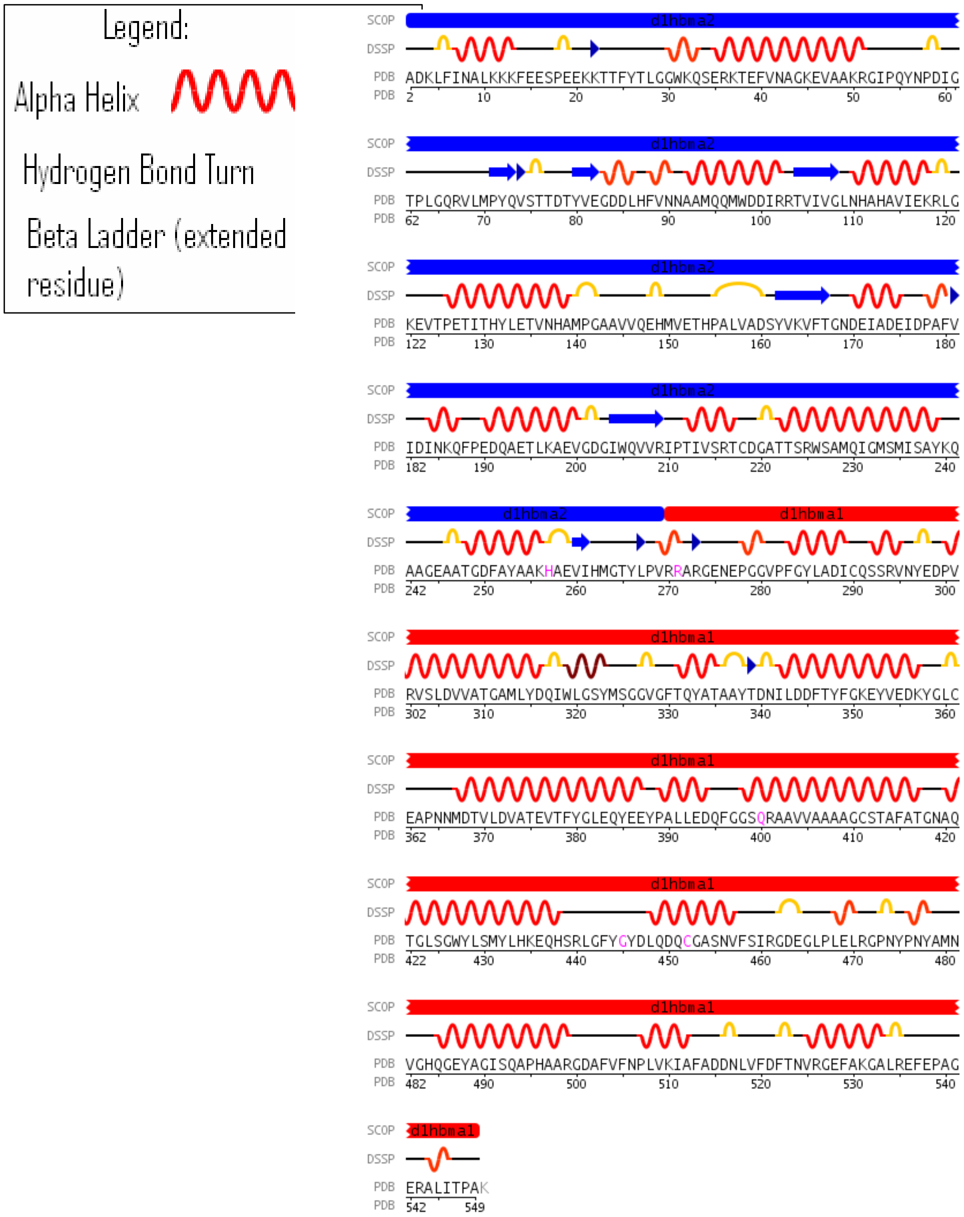
INFORMATION:
Below is the Primary structure sequence for one of the subunits of the protein. This sequence can be found through published sources. This sequence of amino acid chains has polar and nonpolar groups, which affects its function in biological systems. You will use this sequence to see the polar and nonpolar groups later in an exercise. Primary structure sequence for the alpha subunit:

1 mnkknkklfl ealekkfkge speekkttfy cfggwkqser krefveyakk lakkrgipfy
61 npdigvplgq rklmayrisg tdayvegddl hfvnnaaiqq mvddikrtvi vgmdtahavl
121 ekrlgvevtp etineymeti nhalpggavv qehmvevhpg lvddcyakif tgndeladel
181 dkrvlidink efpeeqaeml kkyignrtyq vnrvptivvr ccdggtvsrw samqigmsfi
241 sayklcagea aiadfsfaak hadviemgti lpgrrargpn epggipfgvf adiiqtsrvs
301 ddparislev igaaatlydq vwlgsymsgg vgftqyasat ytddilddfv yygaeyvedk
361 ygfcgvkpsm evvkdiatev tlygleqyee yptlledhfg gsqraavvaa aagcstafat
421 gnsnaginaw ylsqilhkeg hsrlgfygyd lqdqcgasns lsirsdeglv helrgpnypn
481 yamnvghqpe yagiaqapha argdafvvnp likvafadnd lsfdfrwprk eiargalref
541 mpdgertlii pask

INFORMATION:
Below is the secondary structure for the alpha 1 subunit. This subunit consists of an amino acid sequence with alpha helices and beta pleated sheets.

Model 5: Secondary Structure. (for the alpha 1 subunit)

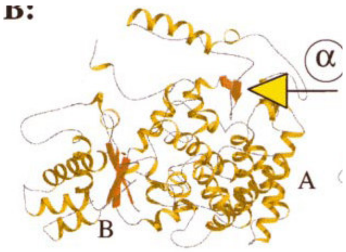


According to Model 5 and the information above, answer the following questions.

11. Circle 2 alpha helices, 2 hydrogen bond turns, and 2 beta ladders in the secondary structure above.

INFORMATION:
Below is the tertiary structure for the alpha 1 subunit. This subunit consists of interactions between the alpha helices and the beta sheets. Within the alpha subunit, there are two sections A and B that are labeled. In addition, the yellow arrow indicates an activation site where molecules typically bind.

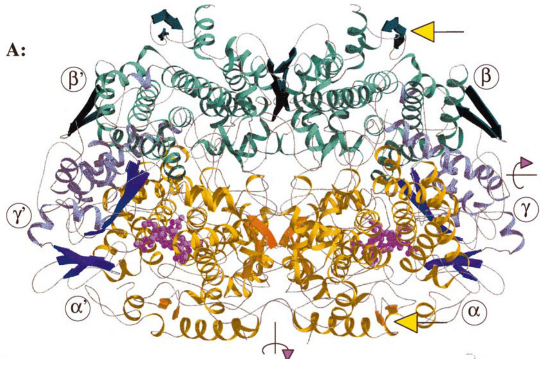
Model 6: Tertiary Structure for the Alpha Subunit:



INFORMATION:

A quaternary structure for a protein consists of several amino acid chains, which can be described as subunits. MCR is a heterohexamer with two copies of the subunits alpha, beta, and gamma. The alpha subunit contains two domains, A and B. Alpha subunit A has many parallel helices, while the alpha B subunit has a four-fold anti-parallel beta sheet. The alpha and beta subunits are perpendicular to the symmetry axis running down the center of the hexamer and are remarkably similar in their three dimensional structures. The last subunit, gamma, contains an alpha/beta fold with two antiparallel beta sheets which are perpendicular to each other.

Model 7: Quaternary Structure of MCR



Grabarse et al, 2001.

According to Model 7 and the information above, answer the following questions.

12. Draw a line for the symmetry axis in the quaternary structure above.
13. Identify the 6 subunits for the quaternary structure.

14. Circle an alpha helix and beta sheet in the structure above.

INFORMATION:
There are many catalytic parameters for the enzyme MCR. The catalytic parameter of Km is an estimate of the dissociation between the enzyme (MCR) from the substrate (coM and coB). A small Km means that the enzyme is tightly bound, while a high Km means that the enzyme is weakly bound. The substrate coenzyme B has a Km value of 0.000023-0.000075 (M) (depending on the literature sources).[2] The substrate methyl coenzyme M has a Km value 0.002-0.004 (M).[2] Therefore, coenzyme B binds more tightly to the substrate while methyl coenzyme M does not bind as tightly.

15. How would the Km value affect the production of methane in the enzyme MCR?

INFORMATION:
The enzyme MCR is also regulated in several different ways. As indicated earlier, the most important aspect of the enzymatic regulation is the necessity for anaerobic conditions. (The reaction is typically coupled with ATP synthesis via the formation of an electrochemical proton gradient). Also, depending on the electronic state of the biological system, the MCR is either in the reductive or oxidative state. Furthermore, the enzyme is regulated by pH and temperature. The optimum pH is around 7.[3] The optimum temperature is around 65 ºC.[3] The greater the temperature, the greater effect MCR reductive state has on the biological system.

16. What is significant about the optimum pH for the MCR enzyme.

17. Why would a greater temperature favor the enzyme and hence the production of methane?

Exercises:

1. A ***Hydropathicity Plot*** is a plot of the primary sequence of an amino acid sequence. The information taken from the primary sequence gives you information about the possible structure of a protein. Each amino acid is given a hydrophobicity score between 4.6 and -4.6. A score of 4.6 indicates that the amino acid is the most hydrophobic and a score or -4.6 indicates that it is the most hydrophilic. Copy the primary sequence from the information in POGIL above in to the hydrophobicity plot at http://gcat.davidson.edu/rakarnik/KD.html. Give a brief interpretation of what you observe.

2. Create a flow chart of the principles discussed in this POGIL. Start with Protein in the middle and include the terms listed below (not limited to). Write on the conection lines how the words relate to each other.

   Some words to use: enzyme, substrate, MCR, methane, structure, primary, secondary, tertiary, quaternary, subunits, temperature, pH, regulated.

References:

1. Grabarse, W., Mahlert, F, Duin, E.C., Goubeaud M., Shima, S., Tauer, R.K., Lamzin, V., & Ermler, U. 2001. On the Mechanism of Biological Methane Formation: Structural Evidence for Conformational Changes in Methyl-coenzyme M Reductase upon Substrate Binding. *J. Mol. Biol.,* 309, 315-330.

2. http://www.brenda-enzymes.info/php/result_flat.php4?ecno=2.8.4.1

3. Bonacker, L.G.; Baudner, S.; Morschel, E.; Bocher, R.; Thauer, R.K.; (1993). Properties of the two isoenzymes of methyl-coenzyme M reductase in Methanobacterium thermoautotrophicum. *Eur. J. Biochem*. 217, 587-595.

4. http://matcmadison.edu/biotech/resources/proteins/labManual/chapter_2.htm

Methanogen Bacteria POGIL-TEACHER’S COPY

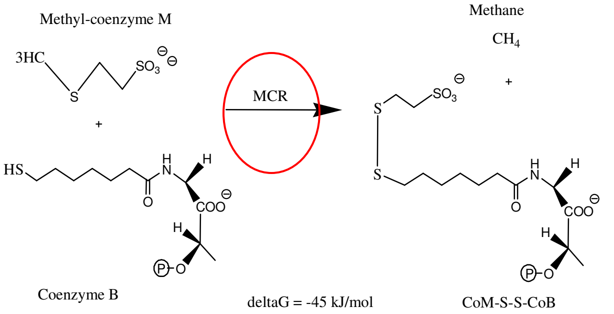
Name:___________________ Date:____________

INFORMATION:
In the past we have discussed about the carbon cycle and how carbon is transferred through various biological systems. We have also discussed what methanogens are and what they produce; methane gas. Methane gas produced by bacteria is actually a bit more complicated.

Enzymes are chemical substances which speed up a chemical reaction. Enzymes are necessary to lower the energy needed for a reaction to proceed, called activation energy. The reactants within enzyme-catalyzed reactions are called substrates. Enzymes bind one or more of the substrates to produce new products.

One such enzyme within the methanogen bacteria is called methyl coenzyme M reductase (MCR). MCR catalyzes the final reaction of the “energy conserving pathway” of methanogenic bacteria. Methyl-coenzyme M (coM) and coenzyme B (coB) are converted to methane and CoM-S-S-CoB.

MODEL 1: Proposed Reaction Catalyzed by MCR



According to Model 1 above, answer the following questions

1. List the reactants in the reaction from Model 1.
Methyl-coenzyme M, Coenzyme B

2. List the products in the reaction from Model 1.
Methane and CoM-S-S-CoB

3. Circle the enzyme used in the reaction from Model 1.

4. What type of linkage is created in the products?
A disulfide linkage.

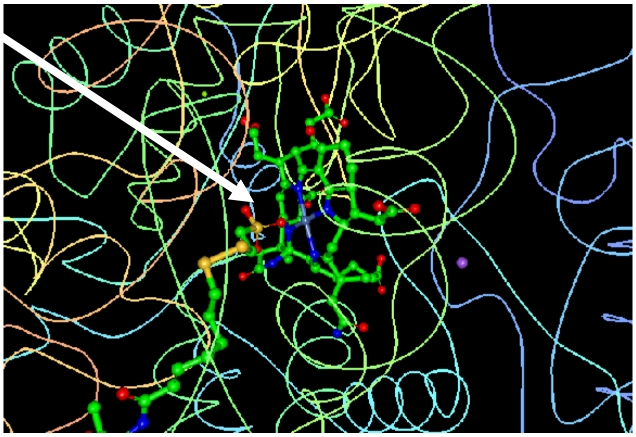
INFORMATION:

Many enzymes can only function under certain conditions. One such condition is the existence of a cofactor. A cofactor, which can be a coenzyme or metal ion work by changing the shape of an enzyme or by actually participating in the enzymatic reaction. MCR uses nickel porphinoid (F_{430}) as the cofactor. Other cofactors associated with MCR include chloride ion, glycerol, magnesium ion, sodium ion, zinc ion.

(Of the 19 magnesium ions, half are coordinated to protein atoms. Of the 11 sodium ions, all are coordinated to the oxygens of the protein located in MCR. A single zinc ion was found along the symmetry axis of MCR. Two chloride ions are also found attached to the beta subunits.)

The most notable cofactor present is the nickel porphinoid F_{430}. Here is an image of the cofactor located within the methyl-coenzyme M reductase (shown in blue and green with arrow pointing towards it).

MODEL 2: Cofactor F_{430}



According to Model 2 and the information above, answer the following questions

5. What is a cofactor and why is it necessary?

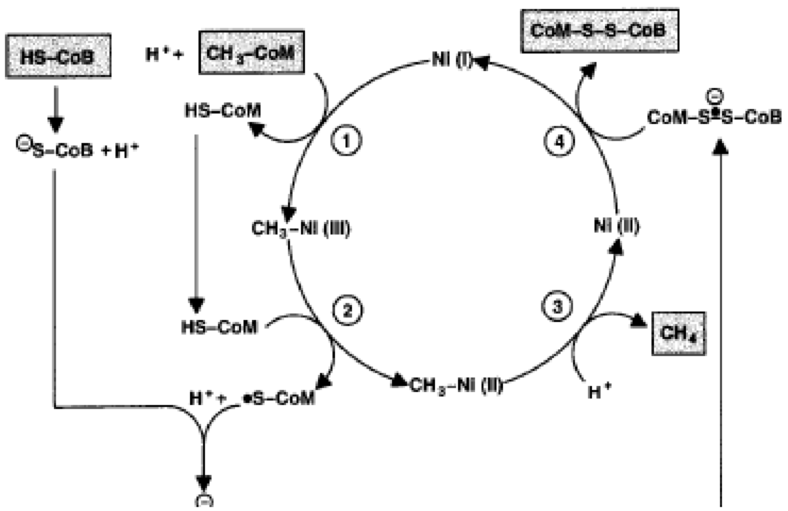
A cofactor is a coenzyme or metal ion that works by changing the shape of an enzyme or participating enzymatic reaction.

6. Describe F430 and its function.

F430 is a nickel based compound that binds to the coenzymes.

INFORMATION:
A more detailed mechanism is found in the literature for how methane is produced in methanogenic bacteria (according to the reaction in model 3 below). The substrates (coM and coB) bind to the cofactor (F_{430}), methyl-Ni (III) in step one. F_{430}, is bound to histadine gamma-156. In step two, methyl-Ni (III) is reduced to methyl-Ni (II). Upon further reduction, methane gas is formed. This reaction above occurs in anaerobic conditions, such as deep ocean sediment. Upon methane production in deep ocean sediment, methane clathrate hydrates can form.

MODEL 3: Hypothetical catalytic reaction mechanism of methyl-coenzyme M.



According to Model 3 and the information above, answer the following questions.

7. How many main steps are there in this proposed reaction mechanism?
Four

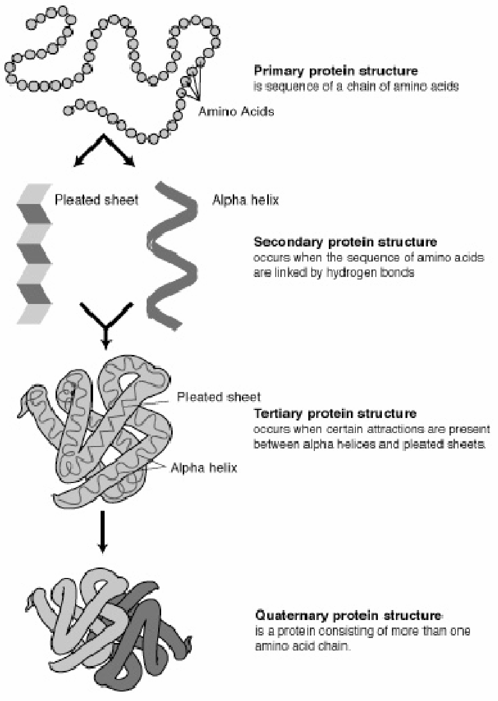
8. What transition metal (the cofactor) is used to bind to the methyl (CH3) group in step 1?
Nickel

9. What is the charge on the nickel between each of the 4 steps? Is the nickel being oxidized or reduced?
1-2 step = +3 charge, 2-3 step = +2 charge, 3-4 step = +2 charge

10. Describe using your own words how methane (CH4) is being produced.
Methane is produced through the reduction of the Ni cofactor.

INFORMATION:
Enzymes, such as MCR act upon proteins within methanogen bacteria. Protein structure is classified into four different levels.

MODEL 4: Four different structures of proteins.



4

INFORMATION:
Below is the Primary structure sequence for one of the subunits of the protein. This sequence can be found through published sources. This sequence of amino acid chains has polar and nonpolar groups, which affects its function in biological systems. You will use this sequence to see the polar and nonpolar groups later in an exercise.

Primary structure sequence for the alpha subunit:

```
  1 mnkknkklfl ealekkfkge speekkttfy cfggwkqser krefveyakk lakkrgipfy
 61 npdigvplgq rklmayrisg tdayvegddl hfvnnaaiqq mvddikrtvi vgmdtahavl
121 ekrlgvevtp etineymeti nhalpggavv qehmvevhpg lvddcyakif tgndeladel
181 dkrvlidink efpeeqaeml kkyignrtyq vnrvptivvr ccdggtvsrw samqigmsfi
241 sayklcagea aiadfsfaak hadviemgti lpgrrargpn epggipfgvf adiiqtsrvs
301 ddparislev igaaatlydq vwlgsymsgg vgftqyasat ytddilddfv yygaeyvedk
361 ygfcgvkpsm evvkdiatev tlygleqyee yptlledhfg gsqraavvaa aagcstafat
421 gnsnaginaw ylsqilhkeg hsrlgfygyd lqdqcgasns lsirsdeglv helrgpnypn
481 yamnvghqpe yagiaqapha argdafvvnp likvafadnd lsfdfrwprk eiargalref
541 mpdgertlii pask
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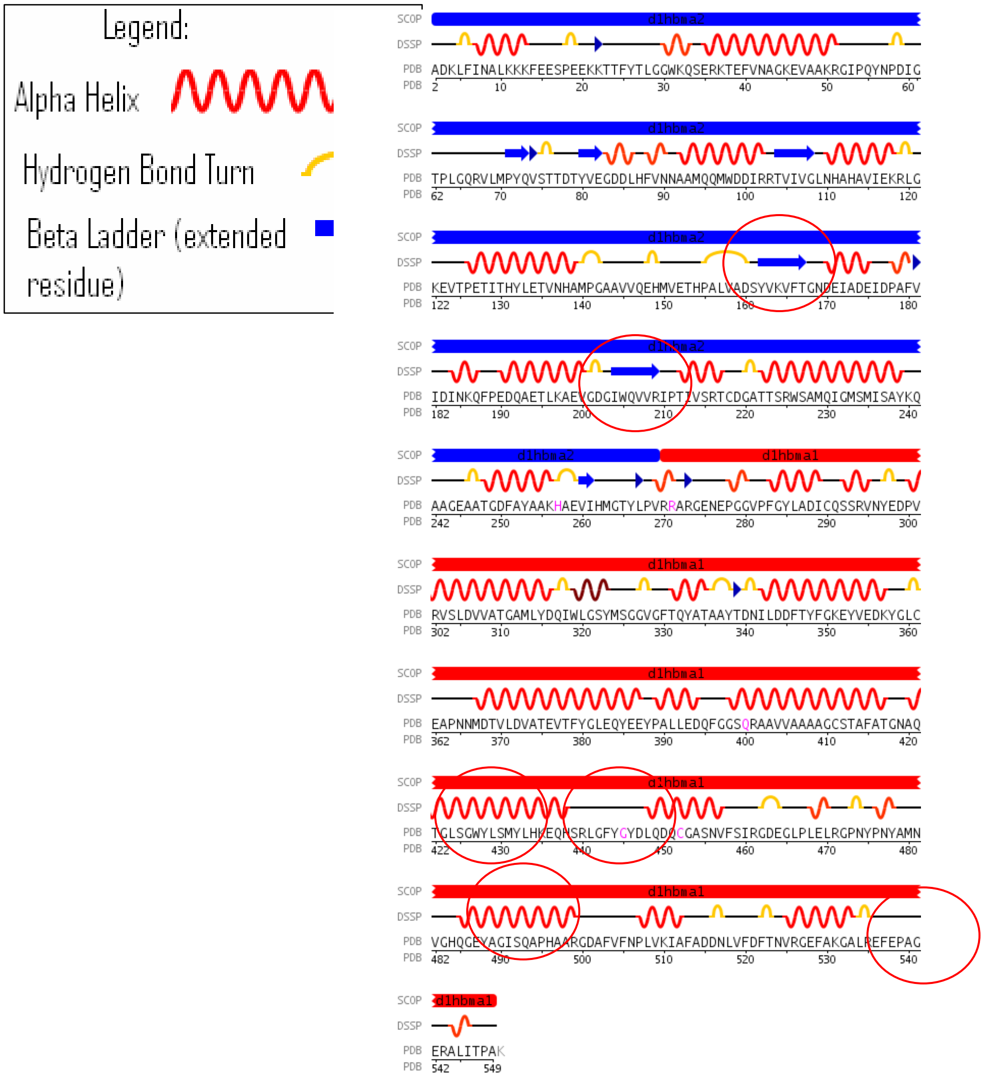
INFORMATION:
Below is the secondary structure for the alpha 1 subunit. This subunit consists of an amino acid sequence with alpha helices and beta pleated sheets.

Model 5: Secondary Structure. (for the alpha 1 subunit)



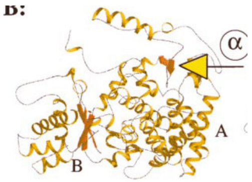
According to Model 5 and the information above, answer the following questions.

11. Circle 2 alpha helices, 2 hydrogen bond turns, and 2 beta ladders in the secondary structure above.

INFORMATION:

Below is the tertiary structure for the alpha 1 subunit. This subunit consists of interactions between the alpha helices and the beta sheets. Within the alpha subunit, there are two sections A and B that are labeled. In addition, the yellow arrow indicates an activation site where molecules typically bind.

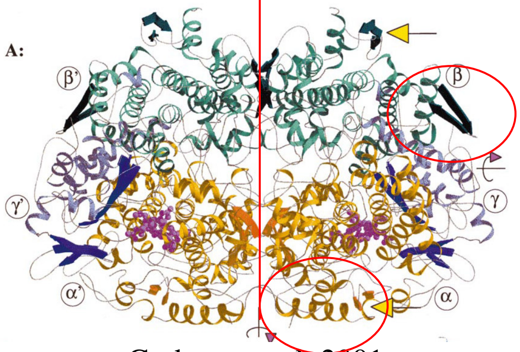
Model 6: Tertiary Structure for the Alpha Subunit:



INFORMATION:

A quaternary structure for a protein consists of several amino acid chains, which can be described as subunits. MCR is a heterohexamer with two copies of the subunits alpha, beta, and gamma. The alpha subunit contains two domains, A and B. Alpha subunit A has many parallel helices, while the alpha B subunit has a four-fold anti-parallel beta sheet. The alpha and beta subunits are perpendicular to the symmetry axis running down the center of the hexamer and are remarkably similar in their three dimensional structures. The last subunit, gamma, contains an alpha/beta fold with two antiparallel beta sheets which are perpendicular to each other.

Model 7: Quaternary Structure of MCR



Grabarse et al, 2001.

According to Model 7 and the information above, answer the following questions.

12. Draw a line for the symmetry axis in the quaternary structure above.
13. Identify the 6 subunits for the quaternary structure.

Alpha, alpha prime, beta, beta prime, gamma, gamma prime

14. Circle an alpha helix and beta sheet in the structure above.

INFORMATION:
There are many catalytic parameters for the enzyme MCR. The catalytic parameter of Km is an estimate of the dissociation between the enzyme (MCR) from the substrate (coM and coB). A small Km means that the enzyme is tightly bound, while a high Km means that the enzyme is weakly bound. The substrate coenzyme B has a Km value of 0.000023-0.000075 (M) (depending on the literature sources).[2] The substrate methyl coenzyme M has a Km value 0.002-0.004 (M).[2] Therefore, coenzyme B binds more tightly to the substrate while methyl coenzyme M does not bind as tightly.

15. How would the Km value affect the production of methane in the enzyme MCR?

If the Km value was small then the enzyme would tightly bind to the substrate and then reduce the production of methane.

INFORMATION:
The enzyme MCR is also regulated in several different ways. As indicated earlier, the most important aspect of the enzymatic regulation is the necessity for anaerobic conditions. (The reaction is typically coupled with ATP synthesis via the formation of an electrochemical proton gradient). Also, depending on the electronic state of the biological system, the MCR is either in the reductive or oxidative state. Furthermore, the enzyme is regulated by pH and temperature. The optimum pH is around 7.[3] The optimum temperature is around 65 ºC.[3] The greater the temperature, the greater effect MCR reductive state has on the biological system.

16. What is significant about the optimum pH for the MCR enzyme.

The optimum pH is close to the pH of water.

17. Why would a greater temperature favor the enzyme and hence the production of methane?

A great temperature would reduce the activation energy for the reaction and help in the production of methane.

Exercises:

1. A ***Hydropathicity Plot*** is a plot of the primary sequence of an amino acid sequence. The information taken from the primary sequence gives you information about the possible structure of a protein. Each amino acid is given a hydrophobicity score between 4.6 and -4.6. A score of 4.6 indicates that the amino acid is the most hydrophobic and a score or -4.6 indicates that it is the most hydrophilic. Copy the primary sequence from the information in POGIL above in to the hydrophobicity plot at http://gcat.davidson.edu/rakarnik/KD.html. Give a brief interpretation of what you observe.

   See Answer below.

2. Create a flow chart of the principles discussed in this POGIL. Start with Protein in the middle and include the terms listed below (not limited to). Write on the conection lines how the words relate to each other.

   Some words to use: enzyme, substrate, MCR, methane, structure, primary, secondary, tertiary, quaternary, subunits, temperature, pH, regulated.

Answers may vary.

References:

1. Grabarse, W., Mahlert, F, Duin, E.C., Goubeaud M., Shima, S., Tauer, R.K., Lamzin, V., & Ermler, U. 2001. On the Mechanism of Biological Methane Formation: Structural Evidence for Conformational Changes in Methyl-coenzyme M Reductase upon Substrate Binding. *J. Mol. Biol.,* 309, 315-330.

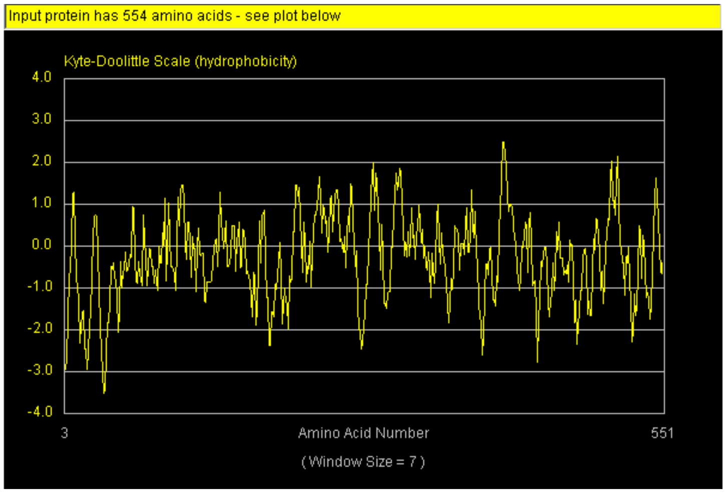
2. http://www.brenda-enzymes.info/php/result_flat.php4?ecno=2.8.4.1

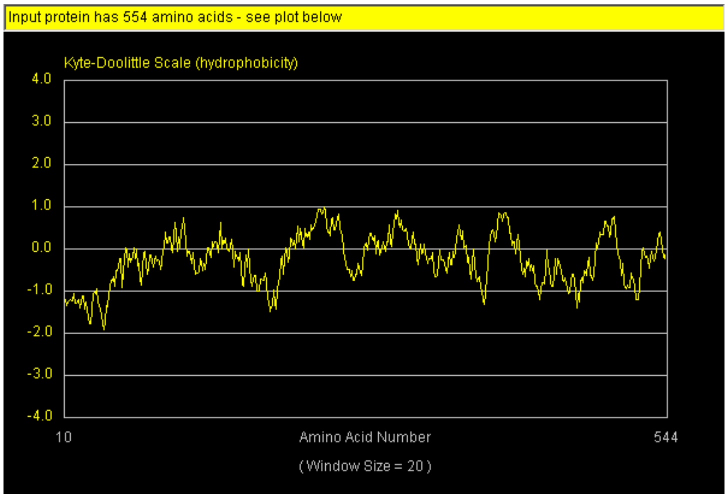
3. Bonacker, L.G.; Baudner, S.; Morschel, E.; Bocher, R.; Thauer, R.K.; (1993). Properties of the two isoenzymes of methyl-coenzyme M reductase in Methanobacterium thermoautotrophicum. *Eur. J. Biochem*. 217, 587-595.

4. http://matcmadison.edu/biotech/resources/proteins/labManual/chapter_2.htm

Answers to exercise #1.

Hydrophobicity Plots:


Input protein has 554 amino acids - see plot below


Input protein has 554 amino acids - see plot below

Hydrophobicity Plots:

According to the plots above, the alpha subunit does not appear to be membrane bound. None of the amino acids are close to the 1.9 threshold, which would indicate a trans-membrane region. The alpha subunit appears to be globular because of the equal amounts of hydrophilic and hydrophobic regions. Amino acids 38 and 388 have large negative values, which correspond to alpha helices in the secondary structure on the outside of the protein (hydrophilic regions). Hydrophobic residues are probably on the inside of the protein where the subunits bind.

Hydrophobic AA (Large y axis values):
negative values for the amino acids of: 25, 38, 190, 198, 388, 439, 474, 529
positive values for the amino acids of: 111, 146, 241, 309, 365, 408, 508