Chapter 24
Marine hydrates – a potentially emerging issue

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Keynote points

- Marine hydrates (mainly methane hydrates) exist primarily on continental slopes where there are large quantities of methane gas in the ocean, the pressure is high enough and the temperature is low enough.
- Concern has been expressed about the climatic risks resulting from the sudden release of large amounts of methane from marine hydrates. However, that hypothesis is not widely supported at present and is not mentioned in the recent special report of the Intergovernmental Panel on Climate Change on the ocean and cryosphere in a changing climate.
- Areas of gas seepage in the deep sea associated with gas hydrates host a very rich level of biodiversity supported by chemosynthetic bacteria.
- Initial successes have recently been noted by China and Japan in producing methane from marine methane hydrates.

1. Introduction

The first *World Ocean Assessment* (United Nations, 2017c) did not contain detailed material on marine hydrates. In the overall summary, it was noted that they were among the deep-water deposits that had generated continuing interest, but were not mined at that time.

It was reported in chapter 21 of the first Assessment that marine hydrates were a potential area for future offshore energy development, and an estimate was provided of the amount of marine hydrates and their carbon equivalent worldwide. While hydrates potentially represent an immense store of hydrocarbons, it was noted in the chapter that methane production from hydrates had not been documented beyond small-scale field experiments and that its relevance to the global gas supply was likely to be overshadowed by the increased development of onshore natural gas.

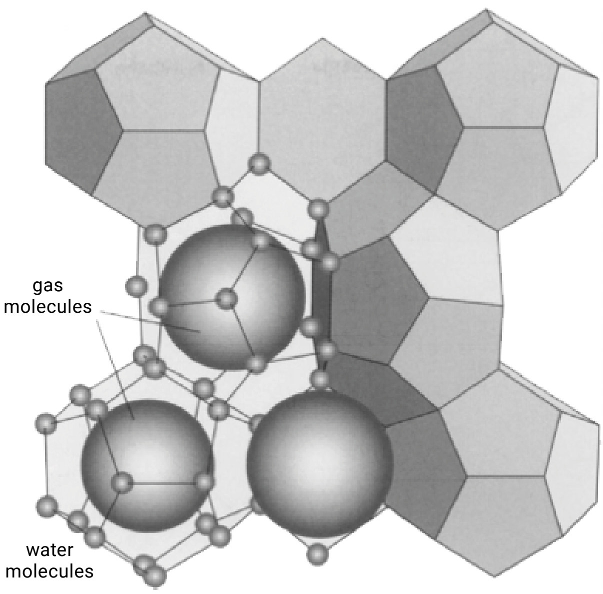
In chapter 35 of the first Assessment, it was noted that, because of the close relationship of gas seeps on continental margins to areas of interest for resource exploration (oil, gas and methane hydrates), an assessment of the nature of the associated rich biodiversity and its role in ecosystem functioning would be important before potential alterations and extractions could be carried out. Such biodiversity is discussed in chapter 7P of the present Assessment on hydrothermal vents and cold seeps.

The present chapter is aimed at providing a fuller assessment of the origin and estimated abundance of marine hydrates, their potential as a source of energy and the associated risks to the Earth's climate, slope stability and human society.

2. What are marine hydrates?

A marine hydrate is a crystalline solid composed of natural gas molecules retained within an ice-like cage of water molecules. The most common form of marine hydrate is methane hydrate, which has the chemical formula $(CH_4)_4(H_2O)_{23}$, or 1 mole of methane for every 5.75 moles of water, corresponding to 13.4 per cent methane by mass (Maslin and others, 2010; Chou and others, 2000). Marine hydrates are often referred to as marine or methane clathrates (from the Latin "clathri", meaning "lattice"), since the water molecules form a lattice within which the gas molecules are held. A schematic drawing of a gas hydrate is shown in figure I.

Figure I
Typical structure of a gas hydrate, with water molecules linked together to form a cage that traps gas molecules, such as methane, within



Source: Maslin and others, 2010.

Methane hydrates were first recognized in the late nineteenth century (Wróblewski, 1882; Villard, 1894). In the 1930s, they were identified in nature when their formation clogged natural gas pipelines in cold weather. In the 1950s, theoretical models for gas hydrates were developed and, in the 1960s, Russian scientists, including Vasiliev, argued that substantial marine deposits existed around the world (Vasiliev and others, 1970). That conclusion was confirmed in the early 1970s by the retrieval of samples of methane hydrates from the seabed in the Black Sea (Yefremova and Zhizhchenko, 1974). Since then, there have been similar retrievals around the world (see figure II), and countries such as Canada, China, Germany, India, Japan and the United States of America have established major hydrate research programmes (Sloan and Koh, 2007; Maslin and others, 2010; Song and others, 2014).

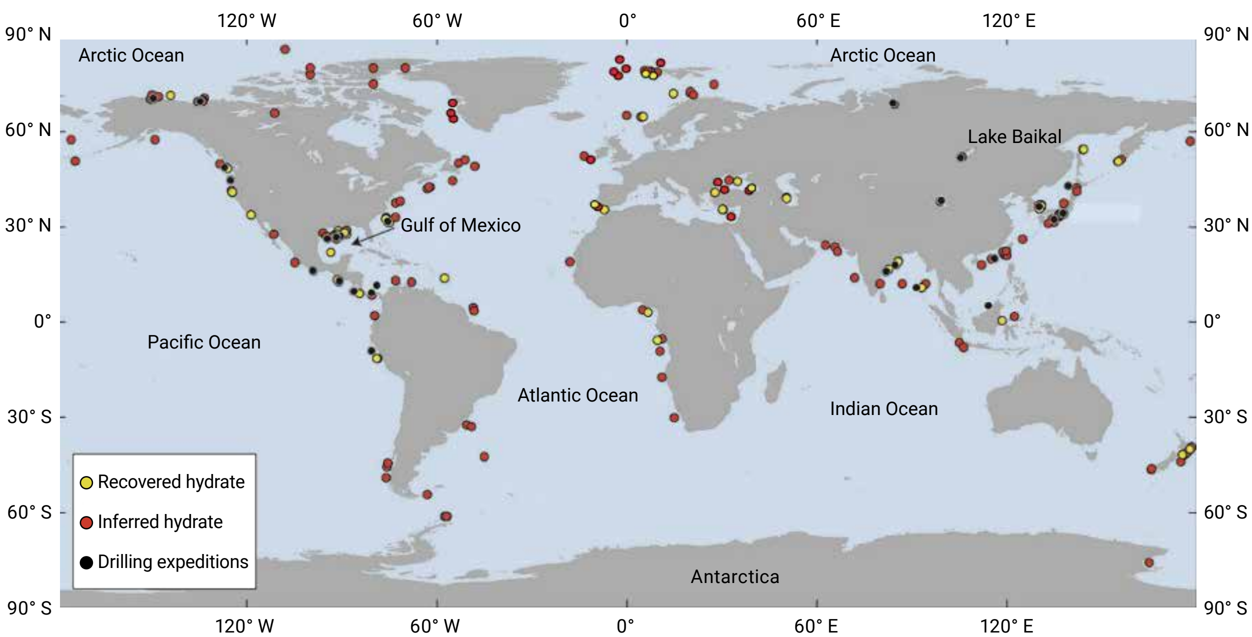
2.1. Location and scale of marine hydrates

Gas hydrates occur in areas of significant gas generation in which the temperature is sufficiently low and the pressure is sufficiently high to form and maintain them. The vast majority of gas hydrates occur as marine hydrates, while just over 1 per cent are located in permafrost soils (Ruppel, 2015). Most marine hydrates are formed by the accumulation of methane produced from the degradation of organic matter in buried sediments. Gas hydrate deposits (often several hundred metres thick) are embedded in sediments (Milkov and Sassen, 2002; Ruppel and Kessler, 2017). Marine hydrates are primarily driven by gas flowing through faults and channels in the sedimentary column and can be found exposed at the sea floor.

Marine hydrate distribution is driven by the combination of a gas source, water depth (usually more than 500 m, but dependent on gas composition) and temperature (geothermal gradient) to stabilize hydrates and the permeability of sediments. The most common way of inferring the presence of gas hydrates is by seismic investigation: the boundary between the gas hydrates and the underlying sediments that contain free gas reflects forms with a negative impedance contrast, which mimics the sea floor (bottom-simulating reflector) and can be interpreted to show the base of the gas hydrate stability zone. Sea floor samples can also be taken directly with cores or other sampling devices, but special steps need to be taken to maintain their stability when they are brought to the surface (Maslin and others, 2010). Seismic data indicate that methane hydrates are found in the sediments of the continental slope, while those in the Arctic Ocean are at lesser depths because of the lower temperature of the water column (Dillon and Max, 2012). In the middle of ocean basins, where the biogenic generation of gas is low owing to a lack of organic material, and in marginal seas where sea floor pressure is lower, hydrates do not form. Hydrates also form in and below the terrestrial permafrost soils of Alaska and Siberia (Maslin and others, 2010). Figure II shows a recent map of known and inferred locations of methane hydrates.

The presence of marine hydrates is constrained by the conditions in which they can persist. First, there needs to be a source of gas, generally methane of biogenic origin, derived from the decaying of organic material trapped in seabed sediments, that leads to the presence of methane in quantities greater than that which is soluble in the surrounding waters. Second, there has to be an appropriate combination of high pressure and low temperature at the sea floor. In Arctic waters, where the temperature is very low, the necessary pressure can, depending on the gas composition, be found at depths as shallow as 400 m. In warmer waters, depth as great as 1,000 m can be required. Third, there is a lower limit to the occurrence of marine hydrates: even at high pressures, the increase in temperature with regard to depth below the sea floor (geothermal gradient) will set a limit on the stability of marine hydrates at approximately 1,600 m (Kvenvolden and Lorenson, 2001; Maslin and others, 2010). The presence of methane hydrates can also act as a seal for free gas, thus retaining substantial amounts of methane in the sediments below them (Hornbach and others, 2004).

Figure II
Map showing locations where gas hydrate has been recovered, where gas hydrate is inferred to be present on the basis of seismic data and where gas hydrate drilling expeditions have been completed in permafrost or deep marine environments, also leading to the recovery of gas hydrate



Source: Ruppel, 2018, amended to reflect Ryu and others, 2013; Minshull and others, 2020.[1]
Note: Any boundaries or names shown and designations used on the map do not imply official endorsement or acceptance by the United Nations.

[1] The writing team is grateful to Chibuzo Ahaneku Valeria for his assistance in updating the map.

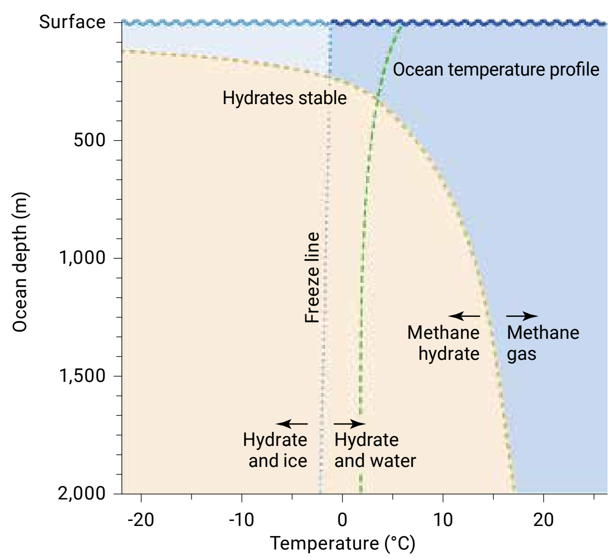
In 1988 and 1990, two independent estimates indicated a total global hydrate quantity of 21 × 10^{15} m^3 (MacDonald, 1990; Kvenvolden, 1999), which became a consensus view. However, in 2011, on the basis of an exhaustive review of other assessments and considering the lessons of many drilling programmes, it was estimated that there was 3 × 10^{15} m^3 of methane gas in place, calculated at the standard temperature and pressure (Boswell and Collett, 2011). That is similar to the lower end of the range (between 1–5 and 15–20 × 10^{15} m^3) calculated by Milkov (2004) and more than 30 times smaller than the 1 × 10^{17} m^3 estimated by Klauda and Sandler (2005). Some experts still support a larger estimate (Kvenvolden, 2012). The Milkov range equates to between 500–1,000 and 7,500–10,000 gigatons of carbon (Maslin and others, 2010). By way of comparison, the United States Geological Survey estimated in 2000 that the total reserves of all other fossil fuels contained 5,000 gigatons of carbon (United States Geological Survey World Energy Assessment Team, 2000). Subsequent work has supported the call for further research into the global total of marine hydrates on the basis of a wide-ranging discussion held at The Royal Society in London in 2010 (Day and Maslin, 2010).

3. Potential risks from marine methane hydrates

3.1. Risks in relation to the atmosphere

Methane is a powerful greenhouse gas with a heat-trapping potential over 100 years, estimated by the Intergovernmental Panel on Climate Change to be 25 times that of carbon dioxide (Intergovernmental Panel on Climate Change (IPCC), 2013). Some more recent calculations suggest that the factor should be higher, possibly by as much as 25 per cent (Etminan and others, 2016). For the decade 2008–2017, global methane emissions were estimated at 0.572 gigatons of methane per year (Saunois and others, 2019). The temperature and pressure dependence of gas hydrate stability, mainly temperature (see figure III), has led to a perception that global warming could cause catastrophic methane release from gas hydrate reservoirs (the clathrate gun hypothesis) (Henriet and Mienert, 1998; Haq, 1999). A similar mechanism has also been proposed as a way of explaining periods of rapid warming during the Quaternary Period (Kennett and others, 2000; Maslin and others, 2004). However, that hypothesis is not widely supported, and empirical evidence is inconclusive (Sowers, 2006; O'Hara, 2008).

Figure III
Methane hydrate stability



Source: https://commons.wikimedia.org/wiki/File:Undersea_methane_hydrate_phase_diagram.svg.

In a recent thorough review of the interaction between climate change and methane hydrates, it was concluded that there was no current evidence from observations that hydrate-derived methane was reaching the atmosphere or that the amounts that could potentially reach the atmosphere were significant enough to affect the overall methane budget. It was further noted that, in considering potential effects on methane flux to the atmosphere from the dissociation of marine methane hydrates, it was essential to consider the processes (sinks) that would intercept the methane before it reaches the atmosphere: in passing through sediment, methane may be broken down though anaerobic oxidation by microbes. In general, the conclusion is that methane from dissociated hydrates would not reach the atmosphere; it might dissolve in water in the sediment or in the water column, and it might be broken down further by microbial oxidation in the water column. However, more observational data and improved numerical models are needed to better characterize the climate-hydrate synergy in the future (Ruppel and Kessler, 2017).

Thus, the role of methane hydrates in contemporary and future climate change is unclear. Rather than with catastrophic, abrupt impacts, the release of methane from marine hydrates in response to rising ocean temperatures may have occurred gradually in the past and may occur over time scales of millenniums or longer (Archer, 2007; Archer and others, 2009).

However, the Arctic Ocean is warming at a faster rate than the rest of the globe (Larsen and others, 2014), and there is evidence of significant methane release into it, which may come from near-shore, submarine permafrost on the East Siberian Arctic Shelf (Shakhova and others, 2014). However, seasonal changes in the mixing of the water column appear to prevent methane from reaching the atmosphere during the summer (Yurganov and others, 2019).

In its recent special report on the ocean and cryosphere in a changing climate (IPCC, 2019), the Intergovernmental Panel on Climate Change did not mention marine hydrates, except to note (in chap. 5 of the report), with low confidence, that rising bottom temperatures or the shifting of warm currents on continental margins could increase the dissociation of buried gas hydrates on margins, potentially intensifying anaerobic methane oxidation (which produces hydrogen sulphide) and expanding the cover of methane-seep communities.

3.2. Risks in relation to seabed stability

When enclosed in sediments, and when the saturation is high enough, gas hydrates can act like cement, compacting and stabilizing the sea floor. However, if formed in deposits that are still unconsolidated, gas hydrates prevent the normal increase in compaction as the weight of the sediment increases. If destabilized by lower pressure or, in particular, by increased sea floor temperature, the gas hydrate can then dissociate. If that occurs, submarine slope failures may occur (Maslin and others, 2010). One particularly notable case in which gas hydrates are thought to have been implicated is the Storegga slide off the middle of the west coast of Norway, dated to about 8,200 years ago. According to calculations, it had a volume of 3,000 km^3 and produced a tsunami that affected Norway, the Faroe Islands (Denmark), Scotland and northern England (United Kingdom of Great Britain and Northern Ireland), with a run-up of up to 20 m. While an earthquake was probably the proximate cause, the dissociation of marine hydrates appears to have contributed significantly to the occurrence (Bondevik and others, 2005; Bryn and others, 2005; Micallef and others, 2009). In general, the consensus at present seems to be that, while the dissociation of marine hydrates can contribute to the scale, and thus the impact, of major slope failures, there is usually a separate trigger in the form of an earthquake or extreme weather event (Tappin, 2010).

4. Marine hydrates as a source of energy

Methane, as natural gas, is a well-known source of energy. Several countries have undertaken large research programmes to investigate the possibilities of using marine hydrates as a source of natural gas. Because of their lack of terrestrial natural gas resources, China and Japan are among the States that have put most effort into such exploration.

Japan established the Research Consortium for Methane Hydrate Resources in Japan (MH21) in 2002 to explore and develop energy from marine hydrates in its seas. The consortium brought together the Japan Oil, Gas and Metals National Corporation, the National Institute of Advanced Industrial Science and Technology and the Engineering Advancement Association of Japan. The work was planned in three phases. The first phase ran from 2002 to 2008 and involved cooperation with a number of other States, including Canada, Germany, India and the United States. The main outcomes were improved knowledge of the marine hydrate resources of Japan and two successful onshore methane hydrate production tests, yielding about 13,000 m^3 of methane. In the second phase, from 2008 to 2015, a successful offshore production test was run, an environmental impact assessment was developed and economic valuation and field verification was completed. The third phase, of which the major focus is to establish a technical platform for commercialization, is still in progress. The significance of the programme has increased since the great east Japan earthquake in 2011, which led to a policy of reducing planned dependence on nuclear energy (Oyama and Masutani, 2017). Through a collaborative effort between the National Energy Technology Laboratory of the Department of Energy, the Japan Oil, Gas and Metals National Corporation, the United States Geological Survey and Petrotechnical Resources of Alaska, in cooperation with Prudhoe Bay unitholders, a natural gas hydrate test well was drilled, which showed two gas hydrate reservoirs suitable for future testing. The Prudhoe well struck reservoirs at about 700 m and 844 m below the surface. According to the United States Geological Survey, gas hydrate was found to be filling 65 to >80 per cent of the spaces, or porosity, between the grains of sand and silt in the upper reservoir that comprise the rock formation. Japan is also collaborating with the United States to carry out production testing within the Prudhoe Bay unit in the fiscal year 2021/22. The experience gained through that collaboration will help Japan in its endeavour to conduct pilot testing in the fiscal year 2027/28.

Energy-related exploration for methane hydrates has been extensive in the Gulf of Mexico. The first leg of the Gulf of Mexico Gas Hydrates Joint Industry Project was undertaken in 2005 to develop technology and collect data to assist in the characterization of naturally occurring gas hydrates in the deep water of the Gulf of Mexico. The primary goal of the programme was to understand the impact of hydrate exploitation on sea floor stability and climate change, along with an assessment of the potential of methane hydrate as a future energy resource. Chevron, ConocoPhillips, Halliburton, Japan Oil, Gas and Metals National Corporation, Reliance Industries, Schlumberger, Total and the United States Mineral Management Service participated in collaboration with the Georgia Institute of Technology, Rice University and the United States Geological Survey. The investigation (Ruppel, 2018) revealed that drilling for gas hydrate in fine-grained sediments can be done safely without the expected disruption of the sea floor owing to hydrate dissociation. The results brought to light the importance of focused gas flow through localized permeability zones such as the sand body or fractures in forming hydrate deposits with a very limited lateral extent. The results also emphasized the relatively lower importance of features of the sea floor, such as mounds, and hydrates in decisions regarding coring sites for larger reserves at greater depths. Coring, drilling and wireline operations were carried out at water depths of more than 500 m, to depths of between 200 m and 459 m below the sea floor. As part of the second leg of the Gulf of Mexico Gas Hydrates Joint Industry Project, in 2009, the primary goal was to collect logging while drilling data through expected gas hydrate-bearing sand reservoirs in seven wells at three locations in the Gulf of Mexico. The findings of the second leg suggest that high-saturation gas hydrate sands free of trapped free gases are safe for exploitation since they do not present drilling hazards. The discovery of thick hydrate-bearing sands at Walker Ridge and Green Canyon validates the integrated geological and geophysical approach used in the pre-drill site selection process, and provides increased confidence in the assessment of gas hydrate volumes in the Gulf of Mexico and other marine sedimentary basins.

The National Gas Hydrate Program of India undertook the second expedition on board the drilling vessel *Chikyu* between March and July 2015 in the deep waters of the Krishna Godavari Basin, in collaboration with the Japan Agency for Marine-Earth Science and Technology and the United States Geological Survey. The objective of the expedition was to confirm the presence of sand-bearing hydrate reservoirs identified from seismic data and to calculate the reserves from the hydrate saturation percentage and sand body dimensions. Pressure coring, logging while drilling, wireline logging and formation testing operations were carried out as part of the programme. The expedition (Collett and others, 2019) confirmed the predicted slope-basin interconnected depositional model with sand-rich channel-levee facies saturated with methane hydrate in the Krishna Godavari Basin. The exceptionally detailed petrophysical information acquired through closely spaced logging while drilling and bore holes in area B of the L1 block gas hydrate accumulation has provided one of the most complete three-dimensional petrophysical-based views of any known gas hydrate reservoir system in the world.

Methane hydrate has been identified as a potential new gas source for China, and the South China Sea is believed to contain some of the world's most promising deposits. In China, a substantial number of institutions have undertaken investigations into the possibility of using marine hydrates as a source of energy, in particular the technology that would be needed to recover them. The methods considered include depressurization and thermal stimulation. Research has also been focused on the security of methane hydrate-bearing sediments during gas production and the related environmental impact (Song and others, 2014). The China Geological Survey conducted an initial production test and recovered 309,000 m^3 of methane from marine hydrates in the Shenhu area of the South China Sea between 10 May and 9 July 2017 (Li and others, 2018). China extracted 861,400 m^3 of natural gas from methane hydrate, known as "flammable ice", during a one-month trial production operation in the South China Sea, following its first experimental gas extraction from methane hydrate in 2017, during which a total of 309,000 m^3 of natural gas was produced in a 60-day period.

5. Key knowledge and capacity-building gaps

There are obvious gaps in knowledge of the global distribution and size of deposits of methane hydrates. The map in figure II shows that, for much of the world, assessments of the presence of gas hydrates are largely based on extrapolation rather than direct observation. Likewise, estimates of the global amounts of hydrate present are largely based on estimates of the volume of the methane hydrate stability zone, regardless of evidence of the presence or absence of gas to form them. Furthermore, abiogenic methane generation by ocean crust serpentinization, a major process in the ocean, has been largely ignored. A review of gas hydrates in Europe has recently been published (Minshull and others, 2020), but there is still no updated review at the global level.

There are also major gaps in understanding how methane hydrates will behave in changing circumstances, especially changes in ocean temperature, the way in which methane hydrates may dissociate and the way in which any methane released will then behave, and its impacts on climate and slope stability. Futhermore, it remains to be determined whether the oxidation of methane venting from the sea floor, presumably some sourced from dissociating hydrates, contributes significantly to ocean acidification. Such knowledge gaps have the possibility of being very significant in relation to the release of oceanic methane into the atmosphere and its consequent function as a greenhouse gas, even though the predominant opinion is that such a possibility is limited (see sect. 4 above).

Capacities are clearly being developed in China, Japan and elsewhere to enable access to methane stored as marine hydrates. At present, these are at the experimental or testing stage but could become important for States with limited access to natural gas.

6. Outlook

The outlook therefore depends very much on demand for natural gas in the context of reducing the consumption of coal and other fossil fuels, on the success of experiments in providing access to methane hydrates and on the further identification of locations of significant methane hydrate deposits that may justify their exploitation.

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