

# **Ocean Acidification & Methane Hydrates**

*By Jenny Griffin*

Continued atmospheric emissions of greenhouse gases such as carbon dioxide, methane and nitrous oxide have trapped heat within the Earth's atmosphere, causing a steady warming of the both the Earth's atmosphere and ocean waters. While warming in itself poses severe threats to the Earth and all its inhabitants, unfortunately it is not the only impact. Climate change involves a series of knock on effects that impact various ecosystems, many of which generate feed back loops that drive the cycle of warming, fueling further climate change.

## ***Carbon Cycle***

Carbon is constantly being exchanged between the three key carbon stores within the context of human induced climate change – the ocean, atmosphere, and terrestrial biosphere.

Dissolved carbon dioxide is assimilated by phytoplankton during the process of photosynthesis, and carbonate ions (in the form of calcium carbonate) are used as building blocks for skeletal and shell formation by zooplankton and other marine organisms, including pteropod snails, mussels, and corals.

When the plankton die their cells sink to the ocean floor taking the converted carbon down to the ocean sediments. Approximately a quarter of all carbon dioxide released into the atmosphere is taken up by the ocean, which effectively acts as a carbon sink, as large amounts of carbon dioxide are locked up in the ocean sediments for very long periods before being released back into the cycle. This process forms part of the natural carbon cycle, initially removing carbon dioxide from the atmosphere and then from the surface of the ocean, allowing more carbon dioxide to be absorbed by the ocean across the ocean-atmosphere interface.

## ***Ocean Acidification***

One of the more serious, though often overlooked, impacts of CO<sub>2</sub> emissions is ocean acidification. As part of the natural carbon cycle, carbon dioxide is absorbed by the oceans, dissolving in seawater to become part of the carbonate system – the largest

carbon pool on Earth – where it occurs in one of three forms: dissolved carbon dioxide, bicarbonate ions, or carbonate ions. When carbon dioxide moves from the atmosphere into seawater it can undergo a chemical reaction with seawater molecules to form carbonic acid, which results in a change in concentration levels of hydrogen carbonate and carbonate ions, which originate from carbonic acid.

As atmospheric CO<sub>2</sub> levels rise, the oceans are absorbing more and more carbon dioxide. However, while this does reduce atmospheric CO<sub>2</sub> levels it is significantly altering ocean chemistry, altering the pH of seawater which is gradually becoming more acidic, with severe implications to marine life and ocean ecosystems. Increasing ocean acidity is already starting to impact biodiversity and food webs in the marine environment, which will ultimately effect land based animals (including humans) that are dependent on these marine resources.

### ***Impact on Marine Life***

A major new international report published by the International Geosphere Biosphere Programme with input from 540 international scientists that attended the world's largest convention on ocean acidification ever – The Third Symposium on the Ocean in a High CO<sub>2</sub> World – held in Monterey, California (September 2012), suggests that ocean acidity may increase by as much as 170% by 2100, resulting in significant economic losses, particularly to communities who depend on the ocean's ecosystem services. People residing in developing countries are particularly vulnerable, according to the report titled: *Ocean Acidification: Summary for Policymakers*, which was presented at the COP19 climate talks held in Warsaw recently.

The report makes 21 statements about ocean acidification with a range of confidence levels from 'very high' to 'low'. These include:

#### **Very high confidence**

- Ocean acidification is caused by carbon dioxide emissions from human activity to the atmosphere that end up in the ocean.
- The capacity of the ocean to act as a carbon sink decreases as it acidifies
- Reducing carbon dioxide emissions will slow the progress of ocean acidification.
- Anthropogenic ocean acidification is currently in progress and is measurable
- The legacy of historical fossil fuel emissions on ocean acidification will be felt for centuries.

## **High confidence**

- If carbon dioxide emissions continue on the current trajectory, coral reef erosion is likely to outpace reef building some time this century.
- Cold-water coral communities are at risk and may be unsustainable.
- Molluscs (such as mussels, oysters and pteropods) are one of the groups most sensitive to ocean acidification.
- The varied responses of species to ocean acidification and other stressors are likely to lead to changes in marine ecosystems, but the extent of the impact is difficult to predict.
- Multiple stressors compound the effects of ocean acidification.

## **Medium confidence**

- Negative socio-economic impacts on coral reefs are expected, but the scale of the costs is uncertain.
- Declines in shellfisheries will lead to economic losses, but the extent of the losses is uncertain.
- Ocean acidification may have some direct effects on fish behaviour and physiology.
- The shells of marine snails known as pteropods, an important link in the marine food web, are already dissolving.

## ***Methane Hydrates***

Methane hydrates are part of a group of substances known as clathrates – substances where one type of molecule forms a crystal-like structure that encages another type of molecule within its structure. In the case of methane hydrates, methane gas is trapped within a cage of crystallized water molecules, sometimes referred to as methane ice.

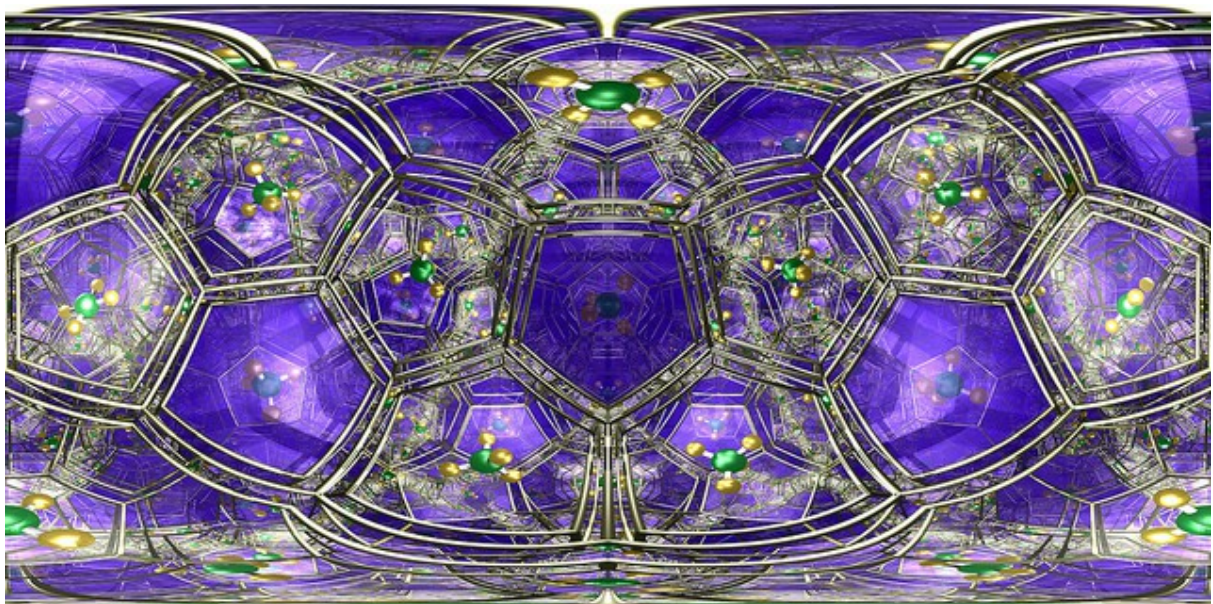


Figure 1(a). Methane Hydrate Interior. Dodecahedral cages are colored by blue - Image by Vitroid, via Flickr

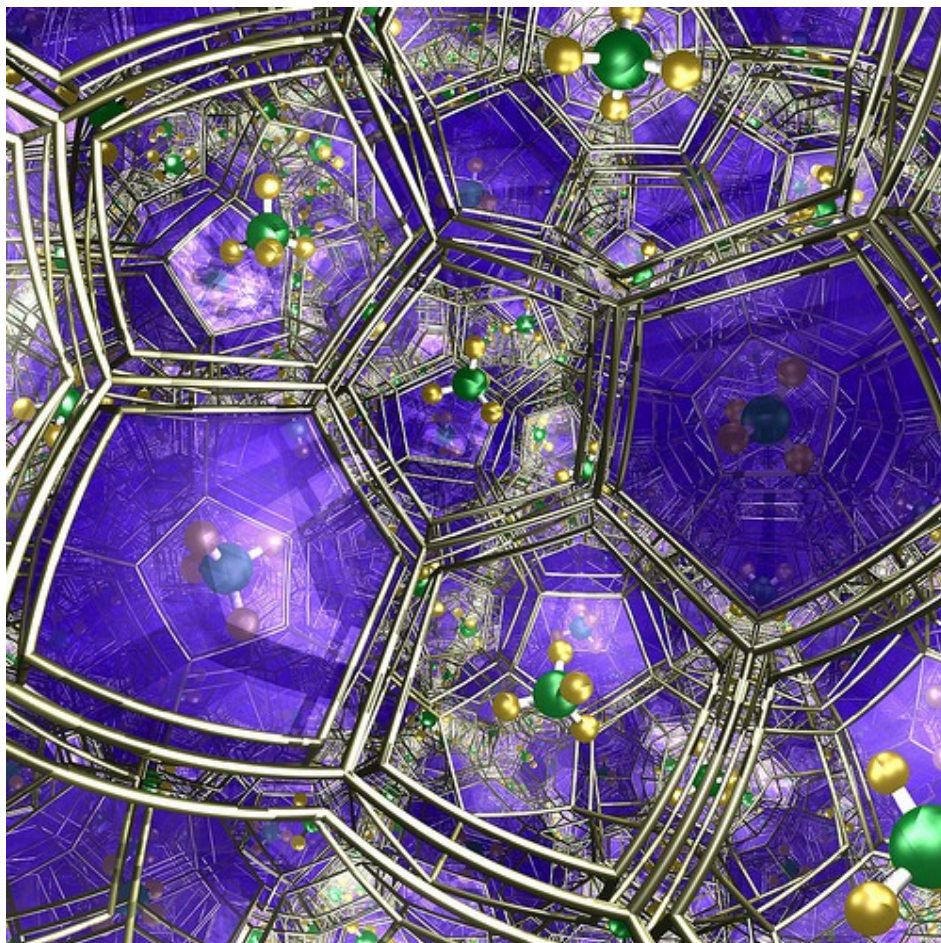


Figure 1(b). Type I clathrate structure of the methane hydrate. Dodecahedral cages are colored by blue –  
Image by Vitroid, via Flickr

## How are Methane Hydrates Formed?

Methane hydrates can only be formed under certain conditions. Conditions where the water temperature is low and the water pressure high are ideal for methane hydrates to form. When water temperatures become warmer, much higher water pressures are required for their formation (Figure 2).

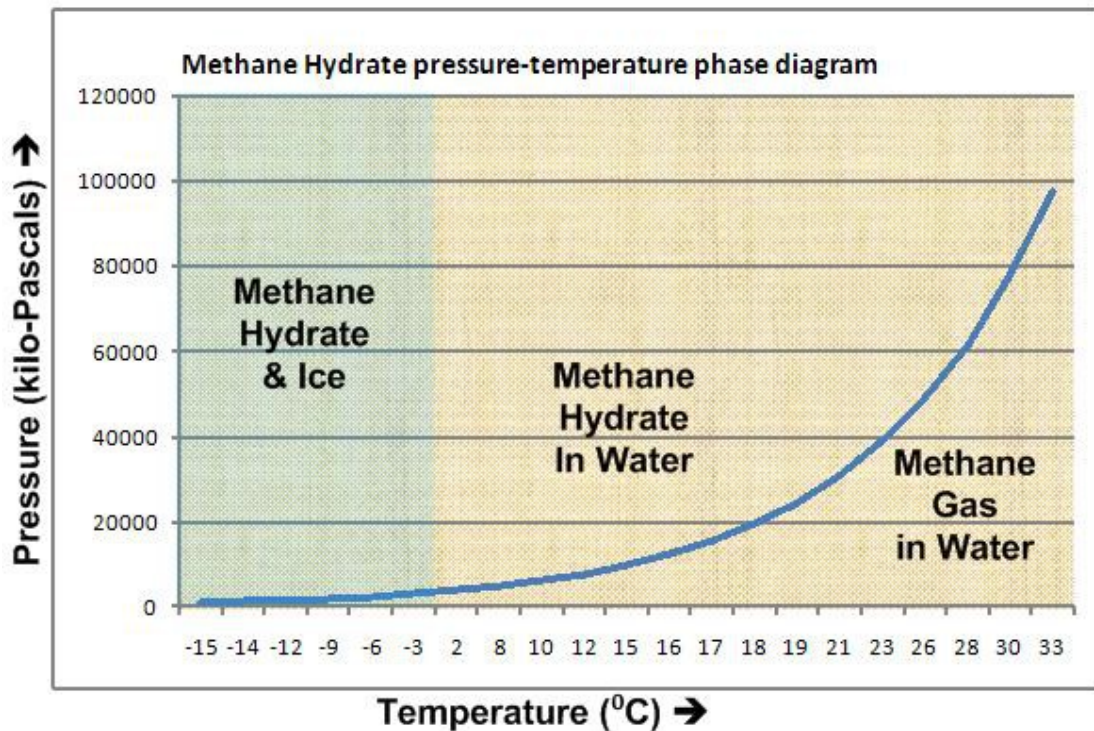


Figure 2. Image By Williamborg [Public domain], via Wikimedia Commons

Consequently methane hydrates are only found at great depths in warmer waters, but when water conditions are extremely cold they are able to form at shallower depths. Methane hydrates form at depths starting around 500 meters in the open ocean, where mean benthic water temperatures typically range between 2-4 degrees Celsius, but can be found at depths of less than 200 meters on the Arctic shelf and even within permafrost of frozen terrestrial soils of the Arctic, where conditions are extremely cold.



*Figure 3. Methane hydrate chunk with dissociating methane gas –  
Image: By U.S. Geological Survey [Public domain], via Wikimedia Commons*



*Figure 4. Structure of a gas hydrate (methane clathrate) block embedded in the sediment of hydrate ridge, off Oregon, USA. The gas hydrates have been found during a research cruise with the German research ship FS SONNE in the subduction zone off Oregon in a depth of about 1200 meters in the upper meter of the sediment – Image By Wusel00, via Wikimedia Commons*

However, in order for methane hydrates to form, there must be a supply of methane. When organic matter from animal waste and dead marine organisms drifts down to the seabed, it is broken down by microbes that release methane as a by-product of the decomposition process. Even though conditions are extremely favorable for the formation of methane hydrates in the deepest regions of the oceans – these areas have extremely cold water

temperatures together with extremely high water pressures – it does not occur here, as there is insufficient methane available. There are two reasons for this: firstly, the open ocean is relatively nutrient poor and thus less productive than the continental shelf; and secondly, in deeper water organic matter is typically broken down before it reaches the seafloor, so less and less organic material reaches the seafloor as it becomes deeper.

### Stability of Methane Hydrates

Because methane hydrates can only form under certain conditions, it is highly likely that ocean warming could cause them to become unstable, releasing the methane gas trapped within the frozen crystalline hydro-structures. Similarly, gas hydrates that exist under Arctic permafrost or ice can be released due to melting caused by warmer air temperatures or rising sea levels and warmer ocean temperatures (Figure 5).

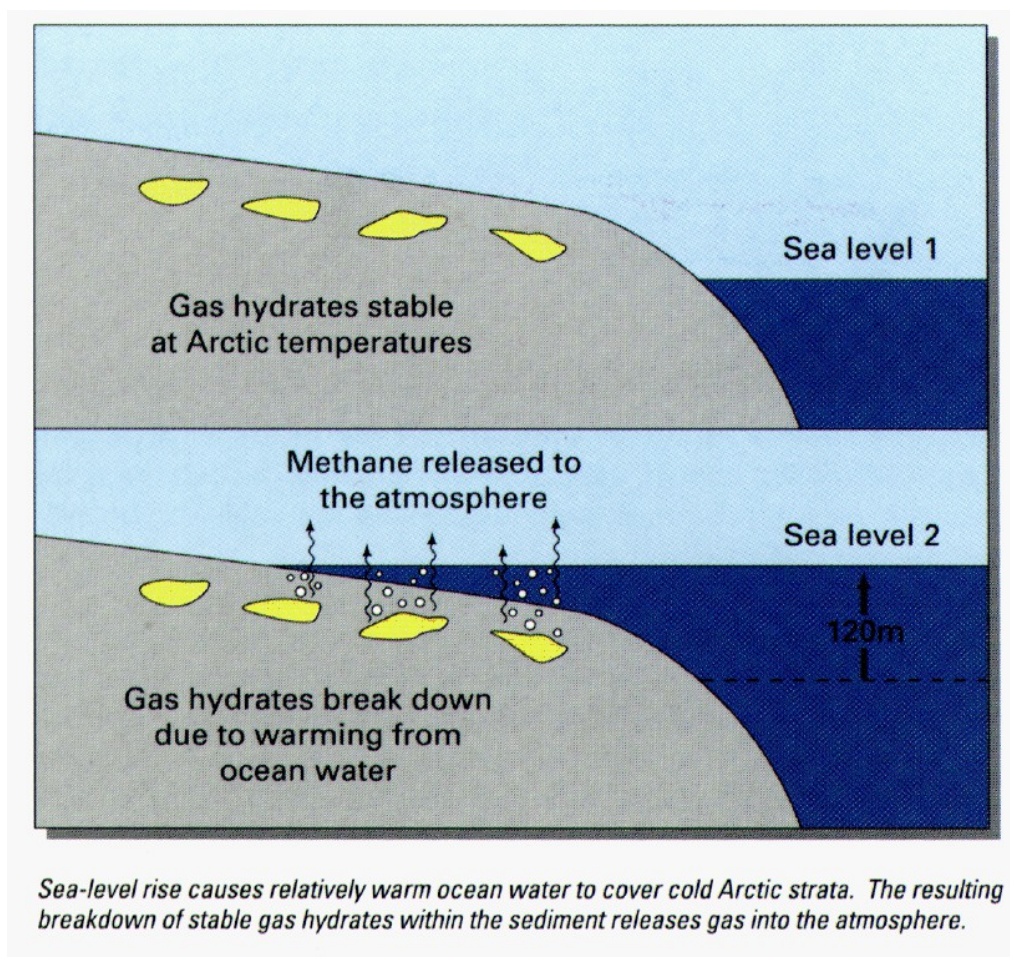


Figure 5. Image: By Dr. William Dillon, U.S. Geological Survey [Public domain], via Wikimedia Commons

Looking back on previous climate change events in the Earth's history, it is evident that climate change can in fact cause methane hydrates to destabilize and release methane.

Considering that methane is a powerful greenhouse gas, 20 times more potent than CO<sub>2</sub> in terms of its warming potential, there is a real concern that this could further enhance global warming, driving climate change over the brink.

It is therefore vitally important that we better understand: 1) the impact of warming on the stability of methane hydrates; and 2) what happens to the methane once it is released from the seabed.

### **What Happens When Methane Hydrates Melt?**

When methane hydrates melt, only some of the methane released is emitted to the atmosphere. Most of the methane that is released is expected to be broken down by bacteria as it rises up through the ocean sediments and through the water column before it reaches the surface of the ocean. The decomposition of methane occurs as the result of two biological processes:

- anaerobic oxidation of methane by bacteria in the sediments of the ocean floor
- aerobic oxidation of methane by bacteria in the water column.

**Anaerobic Oxidation:** When methane is broken down anaerobically by microbes within the ocean sediments they use sulphates in the decomposition process, converting methane to bicarbonate. The bicarbonate may react with calcium ions within seawater forming calcium carbonate, which precipitates to the ocean floor, where it remains stored in the sediments for long periods, effectively rendering the methane harmless in terms of its warming capability. During this process, hydrogen sulphide is formed from the sulphates, providing an energy source for chemosynthetic organisms such as symbiotic tubeworms and clams.

**Aerobic Oxidation:** When methane is broken down aerobically by bacteria in the water column they use oxygen to facilitate the process, producing carbon dioxide which dissolves in the seawater. This process negatively impacts marine environment in two ways:

1. Carbon dioxide promotes ocean acidification.
2. Aerobic oxidation of methane utilizes oxygen within the water column which could result in the expansion of oxygen depleted zones across the ocean. Oxygen depletion can result in mass mortalities of marine organisms – oxygen poor zones are unable to support animals that need oxygen for survival and are thus typically devoid of marine life.



In order for bacteria to decompose methane it must be dissolved in the seawater. Bacteria are able to decompose methane more effectively when it moves through the sediments or water column slowly. Scientists estimate that approximately 90% of methane currently released from the seabed is oxidized either aerobically or anaerobically before it reaches the atmosphere. The concern is that should methane hydrates be rapidly released from the gas hydrates, there is a good possibility that it could ascend to the surface as gas bubbles that the bacteria would not be able to break down. This is of particular concern in areas where methane hydrates occur at shallow depths, as the released methane gas is not able to completely dissolve in the water before it reaches the surface, where it migrates to the atmosphere. Should this occur it could rapidly accelerate global warming, with dire consequences to our planet.

### ***Mass Extinction Event***

Even more alarming is that if ocean acidification is left unchecked it could potentially initiate a Great Mass Extinction Event, as there is increasing evidence pointing to high atmospheric carbon dioxide concentrations and rapidly acidifying oceans having triggered four of the previous five [Great Mass Extinctions](#).

Based on geological records it can be assumed that hydrates have broken down on a large scale numerous times in the Earth's history, leading to extreme global warming and massive extinctions of organisms on the sea floor and beyond.

### ***Conclusion***

While methane may be broken down into a less harmful form, when methane is oxidized the problem doesn't simply go away. Methane oxidizes into carbon dioxide both in seawater and in the atmosphere, adding to the carbon dioxide levels in both these realms. As we have seen, carbon dioxide in seawater contributes to ocean acidity, while atmospheric carbon dioxide traps heat and promotes warming – though not quite to the extent that methane would – and as atmospheric CO<sub>2</sub> levels rise, so too will the CO<sub>2</sub> that is absorbed into the ocean. It is a classic feedback loop that feeds into itself, having the potential to accelerate global warming and climate change to a tipping point – the point of no return.

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