



FROZEN HEAT

A GLOBAL OUTLOOK ON METHANE GAS HYDRATES

VOLUME ONE



UNEP

GRIID
ARENDAL



Beaudoin, Y. C., Waite, W., Boswell, R. and Dallimore, S. R. (eds), 2014.
Frozen Heat: A UNEP Global Outlook on Methane Gas Hydrates. Volume 1.
United Nations Environment Programme, GRID-Arendal.

© United Nations Environment Programme, 2014

ISBN: 978-92-807-3429-4

Job No: DEW/1866/NO

This publication may be reproduced in whole or in part and in any form for educational or non-profit purposes without special permission from the copyright holder, provided acknowledgement of the source is made. The United Nations Environment Programme (UNEP) would appreciate receiving a copy of any publication that uses this publication as a source. No use of this publication may be made for resale or any other commercial purpose whatsoever without prior permission in writing from the United Nations Environment Programme. Applications for such permission, with a statement of purpose and intent of the reproduction, should be addressed to the Division of Communications and Public Information (DCPI), UNEP, P.O. Box 30552, Nairobi 00100, Kenya. The use of information from this publication concerning proprietary products for publicity or advertising is not permitted.

DISCLAIMERS

The contents of this publication do not necessarily reflect the views or policies of UNEP or contributory organizations and neither do they imply any endorsement. The designations employed and the presentation of material in this publication do not imply the expression of any opinion whatsoever on the part of UNEP concerning the legal status of any country, territory or city or its authorities, or concerning the delimitation of its frontiers or boundaries. Mention of a commercial company or product in this publication does not imply endorsement by UNEP.

Edited by Yannick Beaudoin, GRID-Arendal

Guest Editors: William Waite, US Geological Survey

Ray Boswell, US Department of Energy

Scott Dallimore, Geological Survey of Canada – Natural

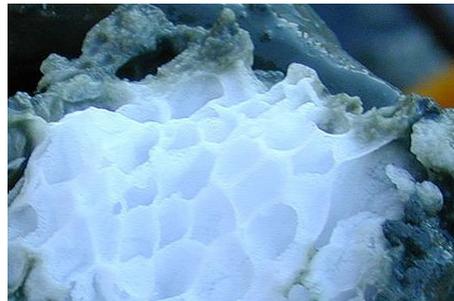
Resources Canada

Design and layout by GRID-Arendal

Printed by Birkeland Trykkeri A/S, Norway



UNEP promotes environmentally sound practices globally and in its own activities. This publication is printed on fully recycled paper, FSC certified, post-consumer waste and chlorine-free. Inks are vegetable-based and coatings are water-based. UNEP's distribution policy aims to reduce its carbon footprints.



FROZEN HEAT

A GLOBAL OUTLOOK ON METHANE GAS HYDRATES

VOLUME ONE

GUEST EDITORS

William Waite, Ray Boswell, Scott Dallimore



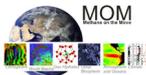
Natural Resources
Canada
GEOLOGICAL SURVEY
OF CANADA



Ressources naturelles
Canada
COMMISSION GÉOLOGIQUE
DU CANADA



JOGMEC



CONTENTS

11

Chapter 1 What are Gas Hydrates?

- 12 1.1 Introduction
- 14 1.2 What are Gas Hydrates?
- 16 1.3 Gas Hydrate Formation, Stability, and Occurrence
- 21 1.4 What Forms Do Gas Hydrates Take in Nature?

31

Chapter 2 Methane Gas Hydrates and the Natural Carbon Cycle

- 33 2.1 Introduction
- 34 2.2 Methane Generation and Consumption
- 40 2.3 A Gas Hydrate Capacitor in the Global Carbon Cycle?
- 42 2.4 Life at Marine Methane Seeps

51

Chapter 3 Assessment of the Sensitivity and Response of Methane Gas Hydrate to Global Climate Change

- 52 3.1 Introduction
- 53 3.2 The Role of Gas Hydrate in Past Climate Change
- 54 3.3 Key Issues for Linking Gas Hydrate with Climate Change
- 55 3.4 Global Climate Change Projections
- 57 3.5 Response of Gas Hydrates to Climate Change
- 68 3.6 Review of Sensitivity of Global Gas Hydrate Inventory to Climate Change
- 71 3.7 Conclusions

FOREWORD



Growing energy demands, uncertainty about supplies, and the urgent need to reduce emissions of greenhouse gases mean that the world faces an uncertain energy future. Many countries have begun to explore alternative energy sources, including so-called unconventional fossil fuels such as natural gas hydrates.

Gas hydrates generally occur in relatively inaccessible polar and marine environments, which is why they have not been extensively studied until recently. Research about naturally occurring gas hydrates has increased markedly over the past two decades, however, and understanding about where hydrates occur and how they might be exploited is growing rapidly. Japan has recently tested offshore production of natural gas from a hydrate reservoir located more than 1,300 metres below the sea's surface and other countries are also actively exploring production potentials.

Continuing a tradition of identifying emerging issues, the Global Outlook on Methane Gas Hydrates is the result of

a rigorous assessment process designed to ensure the availability of scientifically credible and policy-relevant information. This assessment format brings together diverse strands of knowledge and is a key mechanism through which science informs decision-making.

This report provides a basis for understanding how gas hydrates occur and the emerging science and knowledge as to their potential environmental, economic, and social consequences of their use. The intention of this publication is to enable sound policy discourse and choices that take into account a number of important perspectives.

A handwritten signature in black ink that reads "Achim Steiner". The signature is fluid and cursive, with a long horizontal stroke at the end.

Achim Steiner
UN Under-Secretary General
and Executive Director of UNEP

PREFACE

Methane gas hydrates are solid, ice-like combinations of methane and water (Fig. I.1) that are stable under conditions of relatively high pressure and low temperature. Gas hydrates contain most of the world's methane and account for roughly a third of the world's mobile organic carbon. Because gas hydrates tend to occur in relatively inaccessible and harsh polar and marine environments, they were not studied extensively until recently. For more than a century after their first creation in the lab by scientists in the early 1800s, gas hydrates were considered an academic curiosity, with no meaningful occurrence in nature. In the 1930s, they were recognized as an industrial hazard forming blockages in oil and gas pipelines. In the late 1960s, scientists in Russia inferred their occurrence in nature. However, it wasn't until after a series of deep-ocean scientific drilling expeditions in the late 1970s and early 1980s that the abundance of gas hydrates in the natural environment was widely recognized.



Figure I.1: Gas hydrate nodules. Nodules (white) recovered while coring in the East Sea (Sea of Japan) (Courtesy Korea Institute of Geoscience and Mineral Resources)

Growing energy demands and climate concerns have brought increased attention to the potentially immense quantity of methane held in natural gas hydrates. The result has been a significant acceleration of the investigation of gas hydrates over the past two decades (Fig. I.2), and the pace of scientific discovery about naturally occurring gas hydrates continues to increase.

Although industry remains focused primarily on mitigating unwanted gas-hydrate formation in production and transport infrastructure, it is beginning to invest in understanding the hazards that naturally occurring gas hydrates pose to deep-water and Arctic energy development. Academia, supported by national programs, is making significant progress in understanding the basic physics and chemistry of gas hydrates, as well as their impact on the physical properties of sediments. This research furthers our understanding of the role of gas hydrates in global environmental processes, including natural geohazards, long-term carbon cycling and – given that methane is a potent greenhouse gas – global climate change. However, the primary driver for much of the current interest is the prospect of utilizing gas hydrates as an energy resource. For a world in which energy demands are increasing steadily and future energy supplies are uncertain, the widespread occurrence of potentially immense gas resources is motivating intensive investigations in many countries.

Gas hydrate research is shifting from the level of individual scientists to coordinated national research programs. As a result, policy makers, business leaders, and private citizens are now engaged in a discussion about the most appropriate directions for gas hydrate research, as well as about management and funding issues. The large quantities of naturally occurring gas hydrates distributed around the globe give rise to numerous societal and scientific concerns.

To facilitate decisions that must often rely on highly technical and multidisciplinary information, this comprehensive summary of current issues in global gas hydrate research and de-

Gas hydrates landmark findings

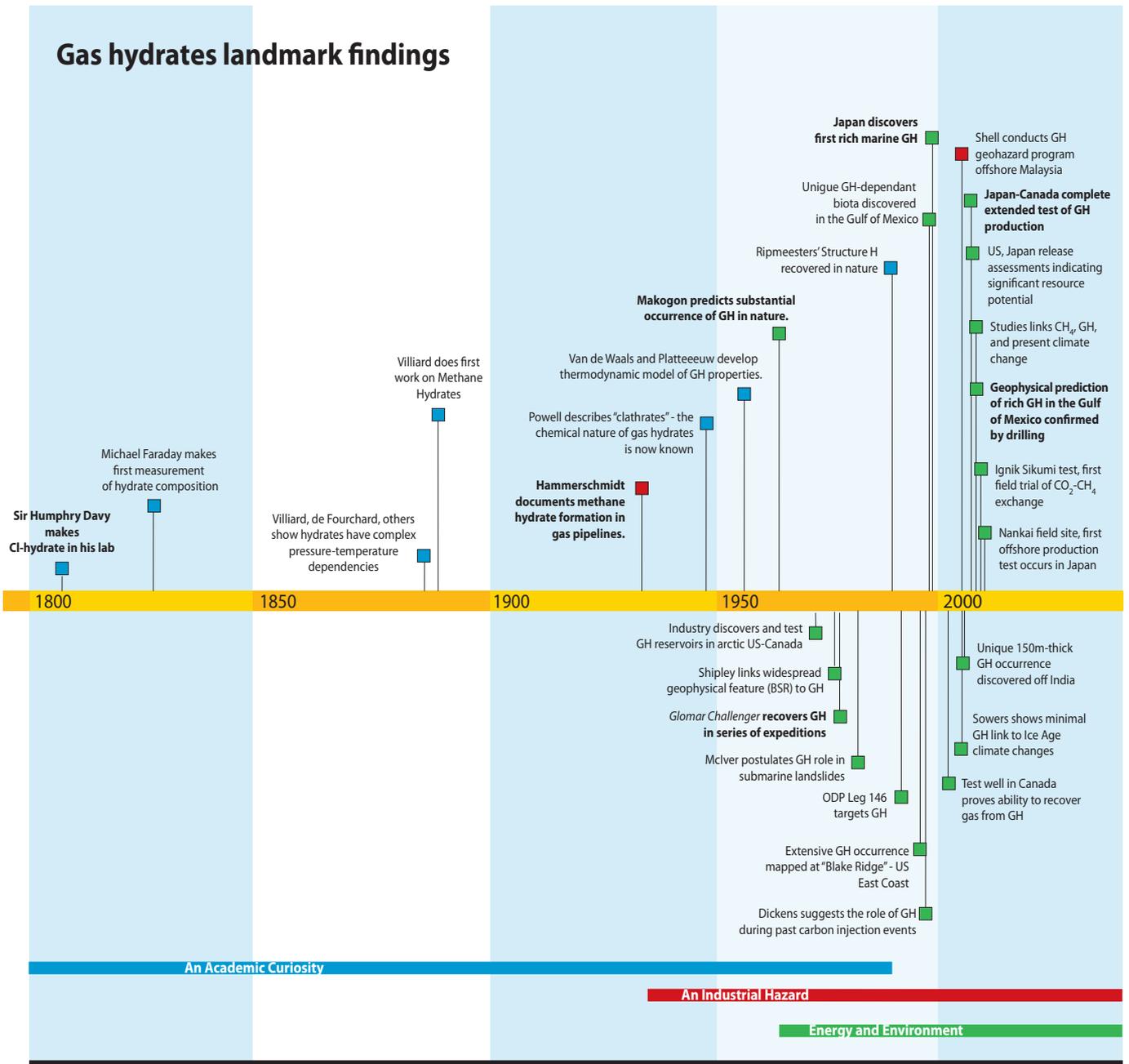


Figure 1.2: Timeline of major milestones in gas hydrate (GH) research.

velopment has been compiled: *Frozen Heat: A global outlook on methane-gas hydrates*. *Frozen Heat* is a two-part review that covers the role of gas hydrates in natural systems (Volume 1) and the potential impact of gas hydrates as a possible new and global energy resource (Volume 2).

Volume 1 Summary

As a basis for understanding how gas hydrates occur and evolve in nature, Chapter 1 describes the crystal structures of gas hydrates, their stability requirements, and the environmental settings in which gas hydrates commonly occur. It also gives estimates of the global quantity and distribution of gas hydrates. These gas hydrate basics provide a context for the central message in Chapter 2: gas hydrates are a key part of the global carbon cycle, storing and releasing vast quantities of methane in response to changing environmental conditions. Chapter 2 summarizes how methane is generated, moved into and out of gas hydrates, and gets consumed. Chapter 2 also discusses the link between gas hydrates and deep marine ecosystems. For example, much of the methane released by gas hydrates into these ecosystems is consumed by microbes in the upper sediment layers and water column and never reaches the atmosphere.

Understanding the behaviour of gas hydrates over long time periods is an important step in understanding how Earth works. As discussed in Chapter 3, the breakdown of gas hydrates due to natural events, such as long-term increases in bottom-water temperature, could release large volumes of gas from marine sediments, potentially transferring significant amounts of methane into the oceans and, to a lesser degree, into the atmosphere. Chapter 3 considers models of past climate change and future climate conditions and how those models might be affected by potential feedbacks from gas hydrates. It is currently thought that methane from gas hydrates likely contributed to, but did not trigger, past global warm-

ing events. Chapter 3 notes that, in the near term, the direct contribution of methane from gas hydrates to Earth's climate warming will likely be of minor significance. Despite the tremendous quantity of methane contained in gas hydrates globally, only a small fraction occurs in environments that will warm sufficiently over the next century to release methane capable of reaching the atmosphere. A more significant near-term result of methane release, particularly in the ocean, may be the oxygen depletion and acidification of the deep ocean that occurs when methane is broken down by microbes. Baseline monitoring studies will be important for understanding the extent of these environmental degradation issues.

Volume 2 Summary

The central message in Volume 2 is that gas hydrates may represent both an enormous potential energy resource and

Figure 1.3: Left: methane from hydrate flared from the Mallik 5L-38 Arctic gas hydrate research well in Canada (Courtesy of the Mallik 2002 Gas Hydrate Production Testing Program). Right: well-logging gas-hydrate-bearing sediment in the Gulf of Mexico (Courtesy R. Boswell, DOE)



source of greenhouse gas for a world with ever-increasing energy demands and rising carbon emissions. Even if no more than a small subset of the global resource is accessible through existing technologies, that portion still represents a very large quantity of gas. The accessible subset could include highly concentrated gas hydrate accumulations in locations where conventional hydrocarbon production is already planned or underway, and more diffuse deposits in areas with strong societal motivations for developing domestic energy resources. To date, a few short-term, pilot-scale methane production tests have been conducted in research wells. The results suggest that larger-scale exploitation may be feasible, but no commercial gas hydrate production has yet occurred. Several nations, however, are currently researching the energy potential of gas hydrates (Fig. I.3). Recent detailed assessments of the energy potential of methane-gas hydrates

concluded that there are no anticipated technical roadblocks to producing gas from hydrate deposits (Expert Panel on Gas Hydrates 2008; Committee on Assessment of the Department of Energy's Methane Hydrate Research and Development Program 2010).

Ultimately, a combination of technological advances and favourable global/regional market conditions could make gas hydrate production economically viable. Therefore, Volume 2 provides a summary of gas-hydrate-based, energy-related information useful in evaluating future energy resource options. Topics addressed in Volume 2 include a review of likely future trends in energy supply, a characterization of prospective gas hydrate resources, technologies for exploration and development, and the potential environmental, economic, and social implications of gas hydrate production.



REFERENCES

Committee on Assessment of the Department of Energy's Methane Hydrate Research and Development Program (2010). Realizing the energy potential of methane hydrate for the United States. 204 p. National Research Council of the National Academies. The National

Academies Press, Washington, D.C.
Expert Panel on Gas Hydrates (2008). Energy from gas hydrates: Assessing the opportunities & challenges for Canada. 222 p. Council of Canadian Academies, Ottawa, Canada

CHAPTER 1

What are Gas Hydrates?



1.1 INTRODUCTION

The English chemistry pioneer Sir Humphry Davy first combined gas and water to produce a solid substance in his lab in 1810. For more than a century after that landmark moment, a small number of scientists catalogued various solid “hydrates” formed by combining water with an assortment of gases and liquids. Sloan and Koh (2007) review this early research, which was aimed at discerning the chemical structures of gas hydrates (Fig. 1.1), as well as the pressures and temperatures at which they are stable. Because no practical applications were found for these synthetic gas hydrates, they remained an academic curiosity.

That perspective changed in 1934. Natural gas was beginning to be used widely as a fuel and was often transported via pipelines. Some pipelines were becoming plugged by what appeared to be ice. E.G. Hammerschmidt (1934) discovered

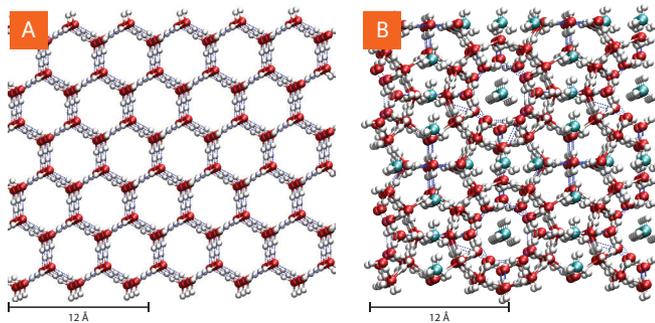


Figure 1.1: Crystal structures of ice and methane gas hydrate. For (A) ordinary hexagonal ice (ice Ih) and (B) structure I methane gas hydrate (sI methane hydrate). Each sphere represents an atom: white for hydrogen, red for oxygen, green for carbon. In hexagonal ice, water molecules (H_2O) are arranged in a hexagonal lattice. In sI methane hydrate, water molecules form a lattice of cages, each cage potentially holding a methane molecule (CH_4). On the right side of (B) and again toward the middle of (B), the cages line up, appearing to hold a line of methane molecules (Figures courtesy B. Anderson, WVU/NETL).

the plugs were not ice, but gas hydrates. This initiated a wave of engineering research – now known widely as flow assurance – dedicated to predicting and preventing the formation of hydrate blockages in industrial equipment. Since then, as hydrocarbon exploration moved into deeper water where hydrates form more readily, the oil and gas industry has invested heavily in flow assurance research.

Much of the early gas hydrate research was empirical in nature, as knowledge of the chemical structures of gas hydrates was still limited. Determining the precise chemical formulation for gas hydrates was challenging. A breakthrough came in the early 1950s, when a relatively new technology, X-ray diffraction, revealed that gas hydrates were in fact clathrates, a term coined a few years earlier to describe solids with no fixed chemical composition in which small guest molecules are trapped within a host lattice. For many years, the combination of the predictive power of a thermodynamic model for clathrate behaviour (van der Waals and Platteeuw 1959) and crystal structure information from X-ray diffraction provided the cornerstone of efforts to predict gas hydrate properties based on their crystal structure (Von Stackelberg and Muller 1951; Davidson 1973).

In the mid-1960s, following research into the pressures and temperatures at which gas hydrates are stable (Pieroen 1955; van der Waals and Platteeuw 1959), Y. Makogon and colleagues in Russia recognized the natural association of methane and water, and that the physical conditions (low temperatures and high pressures) necessary to form gas hydrates should occur naturally on Earth (Makogon 1965). In high-latitude permafrost regions, they predicted, gas hydrates should be found starting hundreds of metres below the ground surface. In marine environments, they should be found in shallow sea-floor sediments beneath cold polar bottom waters where water depths exceed approximately 300 metres, or in the sediments beneath warmer, lower-latitude bottom waters where water depths exceed 450–500 metres. Industry drilling in Arctic permafrost confirmed the existence of naturally-occurring gas hydrates in the early 1970s. It was not until a series of

BOX 1.1 Gas Hydrate and the Deep Sea Drilling Project

The Deep Sea Drilling Project (DSDP) (1968-1983, Legs 1-96) introduced R/V *Glomar Challenger*, the first international drilling platform for global studies of gas hydrates in the marine environment (Figure TB1.1). Over the course of several DSDP legs, scientists obtained the first tangible proof that gas hydrates exist in a variety of geologic settings, evidence that gas hydrates could be nearly ubiquitous in continental-margin and slope sediment around the world.

An objective of DSDP Leg 11 in 1970 was to investigate the nature of the anomalous acoustic reflections (called Bottom Simulating Reflectors or BSRs) that parallel the sea floor. They had been observed on seismic profiles of the passive margin along the Blake Outer Ridge in the Atlantic Ocean. The expedition recovered sediment cores with methane concentrations so high that, in many cases, gas expansion was sufficient to extrude sediment from core liners. Although no obvious gas hydrates were recovered on Leg 11, the high gas concentrations and presence of the BSR were suggestive enough for the R/V *Glomar Challenger* to return in 1980 (DSDP Leg 76) with an objective of recovering gas hydrates. This objective was met with the recovery and testing of a gas hydrate specimen with a high concentration of methane.

A year earlier, in 1979, gas hydrates were recovered in the active margin setting along the landward wall of the Middle America Trench during DSDP Leg 66 off Mexico and Leg 67 off Guatemala. The primary gas from hydrate specimens at both sites was methane, which was confirmed by a massive gas-hydrate specimen recovered in 1983 during Leg 84 near the Leg 66 sites. Although a BSR was present at the Leg 66 hydrate-

recovery sites, the Leg 67 hydrate recoveries were in vitric, or glass-like, sands with no associated BSR.

Yet another hydrate-bearing geologic setting was discovered in 1983, when DSDP Leg 96 recovered gas-hydrate nodules and crystals in Gulf of Mexico mud. Taken together, these sites provided a particularly significant result of the Deep Sea Drilling Project by showing how gas hydrates were present in sediments from a wide range of geologic environments. Extrapolation of these results suggests that gas hydrates are ubiquitous in continental-margin and slope sediment around the world, and this assumption has been confirmed by subsequent investigations.



Figure TB-1.1: The R/V *Glomar Challenger* (Courtesy of the U.S. Geological Survey).

marine discoveries made in the early 1980s during scientific expeditions by the Deep Sea Drilling Program's R/V *Glomar Challenger* (see Text Box 1.1), however, that gas hydrates were recognized as a significant part of the natural environment. It

was soon realized that such a large, and previously unappreciated, storehouse of organic carbon and its inherent energy potential could have profound implications for society and our understanding of Earth (Kvenvolden 1988a, b; 2000).

1.2 WHAT ARE GAS HYDRATES?

In nature, most substances have a fixed composition of building blocks. For example, in the case of methane (CH_4), there is always one carbon (C) atom for every four hydrogen (H) atoms, and these atoms are locked together in a fixed geometric structure by chemical bonds. It was initially assumed each gas-hydrate structure had a fixed ratio of gas molecules to water molecules, but this was later discovered to be incorrect (de Forcrand 1902).

Gas hydrates are classified as clathrates. In a clathrate, the solid lattice of host molecules is physically stabilized by enclosing a sufficient, but not fixed, number of appropriately-sized guest molecules. The guest molecules reside within cages, which are open cavities within the lattice, and the stability of the structure depends on the co-existence of both hosts and guests (Fig. 1.1). This combination occurs without any direct chemical bonding. Furthermore, it is stable even



Figure 1.2: Gas hydrate outcrop on the sea floor of the northern Gulf of Mexico. The hydrate has an orange hue due to the presence of small volumes of oil. This hydrate outcrop hosts pink “methane ice worms.” These worms, discovered in 1997, are generally 2–4 cm in length, and graze upon bacteria living on the hydrate (Fisher *et al.*, 2000). Additional ice worm descriptions are in Volume 1, Chapter 2 (Photo courtesy I. MacDonald, FSU).

if some cages are empty. For methane hydrate to be stable, only 70 per cent of the available cages need to contain methane (Holder and Hand 1982), although typically more than 95 per cent of the cages are filled (Circone *et al.* 2005). The occupancy rate can vary, depending on the pressure, temperature, and the gases present. As a result, clathrates are non-stoichiometric compounds, or compounds without any fixed chemical composition. Composition measurements over a wide range of pressure and temperature conditions, however, show methane hydrate has an average composition of $\text{CH}_4 \cdot 5.99 (+/- 0.07) \text{H}_2\text{O}$ (Circone *et al.* 2005).

Water is the exclusive lattice-building molecule in natural clathrates (hence the popular term, hydrate). Suitable guest molecules include methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), ethane (C_2H_6), propane (C_3H_8), and other low-molecular-weight gases and liquids. Methane has, so far, been the most common clathrate guest molecule observed in nature. Therefore, the term methane hydrate is also common and will be used occasionally in this report and associated web pages.

Naturally occurring clathrates can fit a variety of gases in their structures and create different water lattice shapes or cages to accommodate the different sizes of available gas molecules (Sloan and Koh 2007). The most common clathrate structure forms in the presence of methane and a few other small guest atoms or molecules with diameters between 4.2 and 6 Angstroms (Å). An Angstrom is 1/10 000th of a micron or 10^{-10} metres. This particular clathrate structure is known as Structure I (Fig. 1.1). A unit cell, the smallest repeatable element of the Structure I hydrate lattice, consists of 46 water molecules enclosing 2 smaller cavities and 6 larger cavities. When larger gas molecules (6 to 7 Å), such as ethane and propane, are present in sufficient quantities, a second clathrate structure (Structure II) forms. The unit cell of Structure II hydrate consists of 136 water molecules creating 16 small cavities and 8 large cavities. A third structure, known as Structure H, has also been found in nature and can accommodate larger molecules (7 to 9 Å) when small molecules are

also present. To date, field studies suggest Structure I hydrate occurs most often, Structure II is much less common, and Structure H is extremely rare.

Although people do not ordinarily see methane hydrate in their daily lives, the methane and water molecules that make up methane hydrate are quite ordinary. In fact, approximately 85 per cent of the molecules in gas hydrates are water molecules, and the chemical similarities between methane hydrate and common water ice lead to many similarities in physical properties. For example, the density of both substances (~0.9 grams per cubic centimetre) is less than that of liquid water (~1 gram per cubic centimetre), so both ice and gas hydrates will float in water. Visually, large nodules of methane hydrate tend to look like white, opaque ice, although in nature, small impurities can result in hydrate that ranges in colour from orange (Fig. 1.2) to blue.

Ice and methane hydrate are, however, very different in terms of the conditions at which they are stable. In general, fresh-water-ice stability on Earth is only a function of temperature, with the water-ice to liquid-water transition occurring at 0°C (32°F). As discussed in section 1.3 however, gas hydrate formation requires a suitable combination of temperature, pressure, water chemistry, guest-molecule composition and guest molecule abundance (Thakore and Holder 1987).

Where gas hydrates do exist, they store gas very effectively. Methane hydrate stores so much gas that when exposed to an open flame in controlled conditions, the dissociation, or hydrate breakdown, can free enough flammable methane to create what looks like burning ice, surrounded by a growing pool of water (see front cover of this volume). Dissociating one unit volume of methane hydrate will release approximately 0.8 unit volumes of pure water and, once the gas is brought to atmospheric pressure, 164 to 172 unit volumes of methane, depending on cage occupancy (Kvenvolden 1993; Xu and Germanovich 2006). This is true regardless of how deeply the methane hydrate was initially buried.

1.3 GAS HYDRATE FORMATION, STABILITY, AND OCCURRENCE

Given adequate supplies of gas and water, the fundamental controls on gas-hydrate formation and stability are pressure and temperature. In general, a combination of low tempera-

ture and high pressure is needed to form methane hydrate (Fig. 1.3). Because of Earth's geothermal gradient – the natural increase of temperature with depth below the ground surface

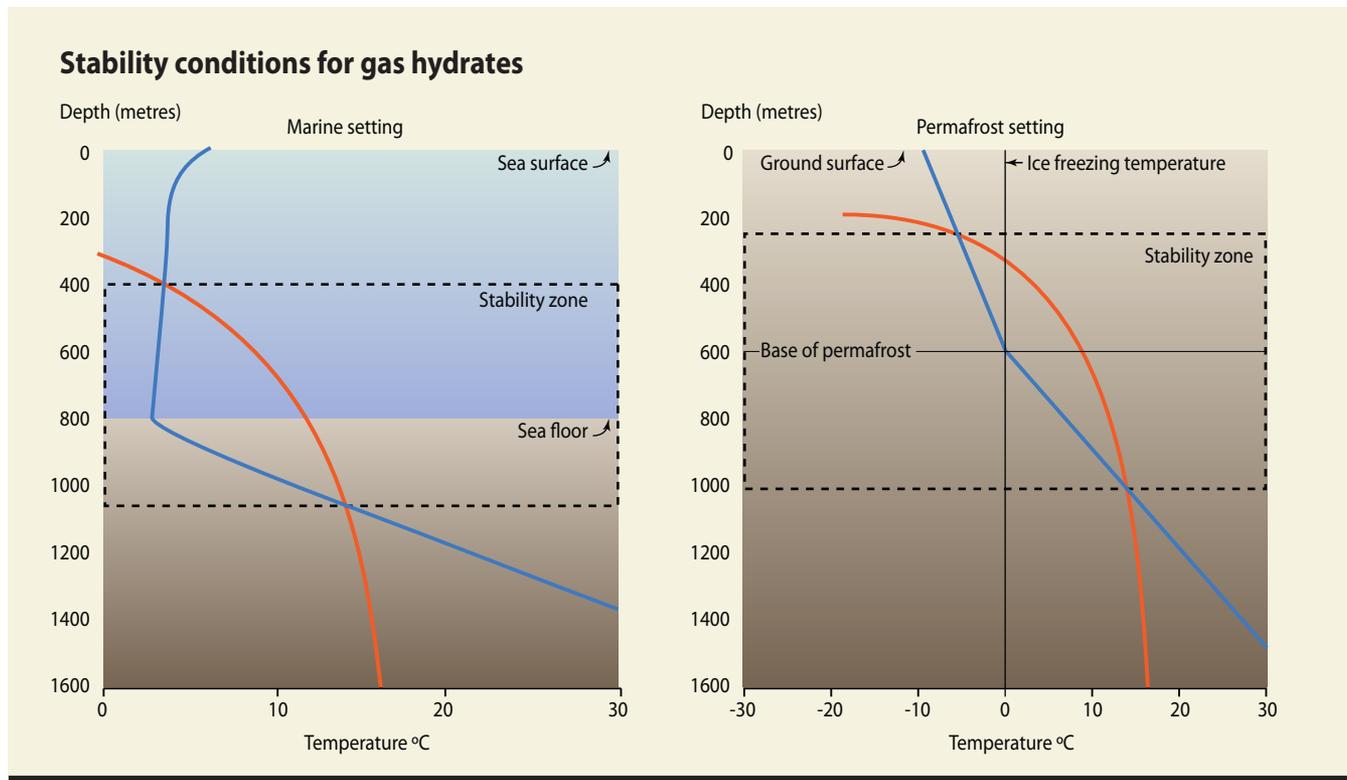


Figure 1.3: Stability conditions for gas hydrates. Idealized phase diagrams illustrating where methane hydrate is stable in marine and permafrost settings. Hydrate can exist at depths where the temperature (blue curve) is less than the maximum stability temperature for gas hydrate (orange curve). Pressure and temperature both increase with depth in the Earth. Although hydrates can exist at warmer temperatures when the pressure is high (orange curve), the temperature at depth (blue curve) gets too hot for hydrate to be stable, limiting hydrate stability to the upper ~1km or less of sediment. The presence of salt, a gas hydrate inhibitor, shifts the gas hydrate stability curve (orange) to lower temperatures, decreasing the depth range of the gas hydrate stability zone. For seawater, this decrease is approximately 1.1°C (Dickens and Quinby-Hunt, 1994) (Figure modified from Kvenvolden (1988a)).

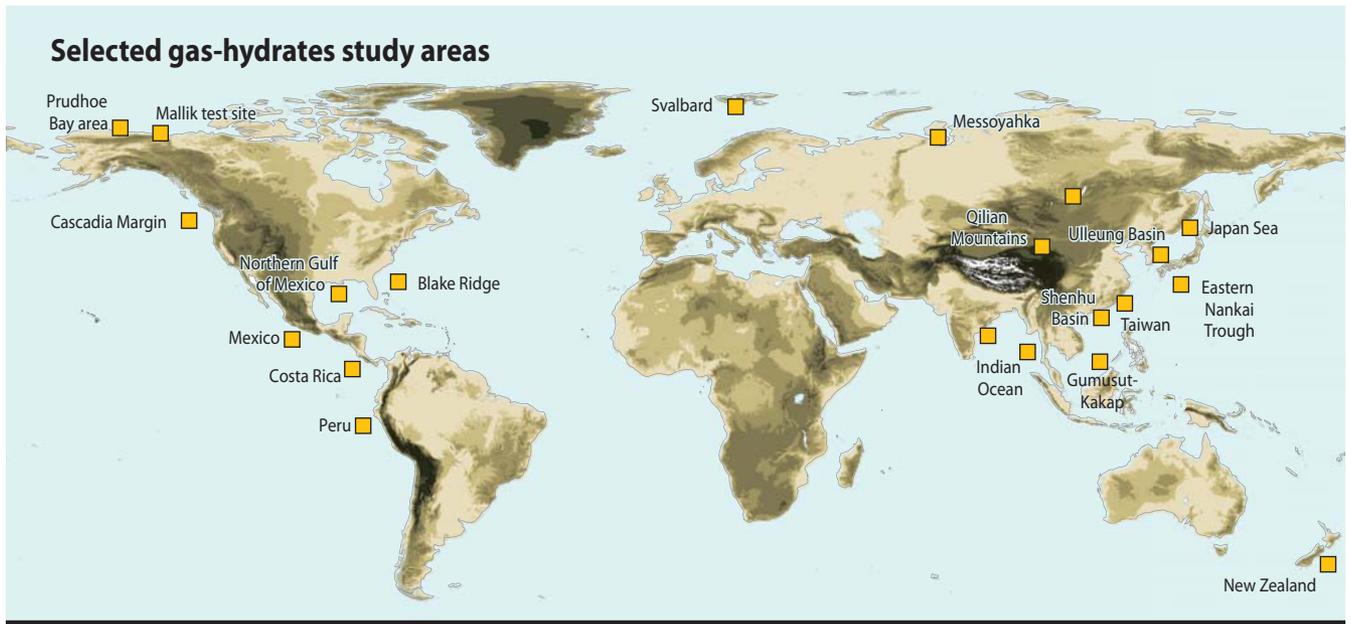


Figure 1.4: Selected gas hydrate study areas. The yellow squares indicate a few of the historically-significant gas hydrate research sites, along with locations where gas hydrates have been recovered from depths greater than 50 meters beneath the sediment surface. Remote sensing studies have inferred the presence of gas hydrate in numerous other locations. Though widespread, methane gas hydrates are restricted to locations where adequate supplies of methane are available, which is generally on or near continents (Figure modified from Ruppel *et al.* 2011).

– gas hydrates are stable only in locations where high pressures can be attained in shallower, cooler sediments. The vertical extent over which these conditions occur at any location is known as the gas hydrate stability zone (GHSZ). In this report, unless otherwise stated, the GHSZ is for Structure I methane hydrate, the most common gas hydrate on Earth.

The GHSZ exists in Arctic regions where cold average air temperatures create thick zones of permanently frozen soils (permafrost). In these regions, the top of the GHSZ typically occurs about 200 to 300 metres below the land surface, often within an interval of permafrost. The GHSZ can extend 500 metres or more below the base of the permafrost (Fig. 1.3).

The GHSZ also exists in oceans or deep inland lakes where high pressures are generated by relatively deep water – typically 300 to 500 metres or more, depending on the bottom-

water temperature. The top of the GHSZ occurs within the water column, with the base of the GHSZ some distance below the sea floor (Fig. 1.3). The thickness of the GHSZ generally increases with increasing water depth. In areas of deep water and low geothermal gradients, the GHSZ can extend 1 000 metres or so below the sea floor (Milkov 2004), with the most deeply buried deposits being as warm as 20°C or more (see Collett *et al.* 2009). Even this maximum depth for gas hydrates is shallow compared to many conventional hydrocarbons, which are now being sought nearly 10 000 metres below the sediment surface (Lewis *et al.* 2007; Mason 2009).

Just because a given location satisfies the pressure and temperature requirements for gas-hydrate stability, there is no guarantee gas hydrates are present. If pressure and temperature were the only determinants, gas hydrates would be virtually ubiquitous throughout oceanic sediment. In ad-

dition to appropriate pressure and temperature conditions, gas hydrate formation requires adequate supplies of water and hydrate-forming guest molecules (Fig. 1.4). The interval in which gas hydrates actually occur within the GHSZ is designated as the gas hydrate occurrence zone or GHOZ. As discussed in Volume 1 Chapter 2, the methane incorporated into gas hydrates comes from organic carbon. In shallow

sediments, the organic carbon is broken down by microbes, with methane being one of the by-products. At significant depths, it is broken down by thermal processes in which heat cracks the organic matter into smaller molecules, such as methane (Fig. 1.5). Organic carbon itself is not uniformly distributed, nor has it always been distributed in the same locations. In modern times, for example, approximately 90

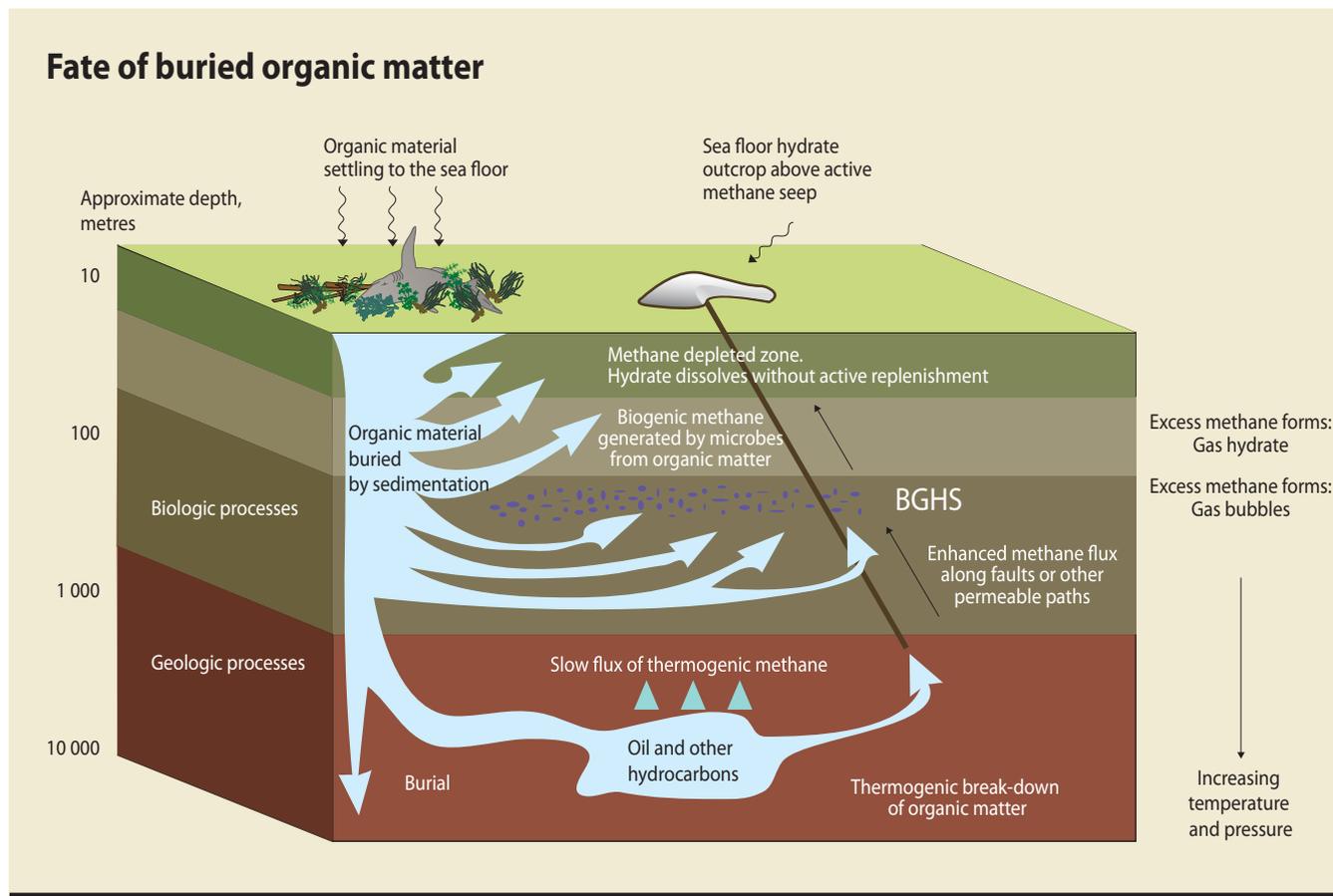


Figure 1.5: Fate of buried organic matter. Buried organic material is degraded by microbes, thermogenically altered by heat and pressure, or buried more deeply and lost to the surface carbon cycle. Methane produced during microbial (also called “biogenic”) and thermogenic decomposition can slowly migrate through overlying sediment with fluids or rise rapidly along faults or other permeable paths. As methane-saturated fluids rise and cool, excess methane forms gas bubbles below the base of gas hydrate stability, BGHS. Above the BGHS, excess methane generally forms methane hydrate, but can also form bubbles (Suess *et al.*, 1999, Liu and Flemings 2006) (Figure modified from Pohlman *et al.* 2009).

per cent of the organic carbon buried in ocean sediment is found beneath relatively shallow water near the continents (Hedges and Keil 1995; Buffett and Archer 2004). In periods of much lower sea levels, however, organic carbon was deposited farther from the continents' current edges, on what is now the continental slope (Muller and Suess 1979; Jasper and Gagosian 1990).

Gas hydrate volume estimates rely on two basic parameters: the amount of pore space, or porosity, available for gas hydrates in the stability zone (Kvenvolden, 1988a; Collett, 1995; Dickens 2001; Klauda and Sandler 2005), and the percentage of that space occupied by gas hydrates, called the gas hydrate saturation. The gas hydrate saturation is related to the amount of methane that can be formed from available organic matter and transported into the GHSZ (Harvey and Huang 1995; Archer *et al.* 2009). Gas hydrates tend to be distributed quite unevenly because the porosity, the permeable paths for liquid and gas flow, and the conditions controlling the conversion of organic material into methane gas can all vary dramatically over short distances (Expert Panel on Gas Hydrates 2008; Frye 2008; Solomon *et al.* 2008).

The Earth's heterogeneous gas-hydrate distribution and uncertainties in porosity and gas hydrate saturation have led to widely varying global estimates of the methane contained in hydrates (Fig. 1.6). Even the lowest estimates, however, are so large they are given in terms of gigatonnes of carbon (GtC). A gigatonne equals 10^9 tonnes, equivalent to 1 petagram or 10^{15} g. A petagram of water, for example, takes up 1 cubic kilometre. For a sense of scale, it is estimated that approximately 1.8 Gt of methane carbon was consumed globally as natural gas in 2011 (U.S. Energy Information Administration 2010).

The earliest global estimates of methane content in gas hydrates were made prior to the first recovery of gas hydrates from marine sediment (green region in Fig. 1.6). These estimates assumed gas hydrates existed wherever pressure and temperature conditions for gas hydrate stability were satisfied. This was equivalent to assuming gas hydrates were present in sediments beneath about 93 per cent of the world's oceans (Milkov 2004).

Estimates of the methane held in hydrates worldwide

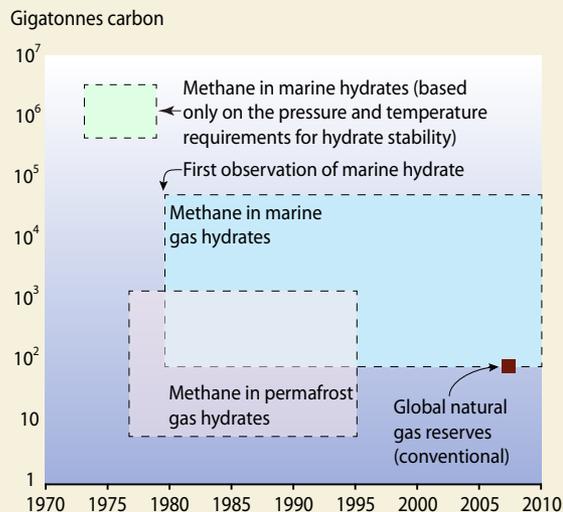


Figure 1.6: Estimates of the methane held in hydrates worldwide. Early estimates for marine hydrates (encompassed by the green region), made before hydrate had been recovered in the marine environment, are high because they assume gas hydrates exist in essentially all the world's oceanic sediments. Subsequent estimates are lower, but remain widely scattered (encompassed by the blue region) because of continued uncertainty in the non-uniform, heterogeneous distribution of organic carbon from which the methane in hydrate is generated, as well as uncertainties in the efficiency with which that methane is produced and then captured in gas hydrate. Nonetheless, marine hydrates are expected to contain one to two orders of magnitude more methane than exists in natural gas reserves worldwide (brown square) (U.S. Energy Information Administration 2010). Continental hydrate mass estimates (encompassed by the pink region) tend to be about 1 per cent of the marine estimates (Figure modified from Boswell and Collett (2011)). Estimates are given in Gigatonnes of carbon (GtC) for comparison with other organic hydrocarbon reservoirs (see Figure 1.7). At standard temperature and pressure, 1 GtC (Gigatonnes of carbon) represents 1.9 Tcm (trillion cubic meters) of methane which has an energy equivalent of approximately 74 EJ (exajoules).

Carbon mass in gas-hydrate-bound methane compared to other sources of organic carbon

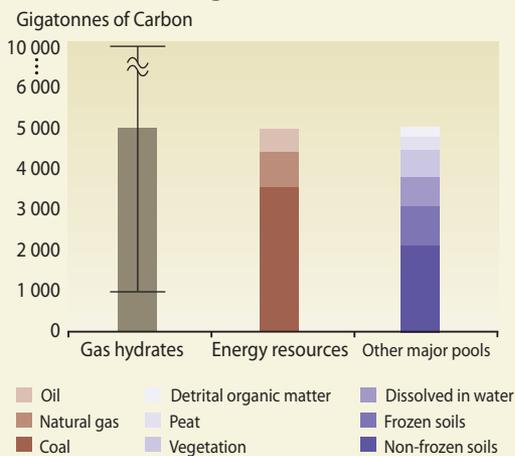


Figure 1.7: Carbon mass in gas-hydrate-bound methane compared to other sources of organic carbon. A 2008 workshop estimated the global methane content in gas hydrates to range from 1 000 to 10 000 gigatonnes of carbon (GtC) (Krey *et al.* 2009). Taking a midrange value of 5 000 GtC as an example, gas hydrates would account for ~33 per cent of Earth’s organic carbon (excluding dispersed carbon such as bitumen and kerogen). Other major carbon pools and their mass estimates in GtC are presented here in top-to-bottom order as they are displayed in the figure. Values for vegetation and non-frozen soil are taken from Sabine *et al.* (2004), frozen soils from Tarnocai *et al.* (2009), peat from Limpens *et al.* (2008b, a), detrital matter from Matthews (1997), and atmospheric values from Blasing (2013). All other values are from Sundquist and Visser (2003).

Estimates of the global methane content in gas hydrates fell as researchers began linking gas hydrate occurrence to the supply of organic material from which methane could be generated. Since the early 1980s, global estimates have varied widely (blue region in Fig. 1.6), reflecting continued uncertainties regarding the amount of methane delivered to, and subsequently stored in, the hydrate stability zone (Buffett and Archer 2004; Wood and Jung 2008).

Significant reduction of the uncertainty associated with global estimates will require additional mapping and coring to define local and regional patterns of gas hydrate distribution (Archer 2007) and to improve our basis for estimating porosity and gas hydrate saturation in unexplored regions. Such assessments are now underway, resulting in more rigorously constrained estimates for some of the world’s promising production regions (see Volume 2 Chapter 2), as well as for regions that are sensitive to climate change (see Volume 1 Chapter 3).

As shown in Figure 1.7, even a median estimate of 5 000 Gt of methane carbon in methane hydrate represents a significant fraction of the world’s organic carbon, and is of similar magnitude to the combined estimates of carbon in traditional global fossil fuel resources, such as oil, coal, and natural gas. Not only is the gas hydrate estimate uncertain, however, but not all gas hydrates are equally accessible as an energy resource (see Volume 2 Chapter 2) (Boswell and Collett 2011). Nonetheless, with annual global consumption estimated at 1.8 Gt of methane carbon in 2011 and 2.15 Gt in 2020 (U.S. Energy Information Administration 2010), recovering even a small fraction of the methane in gas hydrates could significantly affect the global energy mix (see Volume 2).

1.4 WHAT FORMS DO GAS HYDRATES TAKE IN NATURE?

The most visible gas hydrates in nature are massive mounds of solid hydrate, often many metres in diameter, exposed on the sea floor and frequently covered with thin drapes of sediment (Fig. 1.8, bottom row). These mounds mark locations where active fluid vents, or seeps, supply methane directly to the sea floor. Seeps provide the methane for gas-hydrate mounds to form and grow, but this growth must compete not only with temperature changes that can destabilize gas hydrate, but with erosion from the sea water itself, which is undersaturated in methane and will therefore dissolve exposed gas hydrate (Lapham *et al.* 2010; Zhang *et al.* 2011). Gas hydrate mounds have been observed to decay, with chunks of hydrate breaking away from mounds and floating away (MacDonald *et al.*, 1994), but this is not a regular occurrence (MacDonald *et al.*, 2005). Monitoring studies of gas hydrate mounds in the Gulf of Mexico (MacDonald *et al.*, 2005) and offshore of Vancouver Island at the Barkley Canyon site (Lapham *et al.* 2010) demonstrate that gas hydrate mounds can persist for several years at least, in spite of being continually dissolved by seawater and exposed to short-term increases in bottom-water temperature.

The vast majority of gas hydrates, however, lay buried in sediment. The sediment itself is 30 – 70 per cent pore space (Santamarina *et al.* 2001), and as shown in Figs. 1.8–1.10, the manner in which gas hydrates fill or alter that space can be quite different depending on the abundance of available methane and whether the sediment is sandy or more fine-grained (Fig. 1.9).

Hydrate in sands

The relatively high permeability of sands facilitates the flow of water and methane needed for hydrate formation, and gas hydrates have been found filling more than 60 per cent of the available pore space with saturations as high as 90 per cent in some Arctic sands (Collett *et al.* 2009) (Fig. 1.10, class F),

as high as 80 – 90 per cent in Gulf of Mexico sand bodies (Boswell *et al.* 2012) (Fig. 1.10 class C) and as high as 70 per cent in the sandy sections of interbedded sands and muds off Japan's southeastern coast, on the margin of the Nankai Trough (Tsuji *et al.* 2004, 2009) (Fig. 1.10 class C). Though only approximately 10 per cent of the world's gas hydrates likely occur in sands (Collett *et al.* 2009), the high gas hydrate concentrations that can be found in sands have made them research and development targets for potential gas hydrate exploration (see Volume 2).

Hydrate in fine-grained sediment

Marine drilling conducted initially on the Blake Ridge (offshore eastern United States) in 1995 (Paull *et al.* 1998) found gas hydrates occurring as microscopic pore-filling grains in fine-grained sediments (clays and muds) (Fig. 1.10 Class E). These accumulations can cover large areas and extend through thick vertical sequences. It is generally believed the majority of Earth's gas hydrates exist in this dispersed form (Boswell 2009), even though the concentrations are typically low, ranging from 1 or 2 per cent to as high as 12 per cent of the pore volume. These low saturations are probably due to the very small pore size and low permeability of clay-rich sediments, which greatly hinder the mobility of both gas and water. Gas hydrates likely form more readily in zones within these fine-grained environments where porous microfossils or slightly coarser grains provide a small increase in both porosity and permeability (Kraemer *et al.* 2000; Bahk *et al.* 2011).

In areas where methane flux is particularly strong, it is possible for gas hydrates to accumulate to greater concentrations within clay-rich sediments. In 2006, drilling off the coast of eastern India revealed an approximately 150-metre-thick section of fractured clay sediments with gas hydrate saturations of 20 to 30 per cent or more (Collett *et al.* 2008). An expedi-



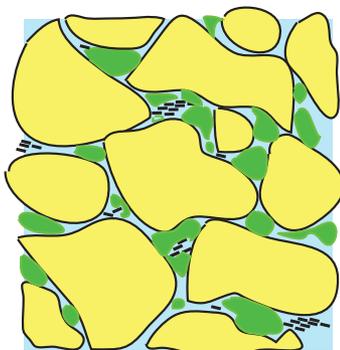
tion to the East Sea of Korea in 2007 found a similar occurrence (Park 2008). X-ray scans conducted on cores from both India and Korea, which were acquired and analyzed at in situ pressures (see Text Box 1.2), showed gas hydrates existing as sporadic lenses of solid hydrate within a pervasive network of thin, nearly vertical fractures (Holland *et al.* 2008; Rees *et al.* 2011) (Fig. 1.8 middle row). Although the mechanisms by which such accumulations form are not clear, it may be that comparatively vigorous gas migration within gas “chimneys” can disrupt the sediment enough to create the local permeability needed for enhanced gas-hydrate formation (Fig. 1.10 class A, B). It is not known how many such occurrences exist, but they could be quite abundant. In 2005, a well-logging expedition in the Gulf of Mexico found a roughly 30-metre interval in which gas hydrates were observed to occupy numerous near-vertical fissures within clay-rich sediments (Ruppel *et al.* 2008). In 2009, a similar gas-hydrate occurrence, about 150 metres thick and widespread, was logged elsewhere in the Gulf of Mexico (Boswell *et al.* 2012). In both settings, the fissures occurred within distinct sedimentary layers and appeared to be controlled by subtle changes in sediment properties. The interpreted gas hydrate saturations were generally low, ranging from 5 per cent to perhaps 10 per cent of the pore volume.

The large size and lateral continuity of typical gas hydrate occurrences in mud-rich sediments are conducive to the generation of anomalous and conspicuous features, seen in seismic data and called bottom-simulating reflectors (BSRs). Initially, BSRs were used widely to assess the distribution of gas hydrates (Shipley *et al.* 1979). However, recent drilling results from Japan (Tsuji *et al.* 2009) and the Gulf of Mexico (Shedd *et al.* 2012) have demonstrated that BSRs can appear in many different forms, and gas hydrates can even occur without a BSR (Paull *et al.* 1996). As discussed in Volume 2, Chapter 2, BSRs are therefore not considered reliable indicators of the nature or concentration of gas hydrates, and more sophisticated geological and geophysical exploration approaches are now being used (Tsuji *et al.* 2009; Boswell and Saeki 2010).

As Chapters 2 and 3 in this volume illustrate, the varied geologic settings in which gas hydrates are found must be considered when evaluating the role of gas hydrates in natural systems such as the natural carbon cycle (Chapter 2), the link to chemosynthetic sea-floor communities (Chapter 2), and past and future climate change (Chapter 3). In Volume 2, the implications of finding high hydrate saturations in sand layers or as veins in fine-grained sediment are discussed in terms of the reservoir’s accessibility and value as a potential energy resource.

Figure 1.8: A selection of gas hydrate forms observed in nature. Unless otherwise noted, gas hydrate is white, and sediment is dark. **Top row:** Pore-filling. Left, Mallik site, Canada (courtesy JOGMEC-NRCan-USGS), and centre, Nankai Trough, offshore Japan (courtesy JOGMEC), show high saturation in sandy sediments. Right (South China Sea, courtesy GMGS-01 Science Party) shows low to moderate saturation in fine-grained sediments. **Middle row:** Grain displacing in fine-grained sediments. Left: massive near-horizontal layers from offshore India (Courtesy NGHP-Expedition-01). Centre: array of thin, near-vertical veins from East Sea (Courtesy UBGH-01). Right: large nodule from Bay of Bengal (Courtesy NGHP-Expedition-01). **Bottom row:** Gas hydrates exposed at the sea floor. Left: massive sea-floor mound stained orange with oil in the Gulf of Mexico (Courtesy I. MacDonald). Centre: massive hydrate mass built from methane gas bubbles under a thin sediment layer at Blake Ridge, offshore USA (Courtesy Woods Hole Oceanographic Institution). Right: massive sea-floor mound offshore Vancouver Island, Canada (Chapman *et al.* 2004).

Silt and Sand-rich Host Sediments



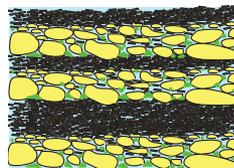
Without Gas Hydrate

Porosity: 30-45%
Permeability: 500-2000 md
Mechanical Strength: Low

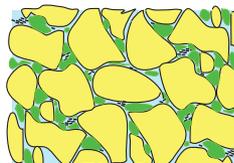
With Gas Hydrate

Porosity: 10-15%
Permeability: 0.1 - 0.5 md
Gas Hydrate Saturation: 50-90%

100 microns



Thinly interbedded
(Nankai Trough; Gulf of Mexico GC955)



Massively-bedded
(Gulf of Mexico WR313; Mallik)

Clay-rich Host Sediments

Pore-filling in undisrupted sediments (Blake Ridge)



Without Gas Hydrate

Porosity: 50-70%
Permeability: Diminishes with Depth to very low values (0.0001 md)
Mechanical Strength: Very Low

With Gas Hydrate

Porosity: 45-60%
Permeability: Nil (0.0001 md)
Gas Hydrate Saturation: 1-10%

100 microns

Grain-displacing in disrupted, deformed sediments (KG Basin, Ulleung Basin)



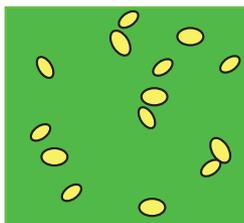
With Gas Hydrate

Porosity: 45-60%
Permeability: Nil (0.0001 md)
Gas Hydrate Saturation: 5-40%

100 microns

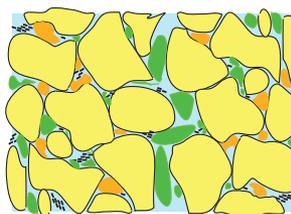
Massive Occurrences (no host sediment)

(Gulf of Mexico, Cascadia, others)



Consolidated host sediments (rock)

(Messoyahki, Barrow (AK), Qilian Mtns (Tibet))



Variety of Lithologies

Porosity: Reduced due to grain compaction, cementation
Permeability: Reduced 500-2000 md
Mechanical Strength: Very high

Figure 1.9: Summary of how the host sediment controls the form of gas hydrate occurrence. Gas hydrates are primarily found in unconsolidated sands (upper row) or clays (centre row). Hydrates also commonly occur in thin, hydrate-bearing sand layers separated by fine-grained sediment (upper right), and can even form in sands that have themselves been consolidated, or packed more tightly together, to form a rock (lower right). In clays, gas hydrates can exist in low concentrations in the small pores between grains (centre left). Gas hydrates in higher concentrations tend to displace grains to form veins, lenses, and nodules (centre right), and those veins, lenses or nodules can occasionally grow large enough to appear as a massive hydrate occurrences (lower left) (adapted from Boswell *et al.* 2011).

Box 1.2 Identifying gas hydrate in specimens of natural sediment

Gas hydrates are now considered one of the largest storehouses of potentially mobile organic carbon on the planet. However, their very existence on Earth was not confirmed until the first samples were observed during scientific drilling programs in the early 1980s (see TEXT BOX 1.1). One reason gas hydrates eluded detection for so long is that the unique combination of high-pressure/low-temperature conditions required for their stability is restricted to some of the more remote places on Earth, including in and beneath permafrost in Arctic regions and within the marine sediments of continental margins. Like water ice, when a gas hydrate is removed from the environment in which it is stable, it melts into a liquid water phase. Gas hydrate also releases its trapped methane gas in the process. Since gas hydrates achieve this phase change rather quickly, much of the gas hydrate present in specimens collected at or below the sea floor in conventional marine studies will have disappeared (dissociated) by the time the specimens arrive on deck for inspection. Only the largest solid masses persist long enough to be physically observed.

Initially, scientists developed special means to infer the presence of gas hydrates from the impact their dissociation has on the chemistry of the surrounding sediment: that is, the stronger the shift of pore-water salinity to fresher values as compared to the local background condition, the greater the gas-hydrate volume that had recently been present. In addition, infrared scanners are used to detect cold spots in recovered cores. These spots indicate where gas hydrates have been and where their melting has cooled the surrounding sediment. The ability to conduct direct measurements in situ using geophysical well-logging tools has advanced significantly (Tsuji *et al.* 2009), and currently much can be determined with great confidence using such tools, particularly when gas-hydrate concentrations are high. Predicting gas-hydrate occurrence using remote sensing (such as seismic or electromagnetic surveys conducted from the surface) is possible, and this ability becomes more accurate with each detailed field study.



To fully assess gas-hydrate-bearing sediments, scientists have devised pressure-coring technologies that allow samples to be collected and retrieved without ever exiting gas-hydrate stability conditions. This technology continues to advance, with increasingly complex measurements being made on acquired samples. X-ray images taken of such samples have demonstrated the wide variety of forms gas hydrates can take in the subsurface, ranging from broadly disseminated pore-filling grains to complex arrays of delicate tabular veins and fracture-filling forms (see Fig. TB-1.2) (Holland *et al.* 2008; Rees *et al.* 2011). Such measurements and images provide critical ground-truth data to confirm the impact of gas-hydrate occurrence on the physical properties of the sediment.

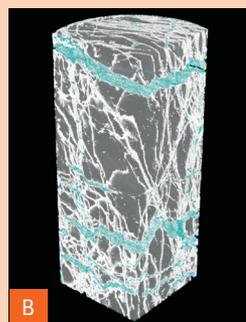


Figure TB-1.2: X-Ray-computed tomography images for gas-hydrate-bearing clays from the Krishna-Godavari Basin offshore eastern India. Gas hydrates are shown in white, clay is shown in grey, and blue represents ice. (A) Gas hydrates are generally observed as near-vertical veins in this 90-centimetre-long core. The diameter is 5.7 centimetres (Holland *et al.* 2008). (B) In this micro-computed tomography scan (Rees *et al.* 2011), a 23-centimetre-long sample, also 5.7 centimetres in diameter, illustrates how the large gas hydrate veins observed in the full-core scan are themselves made up of small, interconnected veins. Ice has formed in this specimen during sample transfer and handling, and it is not representative of the in situ environment, which is well above the freezing temperature of water. (C) A natural-light image of gas-hydrate-bearing clay from the region.

General schematic showing typical modes of gas hydrate occurrence relative to the geologic environment

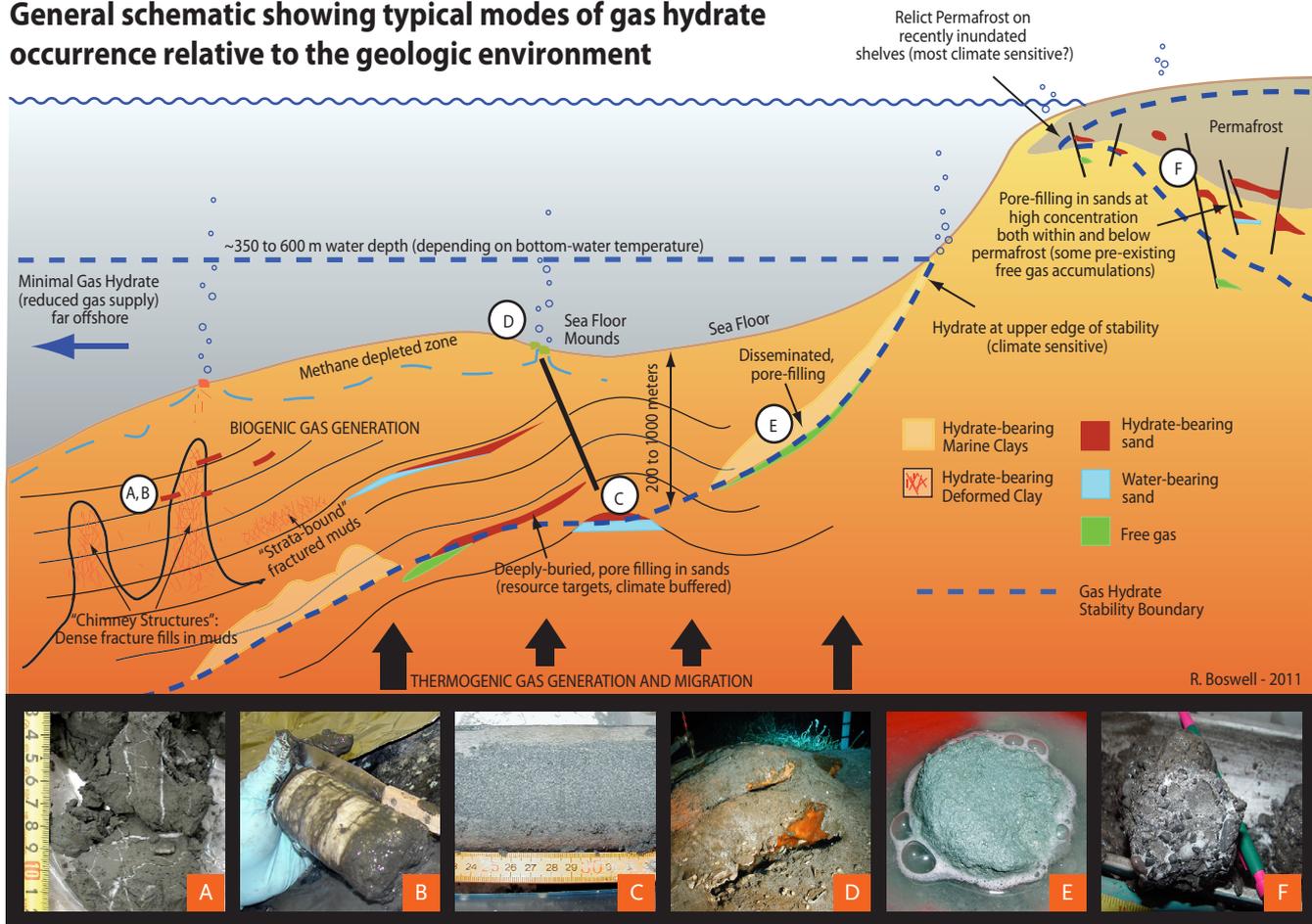


Figure 1.10: General schematic showing typical modes of gas hydrate occurrence relative to the geologic environment. Thin (A) and thickly veined (B) sediment-displacing gas hydrates (white) in fine-grained sediment (grey); (C) pore-filling gas hydrates in sand; (D) gas hydrate mounds on the sea floor (hydrate has an orange coating from oil and is draped with grey sediment); (E) disseminated gas hydrates (white specks) in fine-grained sediment (grey); (F) gas hydrates (white) in coarse sands (grey) (adapted from Boswell 2011).



REFERENCES

- Archer, D. (2007). Methane hydrate stability and anthropogenic climate change. *Biogeosciences*, 4, 521-544
- Archer, D., Buffett, B. and Brovkin, V. (2009). Ocean methane hydrates as a slow tipping point in the global carbon cycle. *P. Natl. Acad. Sci. USA*, 106, 20596-20601
- Bahk, J.J., Chun, J.H., Kim, D.H., Kim, J.H., Torres, M.E., Schultheiss, P., Ryu, B.J., Collett, T.S. and Riedel, M. (2011). Gas hydrate occurrences and their relation to hosting sediment properties: Results from UBGH2, East Sea. 7th International Conference on Gas Hydrates. 8 p. Edinburgh, Scotland.
- Blasing, T.J. (2013). "Recent greenhouse gas concentrations". Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory. http://cdiac.ornl.gov/pns/current_ghg.html
- Boswell, R. (2011). Gas Hydrates: Research Status and Potential Source of Future Energy Supply for the United States. Topical Paper #1-11: NPC 2011 natural gas report., 24 p
- Boswell, R. (2009). Is gas hydrate energy within reach? *Science*, 325, 957-958
- Boswell, R., Collett, T., Frye, M., Shedd, B., McConnell, D. and Shelander, D. (2012). Subsurface gas hydrates in the northern Gulf of Mexico. *J. Mar. Pet. Geol.*, 34, 4-30.
- Boswell, R., Moridis, G., Reagan, M. and Collett, T. (2011). Gas hydrate accumulation types and their application to numerical simulation. Proceedings, 7th International Conference on Gas Hydrates. Edinburgh, Scotland
- Boswell, R. and Collett, T.S. (2011). Current perspectives on gas hydrate resources. *Energy Environ. Sci.*, doi: 10.1039/C1030EE00203H, 10p.
- Boswell, R., Saeki, T. (2010). Motivations for the geophysical investigation of gas hydrates. In: *Geophysical Characterization of Gas Hydrates* (Riedel, M., Willoughby, E.C. and Chopra, S., eds.), SEG Geophysical Developments Series No. 14, Society of Exploration Geologists, Tulsa
- Buffett, B. and Archer, D. (2004). Global inventory of methane clathrate: Sensitivity to changes in the deep ocean. *Earth Planet Sc. Lett.*, 227, 185-199
- Chapman, R., Pohlman, J., Coffin, R., Chanton, J. and Lapham, L. (2004). Thermogenic gas hydrates in the Northern Cascadia Margin. *EOS*, 85, p. 361, 365
- Circone, S., Kirby, S.H. and Stern, L.A. (2005). Direct measurement of methane hydrate composition along the hydrate equilibrium boundary. *J. Phys. Chem. B*, 109, 9468-9475
- Collett, T.S., 1995, Gas hydrate resources of the United States, in Gautier, D.L., Dolton, G.L., Takahashi, K.I., and Varnes, K.L., eds., 1995 National assessment of United States oil and gas resources on CD-ROM: U.S. Geological Survey Digital Data Series 30.
- Collett, T.S., Johnson, A., Knapp, C. and Boswell, R. (2009). Natural gas hydrates – A review. In *Natural gas hydrates - energy resource and associated geologic hazards* (eds. T. Collett, A. Johnson, C. Knapp and R. Boswell). pp. 146-220. AAPG/NETL/AAPG Foundation/AAPG EMD
- Collett, T.S., M., R., Cochran, J., Boswell, R., Kumar, P. and Sathe, A. (2008). Indian continental margin gas hydrate prospects: Results of the Indian National Gas Hydrate Program (NGHP) Expedition 01. Paper 5365. Proceedings of the 6th International Conference on Gas Hydrates (eds. P. Englezos and J. Ripmeeser). 10 p. Vancouver, Canada
- Davidson, D.W. (1973). Clathrate hydrates. In *Water: A comprehensive treatise* (ed. F. Franks). pp. 115-234. Plenum Press, New York
- de Forcrand, R. (1902). On the composition of hydrates of gas. *C. R. Acad. Sci.*, 134, 835-838
- Dickens, G.R. (2001). The potential volume of oceanic methane hydrates with variable external conditions. *Org. Geochem.*, 32, 1179-1193
- Dickens, G. R., and M. S. Quinby-Hunt (1994), Methane hydrate stability in seawater, *Geophysical Research Letters*, 21(19), 2215-2218.
- Expert Panel on Gas Hydrates (2008). Energy from gas hydrates: Assessing the opportunities and challenges for Canada. 222 p. Council of Canadian Academies, Ottawa, Canada
- Fisher, C.R., MacDonald, I.R., Sassen, R., Young, C.M., Macko, S.A., Hourdez, S., Carney, R.S., Joye, S.B. and McMullin, E. (2000). Methane ice worms: *Hesiocoea methanicola* colonizing fossil fuel reserves. *Naturwissenschaften*, 87, 184-187
- Frye, M. (2008). Preliminary evaluation of in-place gas hydrate resources. Report No. MMS 2008-004. 136 p. Minerals Management Service
- Hammerschmidt, E.G. (1934). Formation of gas hydrates in natural gas transmission lines. *Ind. Eng. Chem.*, 26, No. 8, 851-855
- Harvey, L.D.D. and Huang, Z. (1995). Evaluation of the potential impact of methane clathrate destabilization on future global warming. *J. Geophys. Res.-Atmos.*, 100, 2905-2926
- Hedges, J.I. and Keil, R.G. (1995). Sedimentary organic-matter preservation – An assessment and speculative synthesis. *Mar. Chem.*, 49, 81-115
- Holder, G.D. and Hand, J.H. (1982). Multiple-phase equilibria in hydrates from methane, ethane, propane and water mixtures. *AIChE J.*, 28(3), 440-447
- Holland, M., Schultheiss, P., Roberts, J. and Druce, M. (2008). Observed gas hydrate morphologies in marine sediments. Paper 5691. Proceedings of the 6th International Conference on Gas Hydrates (eds. P. Englezos and J. Ripmeeser). 7 p. Vancouver, Canada
- Jasper, J.P. and Gagosian, R.B. (1990). The sources and deposition of organic matter in the Late Quaternary Pinyon Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta*, 54, 1117-1132
- Klauda, J.B. and Sandler, S.I. (2005). Global distribution of methane hydrate in ocean sediment. *Energy Fuels*, 19, 459-470

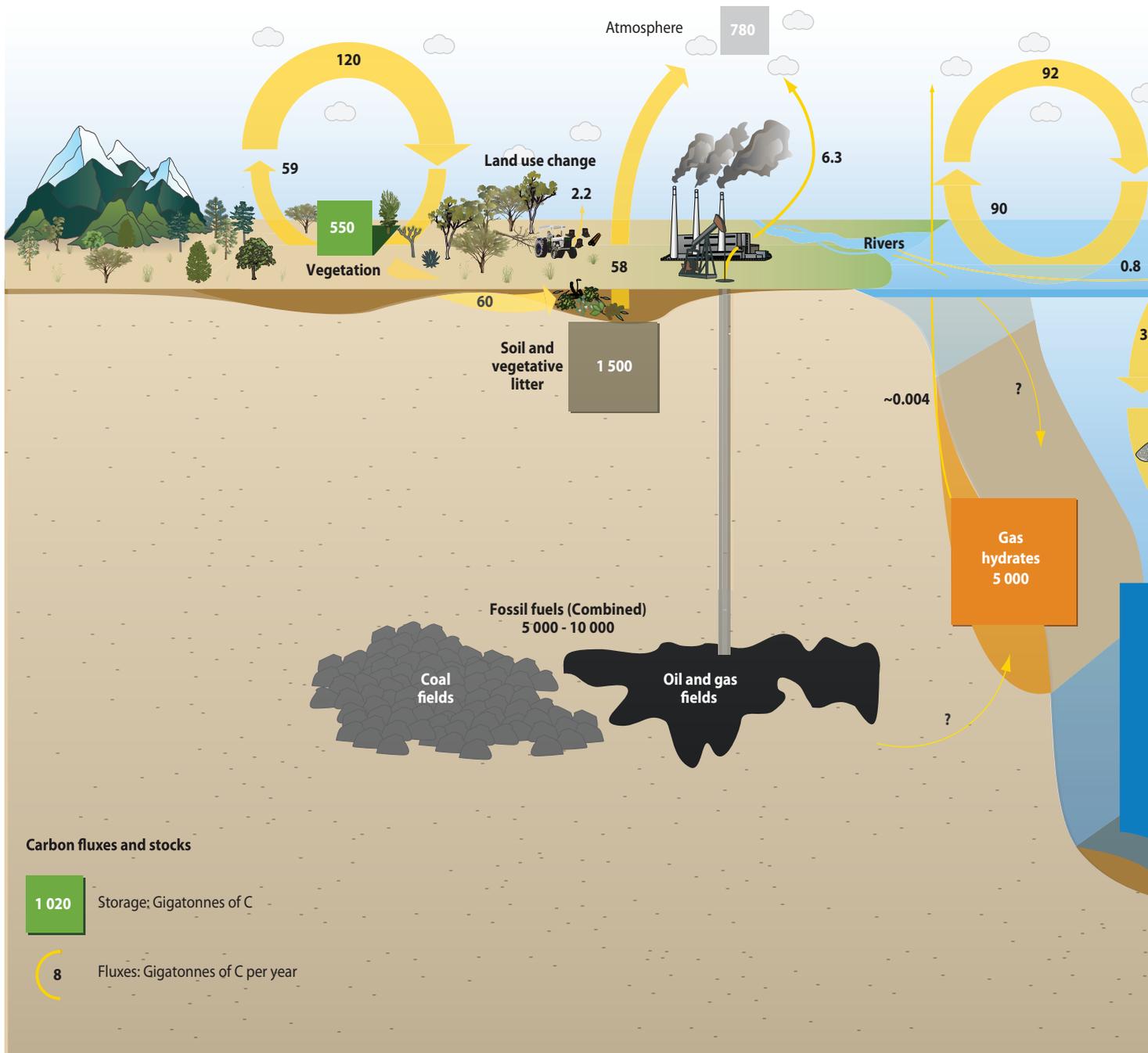
- Kraemer, L.M., Owen, R.M. and Dickens, G.R. (2000). Lithology of the upper gas hydrate zone, Blake Outer Ridge: A link between diatoms, porosity, and gas hydrate. In Proceedings of the Ocean Drilling Program: Leg 164 scientific results (eds. C.K. Paull, R. Matsumoto, P.J. Wallace and W.P. Dillon). pp. 229-236.
- Krey, V., Canadell, J.G., Nakicenovic, N., Abe, Y., Andruleit, H., Archer, D., Grubler, A., Hamilton, N.T.M., Johnson, A., Kostov, V., Lamarque, J.-F., Langhorne, N., Nisbet, E.G., O'Neill, B., Riahi, K., Riedel, M., Wang, W. and Yakushev, V. (2009). Gas hydrates: Entrance to a methane age or climate threat? *Environ. Res. Lett.*, 4, 034007, doi: 10.1016/j.esr.2009.03.007
- Kvenvolden, K.A. (1988a). Methane hydrate – A major reservoir of carbon in the shallow geosphere? *Chem. Geol.*, 71, 41-51
- Kvenvolden, K.A. (1988b). Methane hydrates and global climate. *Global Biogeochem. Cy.*, 2(3), 221-229
- Kvenvolden, K.A. (1993). Gas Hydrates – Geological perspective and global change. *Rev. Geophys.*, 31, 173-187
- Kvenvolden, K.A. (2000). Gas hydrate and humans. *Ann. N. Y. Acad. Sci.*, 912, 17-22
- Lapham, L.L., Chanton, J.P., Chapman, R. and Martens, C.S. (2010). Methane under-saturated fluids in deep-sea sediments: Implications for gas hydrate stability and rates of dissolution. *Earth Planet Sc. Lett.*, 298, 275-285. doi: 10.1016/j.epsl.2010.07.016
- Lewis, J., Clinch, S., Meyer, D., Richards, M., Skirius, C., Stokes, R. and Zarra, L. (2007). Exploration and appraisal challenges in the Gulf of Mexico Deep-Water Wilcox: Part 1 – Exploration overview, reservoir quality, and seismic imaging. The Paleogene of the Gulf of Mexico and Caribbean Basins: Processes, Events and Petroleum Systems, 27th Annual Gulf Coast Section SEPM Foundation, Bob F. Perkins Research Conference (eds. L. Kennan, J. Pindell and N.C. Rosen), pp. 398-414. Houston, TX
- Limpens, J., Berendse, F., Blodau, C., Canadell, J.G., Freeman, C., Holden, J., Roulet, N., Rydin, H. and Schaepman-Strub, G. (2008a). Corrigendum to “Peatlands and the carbon cycle: from local processes to global implications – A synthesis”. *Biogeosciences*, 5, 1739
- Limpens, J., Berendse, F., Blodau, C., Canadell, J.G., Freeman, C., Holden, J., Roulet, N., Rydin, H. and Schaepman-Strub, G. (2008b). Peatlands and the carbon cycle: From local processes to global implications – A synthesis. *Biogeosciences*, 5, 1475-1491
- Liu, X.L. and Flemings, P.B. (2006). Passing gas through the hydrate stability zone at southern Hydrate Ridge, offshore Oregon. *Earth Planet Sc. Lett.*, 241, 211-226
- Macdonald, I., Bender, L., Vardaro, M., Bernard, B. and Brooks, J. (2005). Thermal and visual time-series at a seafloor gas hydrate deposit on the Gulf of Mexico slope, *Earth and Planetary Science Letters*, 233(1-2), 45-59.
- MacDonald, I. R., Guinasso, N. L., Sassen, R., Brooks, J. M., Lee, L. and Scott, K. T. (1994). Gas hydrate that breaches the sea floor on the continental slope of the Gulf of Mexico, *Geology*, 22, 699-702.
- Makogon, Y.F. (1965). Hydrate formation in the gas-bearing beds under permafrost conditions. *Gazovaya Promyshlennost*, 5, 14-15
- Mason, R. (2009). “BP’s 35,000 ft well could produce 3bn barrels of oil”. *The Daily Telegraph*, <http://www.telegraph.co.uk/finance/newsbysector/energy/6128323/BPs-35000ft-well-could-produce-3bn-barrels-of-oil.html>
- Mathews, E. (1997). Global litter production, pools, and turnover times: Estimates from measurement data and regression models. *J. Geophys. Res.*, 102, 18,771-718,800
- Milkov, A. (2004). Global estimates of hydrate-bound gas in marine sediments: How much is really out there? *Earth-Sci. Rev.*, 66, 183-197
- Muller, P.J. and Suess, E. (1979). Productivity, sedimentation rate, and sedimentary organic matter in the oceans – I. Organic carbon preservation. *Deep-Sea Res.*, 26, 1347-1362
- Park, K. (2008). Gas hydrate exploration activities in Korea. Paper 5369. Proceedings of the 6th International Conference on Gas Hydrates (eds. P. Englezos and J. Ripmeester). 7 p. Vancouver, Canada
- Paull, C.K., Borowski, W.S. and Rodriguez, N.M. (1998). Marine gas hydrate inventory: Preliminary results of ODP Leg 164 and implications for gas venting and slumping associated with the Blake Ridge gas hydrate field. *Geol. Soc. Spec. Publ.*, 137, 153-160
- Paull, C.K., Matsumoto, R., Wallace, P.J., *et al.*, 1996. Site 996. Proceedings of the Ocean Drilling Program, Initial Reports 164, 241-275.
- Pieroen, A.P. (1955). Gas hydrates - approximate relations between heat of formation, composition and equilibrium temperature lowering by “Inhibitors”. *Recl. Trav. Chim. Pay-Bas*, 74, 995-1002
- Pohlman, J.W., Bauer, J.E., Canuel, E.A., Grabowski, K.S., Knies, D.L., Mitchell, C.S., Whiticar, M.J. and Coffin, R.B. (2009). Methane sources in gas hydrate-bearing cold seeps: Evidence from radiocarbon and stable isotopes. *Mar. Chem.*, 115, 102-109. doi: 10.1016/j.marchem.2009.07.001
- Rees, E.V.L., Priest, J.A. and Clayton, C.R.I. (2011). The structure of methane gas hydrate bearing sediments from the Krishna-Godavari Basin as seen from Micro-CT scanning. *Mar. Petrol. Geol.*, 28, 1283-1293. doi: 10.1016/j.marpetgeo.2011.03.015
- Ruppel, C., T. Collett, R. Boswell, T. Lorenson, B. Buczkowski, and W. W. (2011). A new global gas hydrate drilling map based on reservoir type, *Fire in the Ice: Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, Methane Hydrate News Letter*, 11, 13-17
- Ruppel, C., Boswell, R. and Jones, E. (2008). Scientific results from Gulf of Mexico Gas Hydrates Joint Industry Project Leg 1 drilling:

- Introduction and overview. *Mar. Petrol. Geol.*, 25, 819-829. doi: 10.1016/j.marpetgeo.2008.02.007
- Sabine, C.L., Heimann, M., Artaxo, P., Bakker, D.C.E., Chen, C.T.A., Field, C.B., Gruber, N., Le Quere, C., Prinn, R.G., Richey, J.E., Lankao, P.R., Sathaye, J.A. and Valentini, R. (2004). Current status and past trends of the global climate cycle. In *The Global Climate Cycle: Integrating Humans, Climate and the Natural World* (eds. C.B. Field and M.R. Raupach). pp. 17-44. Island Press, Washington D.C.
- Santamarina, J.C., Klein, K.A. and Fam, M.A. (2001). *Soils and Waves: Particulate materials behavior, characterization and process monitoring*. 488 p. John Wiley & Sons, Ltd., New York
- Shedd, W., Boswell, R., Frye, M., Godfriaux, P. and Kramer, K. (2012). Occurrence and nature of "bottom simulating reflectors" in the northern Gulf of Mexico. *Mar. Petrol. Geol.*, 34, 31-40. doi: 10.1016/j.marpetgeo.2011.08.005
- Shipley, T.H., Houston, M.H. and Buffler, R.T. (1979). Seismic evidence for widespread possible gas hydrate horizons on continental slopes and rises. *AAPG Bull.*, 63, 2204-2213
- Sloan, E.D. and Koh, C.A. (2007). *Clathrate hydrates of natural gases*, third edition. 721 p. CRC Press, Boca Raton
- Solomon, E.A., Spivack, A.J., Kastner, M., Torres, M., Borole, D.V., Robertson, G. and Das, H.C. (2008). Hydrogeochemical and structural controls on heterogeneous gas hydrate distribution in the K-G Basin offshore SE India. Paper 5509. 6th International Conference on Gas Hydrates (eds. P. Englezos and J. Ripmeester). 10 p. Vancouver, Canada
- Suess, E., M. E. Torres, G. Bohrmann, R. W. Collier, J. Greinert, P. Linke, G. Rehder, A. Trehu, K. Wallmann, G. Winckler, and E. Zuleger (1999). Gas hydrate destabilization: enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin, *Earth and Planetary Science Letters*, 170(1-2), 1-15.
- Sundquist, E.T. and Visser, K. (2003). The geologic history of the carbon cycle. In *Biochemistry: Treatise on Geochemistry* (ed. W. Schlesinger, exec. eds. H.D. Holland, K.K. Turekian). pp. 425-472. Elsevier, New York
- Tarnocai, C., Canadell, J.G., Schuur, E.A.G., Kuhry, P., Mazhitova, G. and Zimov, S. (2009). Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochem. Cy.*, 23, GB2023, doi: 2010.1029/2008GB003327
- Thakore, J.L. and Holder, G.D. (1987). Solid-vapor azeotropes in hydrate-forming systems. *Ind. Eng. Chem. Res.*, 26, 462 - 469
- Tsuji, Y., Fujii, T., Hayashi, M., Kitamura, R., Nakamizu, M., Ohbi, K., Saeki, T., Yamamoto, K., Namikawa, T., Inamori, T., Oikawa, N., Shimizu, S., Kawasaki, M., Nagakubo, S., Matsushima, J., Ochiai, K. and Okui, T. (2009). Methane-hydrate occurrence and distribution in the eastern Nankai trough, Japan: Findings of the Tokai-oki to Kumano-nada methane-hydrate drilling program. In *Natural Gas Hydrates - Energy Resource and Associated Geologic Hazards* (eds. T. Collett, A. Johnson, C. Knapp and R. Boswell). pp. 228-246. AAPG/NETL/AAPG Foundation/AAPG EMD
- Tsuji, Y., Fujii, T., Hayashi, M., Kitamura, R., Nakamizu, M., Ohbi, K., Saeki, T., Yamamoto, K., Namikawa, T., Inamori, T., Oikawa, N., Shimizu, S., Kawasaki, M., Nagakubo, S., Matsushima, J., Ochiai, K. and Okui, T. (2009). Methane-hydrate occurrence and distribution in the eastern Nankai trough, Japan: Findings of the Tokai-oki to Kumano-nada methane-hydrate drilling program. In *Natural Gas Hydrates - Energy Resource and Associated Geologic Hazards* (eds. T. Collett, A. Johnson, C. Knapp and R. Boswell). pp. 228-246.
- Tsuji, Y., Ishida, H., Nakamizu, M., Matsumoto, R. and Shimizu, S. (2004). Overview of the MITI Nankai Trough wells: A milestone in the evaluation of methane hydrate resources. *Resour. Geol.*, 54, 3-10
- U.S. Energy Information Administration (2010). *International energy outlook 2010*. Report No. DOE/EIA-0484(2010). Department of Energy, Washington, D.C.
- van der Waals, J.H. and Platteeuw, J.C. (1959). Clathrate solutions. In *Advances in Chemical Physics* (ed. I. Prigogine). pp. 1-57. John Wiley and Sons
- Von Stackelberg, M. and Muller, H.R. (1951). On the structure of gas hydrates. *J. Chem. Phys.*, 19, 1319-1320
- Wood, W.T. and Jung, W.-Y. (2008). Modeling the extent of Earth's marine methane hydrate cryosphere. Paper 5813. Proceedings of the 6th International Conference on Gas Hydrates (eds. P. Englezos and J. Ripmeester). 8 p. Vancouver, Canada
- Xu, W. and Germanovich, L.N. (2006). Excess pore pressure resulting from methane hydrate dissociation in marine sediments: A theoretical approach. *J. Geophys. Res.*, 111, B01104, doi:10.1029/2004JB003600
- Zhang, X., Hester, K.C., Ussler, W., Walz, P.M., Peltzer, E.T. and Brewer, P.G. (2011). In situ Raman-based measurements of high dissolved methane concentrations in hydrate-rich ocean sediments. *Geophys. Res. Lett.*, 38. doi: 10.1029/2011gl047141

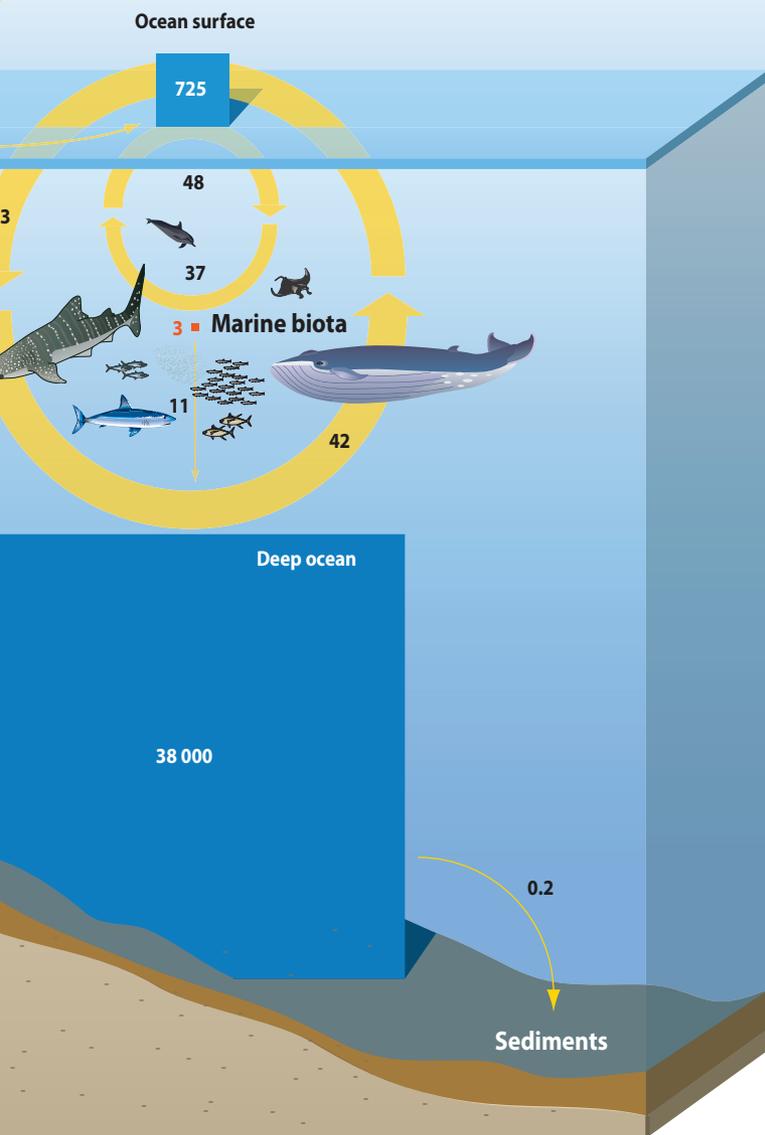
CHAPTER 2

Methane Gas Hydrates and the Natural Carbon Cycle





Carbon cycle



2.1 INTRODUCTION

Methane is a significant component of the near-surface global carbon pool, and it can exist as a free gas, dissolved in water, or held in gas hydrate. Prior to the Industrial Revolution, methane accounted for 0.05 Gigatonnes of carbon (GtC) in the oceans, and 1.5 GtC in the atmosphere (Sundquist and Visser, 2003). Modern estimates suggest methane now accounts for 3.7 GtC in the atmosphere (IPCC, 2007). By comparison, midrange estimates discussed in Volume 1, Chapter 1 suggest global methane hydrates sequester ~5000 GtC, representing about a third of the ~15 000 Gt of organic carbon near the Earth's surface. Methane in hydrates also accounts for approximately 10 per cent of the total near-surface carbon pool (organic and inorganic), which is on the order of 41 000 GtC, with another 5 000 to 10 000 GtC held in coal, gas and oil (Houghton, 2007).

This chapter focuses on the marine environments, where ~99 per cent of the Earth's methane hydrate exists (See Volume 1, Chapter 1). A summary of how and where methane is formed and consumed is presented, along with a discussion of how gas hydrates, and also sea floor chemosynthetic communities, fit into methane's contribution to carbon cycling between the atmosphere, hydrosphere, geosphere, and biosphere.

Figure 2.1: Global carbon cycle. Carbon moves through the atmosphere, biosphere, geosphere, and hydrosphere. Gas hydrates (orange) are shown in marine sediments, but are also buried beneath permafrost sediment in Arctic regions. The 5 000 GtC cited for gas hydrates is a midrange estimate from recent global assessments, and the ~.004 GtC/year carbon flux from hydrates is taken from the Intergovernmental Panel on Climate Change (IPCC, 2007). All other values are compiled from Houghton (2004). Although gas hydrates are a significant global carbon pool, the precise amount of carbon, the amount of carbon released from gas hydrates to the atmosphere, and the extent to which that release could increase as the global climate changes are all under active debate. Improving upon the values for gas hydrates used in this figure will require extensive mapping and research efforts around the world.

2.2 METHANE GENERATION AND CONSUMPTION

Methane is the third-most abundant greenhouse gas in Earth's atmosphere, after water vapour and carbon dioxide. Although the concentration of carbon dioxide in the atmosphere is more than 200 times that of methane (Blasing 2013), the impact of methane is magnified because it is about 23 times more potent than carbon dioxide as a greenhouse gas. This potency is related to methane's radiative forcing capacity, which refers to the ability of a gas to absorb and trap heat radiating off Earth's surface (Lacis *et al.* 1981; Hansen *et al.* 1988). Methane has a relatively short lifetime in the atmosphere (Boucher *et al.* 2009), because within about a decade, a combination of sunlight and chemical processes cause methane molecules in the atmosphere to break down to water and carbon dioxide, the two most abundant greenhouse gases.

As reviewed by the IPCC (2007), the total flux of methane carbon to the atmosphere from all sources is currently around 0.45 GtC/year, or 450 TgC/year ($Tg = 10^{12}$ grammes) (See Fig. 2.2). This flux is more than double the pre-industrial flux, and about 70 per cent of the emissions are due to human activity (Reeburgh 2007; Colwell and Ussler III 2010). Gas hydrates are estimated to account for only about 1 per cent of the annual methane emissions to the atmosphere (Forster *et al.* 2007), but as discussed below, hydrates' true methane contribution is not precisely known.

Since most methane hydrates occur in marine sediments at water depths greater than ~500 metres, a key factor affecting how much methane released from dissociating gas hydrates reaches the atmosphere is the efficiency of transferring methane through the water column. For most bubbles released from the sea floor at water depths greater than 100 meters, the methane will be replaced by other gases during bubble ascent, and the methane will dissolve in the surrounding waters (McGinnis *et al.* 2006) and can be consumed by microbes (see Section 2.2.2). Direct transfer of methane to

the atmosphere via bubbles is most relevant in shallow lakes, estuaries, and river deltas, and on continental shelves. Only in the case of Arctic Ocean continental shelves (Shakhova *et al.* 2010; Biastoch *et al.* 2011) could these methane release processes at shallow water depths be related to gas hydrates.

In special cases, gas hydrate could play a role in enhancing transport of methane to the ocean-atmosphere interface. For example, bubbles released from the sea floor within the gas hydrate stability zone (greater than 500 metres) could form gas hydrate shells in the water column. With such armouring, the bubbles may retain methane to shallower water depths during bubble ascent. Another enhanced transfer mechanism involves chunks of gas hydrate, which can occasionally break off from sea floor gas hydrate mounds (MacDonald *et al.* 2005). Because gas hydrate is buoyant, these chunks may reach the sea surface relatively intact before releasing their methane. Sea floor gas hydrate mounds are not widespread, and this process is not an important factor in transfer of methane to the atmosphere. (For additional discussion of bubble transfer, see Volume 1 Chapter 3).

2.2.1 MARINE METHANE SOURCES: HOW IS METHANE PRODUCED?

Most methane that reaches the Earth's surface is produced by microbial activity in sediments, where a special group of archaea called methanogens produce methane via anaerobic (without oxygen) decomposition of organic material. Intense heating of organic carbon also produces hydrocarbon liquids (e.g., petroleum) and gases, including methane. These formation mechanisms are summarized here.

Microbial methane production

Methanogens generate methane in organic-rich sediments in many settings (e.g., marshes, rice paddies, estuaries, landfills, river deltas, and continental margins). We focus

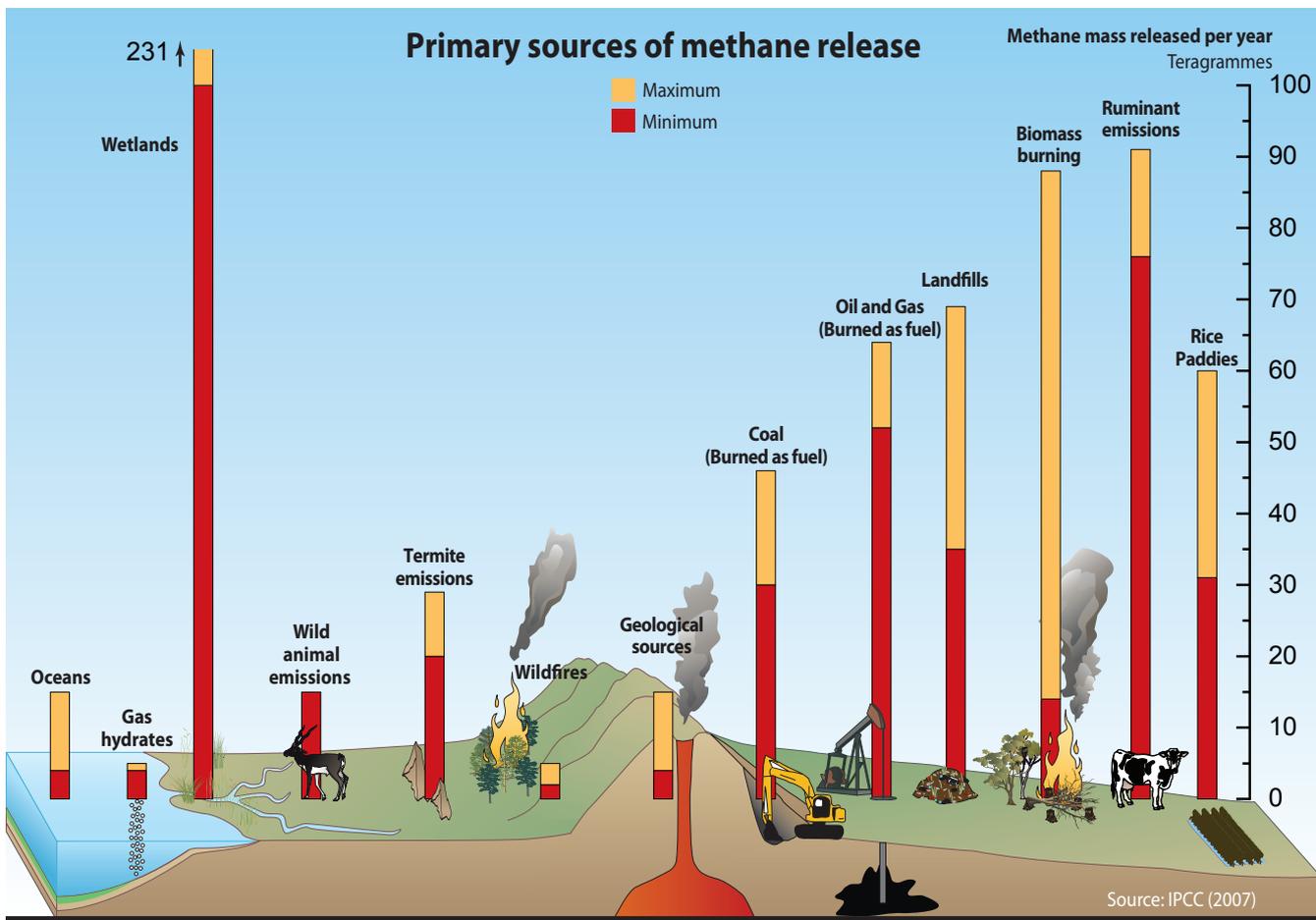


Figure 2.2: Primary methane emissions to the atmosphere per year. Methane emissions due to human-related activities, shown to the right of the volcano, account for approximately 70 per cent of the total emissions (Reeburgh 2007; Colwell and Ussler III 2010). Gas Hydrates are currently estimated to contribute about 5 Tg (Tg = 10^{12} grammes) of methane (3.5 Tg carbon) per year to the atmosphere (IPCC, 2007). Emission rates for gas hydrates are highly speculative, however, and may overestimate the atmospheric methane contribution by not fully accounting for methane consumed by microbes in the sediment and water column (Fig. 2.3). Additional research will be required to constrain the methane flux from gas hydrates that reaches the atmosphere.

here on continental margin settings, which combine the appropriate pressure and temperature conditions for methane hydrate formation with regions of high sedimentation rates and elevated “primary productivity,” which is the rate at which organic carbon is produced in surface waters (Reeburgh 2007). As discussed in Volume 1, Chapter 1, the rapid burial of organic carbon that “rains” to the sea floor can promote microbial breakdown of that organic material, with methane as a key by-product. At the appropriate pressure and temperature conditions, this methane can be

incorporated into methane hydrates within the sediments, usually at water depths greater than ~500 m. Because the combination of high primary productivity and high organic-carbon burial rate is mostly confined to continental margins (Hedges and Keil 1995; Buffett and Archer 2004), continental margins host most of the world’s gas hydrate while sediments of deep ocean basins are relatively free of methane hydrate, even though the deep-ocean pressure and temperature conditions are suitable for gas-hydrate formation (See Volume 1 Chapter 1).

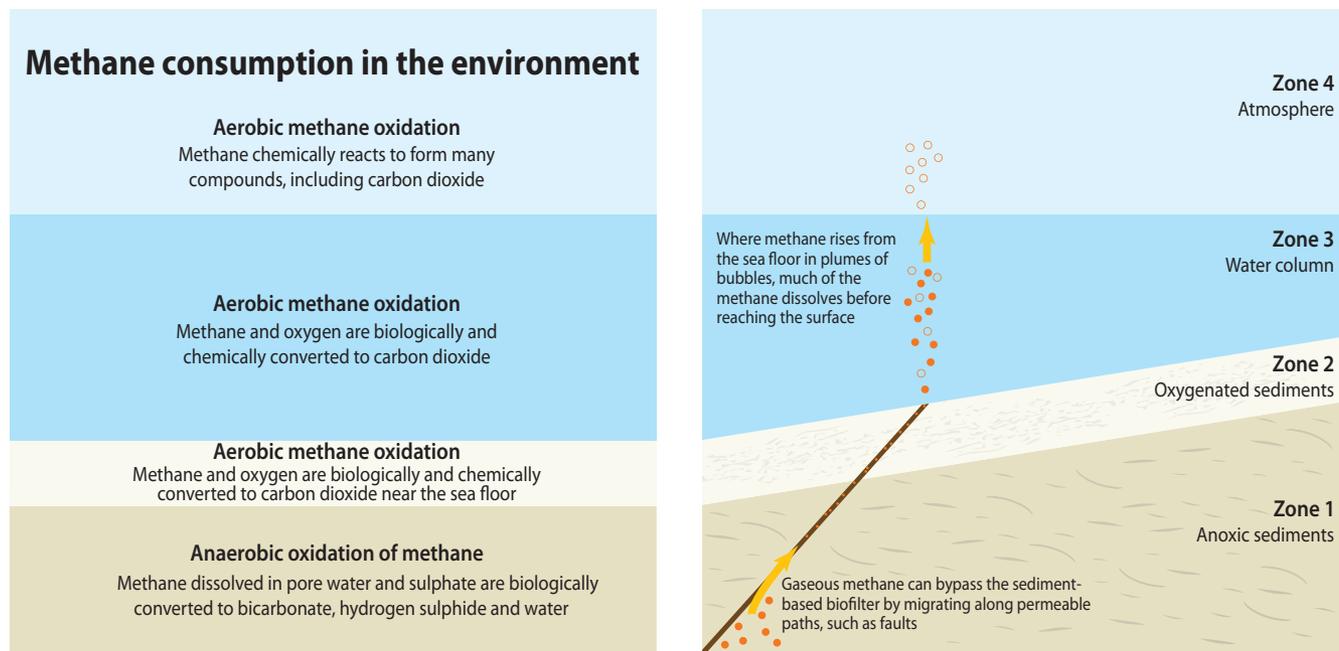


Figure 2.3: Methane consumption in the environment. Near sea-floor methane hydrate is being continuously broken down, releasing methane dissolved in pore water. As methane moves through sediment into the water column and atmosphere, it is consumed in a variety of chemically and microbially controlled reactions. As listed on the left, dissolved-phase methane can then be consumed by microbes as part of an extended chemosynthetic food chain (see also Fig. 2.7) or consumed chemically. As shown on the right, gaseous methane can bypass the microbially controlled reactions in the sediment because microorganisms can access only dissolved methane (Treude *et al.* 2005b; Treude and Ziebis 2010). Methane in bubbles entering the water column tends to dissolve into the water, where it can then be consumed by aerobic microbes. The methane “biofilter” removes much of the methane that would otherwise be transported into the atmosphere. Figure is not drawn to scale. For hydrates in the marine environment, the water depth (Zone 3) would generally be 300-500 metres or more, Zone 2 would be on the order of 1 centimetre thick, and Zone 1 would be on the order of 10 metres thick.

Thermal methane production

Organic material must be buried beneath a few thousand metres of sediment to reach the temperatures necessary to produce methane at significant rates. A portion of the hydrocarbons formed at depth can migrate up toward the sea floor via faults, fractures, and high permeability sediments. Along the way, the gases can become trapped in subsurface structures, be incorporated into gas hydrates, or be released via seeps at the surface. Thermogenic methane, and the associated methane hydrates, are most common in active petroleum areas, such as the Gulf of Mexico (Sassen *et al.* 2001; Boswell *et al.* 2012).

2.2.2 MARINE METHANE SINKS: THE CONVERSION OF METHANE TO OTHER FORMS OF CARBON

Methane can be removed from the global inventory through biological, chemical, and physical sinks (summarized in Fig. 2.3) (Reeburgh 2003). For example, in the atmosphere, methane oxidizes to carbon dioxide in about ten years due to a photolytic process. For methane in the marine realm, the primary methane sinks are anaerobic (without oxygen) oxidation of methane (AOM) and aerobic (with oxygen) oxidation of methane. On present-day Earth, AOM probably dominates on a global basis (Dickens 2003; Reeburgh 2007).

Anaerobic oxidation of methane (AOM): Microbes that consume methane without needing oxygen

Microorganisms consume an estimated 80 to 90 per cent of the methane that reaches shallow sub-sea floor sediments (Reeburgh 1996; Dickens 2003; Reeburgh 2007). The primary sink for this methane is AOM (Zone 1 in Fig. 2.3), a reaction that is accomplished by a consortium of two types of microorganisms: methanotrophic archaea (called ANME from anaerobic methanotrophs) and sulphate-reducing bacteria (Knittel and Boetius 2009). Sulphate, which is abundant in seawater, penetrates the sediments and is consumed in the methane oxidation process. The thickness of Zone 1 in Fig. 2.3 is related to the rate of AOM and the upward flux of methane. This zone can be thin (< 10 metres) where upward methane flux is high and thicker in areas of low methane flux (Borowski *et al.* 1999; Davie and Buffett 2003; Treude *et al.* 2003; Kastner *et al.* 2008).

Some methane can still escape the sediment AOM sink. Where methane flux is very high, such as in fault zones or at mud volcanoes, sulphate cannot penetrate the sediment (Niemann *et al.* 2006; Joye *et al.* 2009). In these locations, AOM is not an efficient benthic filter, and methane vents directly into the water column (MacDonald *et al.* 2002; Liu and Flemings 2006; Solomon *et al.* 2008).

Aerobic oxidation of methane: Microbes that consume methane but also need oxygen

A second sink for methane is aerobic oxidation. This process occurs in near-sea-floor sediments that contain both oxygen and methane (Zone 2 in Fig. 2.3), consuming some of the methane that remains following AOM (Sommer *et al.* 2006; Ding and Valentine 2008). Aerobic oxidation of methane is also a dominant methane sink in the water column (Zone 3 in Fig. 2.3) (e.g. Mau *et al.* 2007), but the accompanying processes remain poorly understood outside a few areas where sensitive radiotracer techniques have been applied.

Aerobic methane oxidation is believed to be carried out by methanotrophic bacteria that use methane as their sole source of energy and as a primary source of structural carbon (Hanson and Hanson 1996). A fraction of the oxidized methane is converted to bacterial biomass, while the remainder is released as dissolved inorganic carbon. In contrast to AOM, which has bicarbonate as its main inorganic carbon product, aerobic oxidation of methane yields primarily carbon dioxide, which increases ocean acidity (See Text Box 2.1). In the water column, aerobic methane oxidation requires time and space for microbes to effectively consume methane. As reviewed by Hu *et al.* (2012), aerobic oxidation is quite efficient when methane is diffusing through water deep enough to stabilize gas hydrates (300-500 metres).

Box 2.1 Could microbial methane oxidation boost acidification and oxygen depletion in the ocean?

Methane consumption by methane-eating microbes in sediments and in the water column is an important global mechanism that prevents methane from reaching the atmosphere. There are two main processes by which methane is consumed: aerobic and anaerobic methane oxidation. But do these processes generate ecological issues of their own?

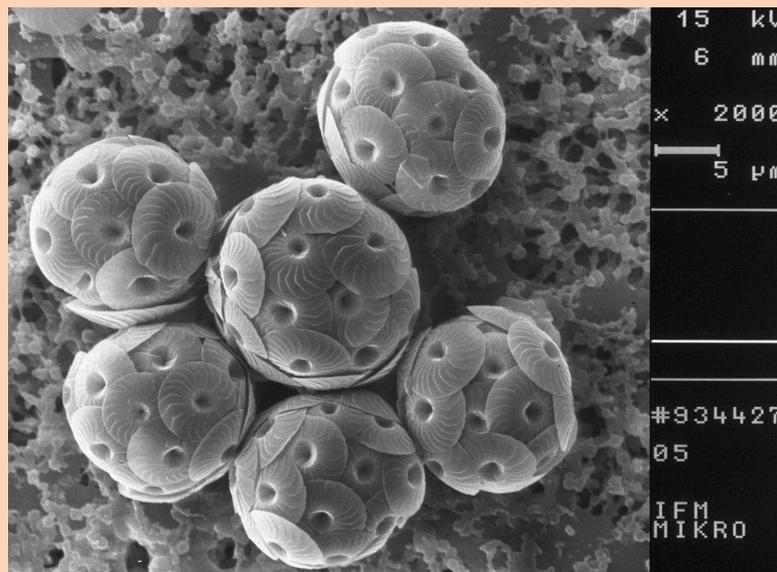
Aerobic oxidation of methane consumes both oxygen and methane to produce carbon dioxide. Excessive oxygen consumption, particularly in the deep ocean where it is not easily replenished, can be detrimental to oxygen-breathing life forms. Carbon dioxide dissolves in water to form carbonic acid, acidifying the water. In theory, if methane vents rapidly into the water column, aerobic oxidation of methane could cause significant local decreases in oxygen levels and increased acidity (lower pH values, see Fig. TB2.1 for an example of potential acidification effects).

There are indications in the geologic record that massive methane releases from gas hydrates might have driven ocean acidification in the past (Zachos *et al.* 2005; Pelejero *et al.* 2010). Model predictions for the future (Biaostoch *et al.* 2011) suggest that methane consumption could lead to pH values dropping by up to 0.25 units within the next century in some deep areas of the Arctic Ocean. In addition, microbial consumption of methane could decrease local bottom-water oxygen concentrations by up to 25 per cent. Regional methane-induced sea-water acidification from the sea floor would occur, in addition to ocean-wide acidification caused by the uptake of anthropogenic carbon dioxide from the atmosphere. The combined effect of the two processes would accelerate acidification in parts of the Arctic Ocean, including in deeper waters. Research has so far been based on the premise of a projected pH decrease due to the anthropogenic carbon dioxide uptake of about 0.3 units by the end of this century. Methane-induced acidification could nearly double the pH decrease in parts of the Arctic Ocean (Biaostoch *et al.* 2011).

The effects of anaerobic oxidation of methane (AOM) in sediments are not as easily predicted. AOM consumes no oxygen and produces bicarbonate instead of carbon dioxide (Barnes and Goldberg 1976).

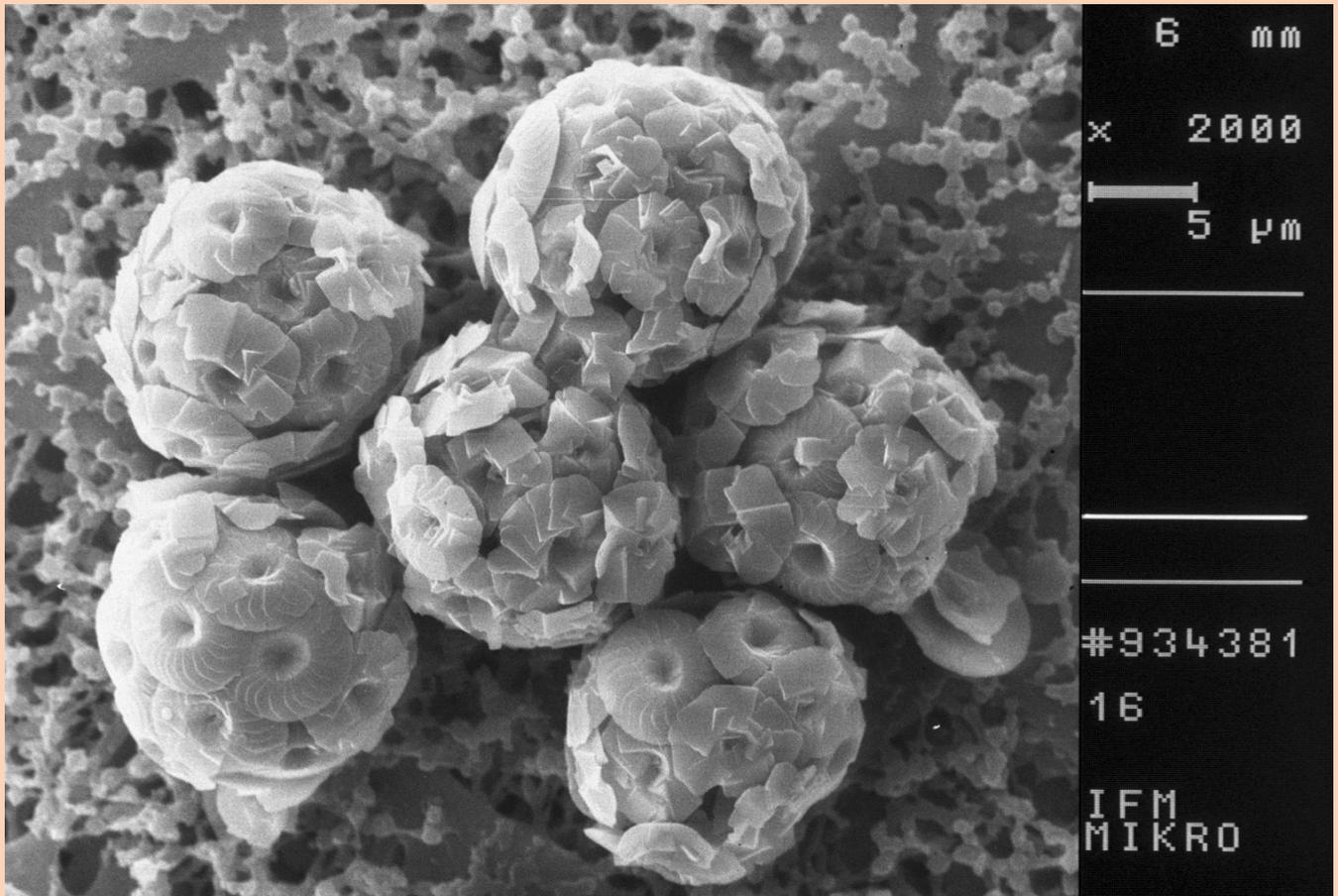
However, sulphide, another end-product of AOM, might be re-oxidized with oxygen by chemoautotrophic organisms (Jørgensen and Nelson 2004) or simply through abiotic chemical reactions. So although the microbial process itself does not directly consume oxygen, consumption occurs during re-oxidation of sulphide at the sediment-water interface.

Figure TB-2.1: Potential effects of ocean acidification on marine organisms. The planktonic coccolithophore *Calcidiscus leptoporus* cultured under present-day carbon dioxide conditions ($p\text{CO}_2 \sim 380 \mu\text{atm}$, left panel) and under conditions projected for the end of this century, assuming business-as-usual carbon dioxide emissions ($p\text{CO}_2 \sim 780 \mu\text{atm}$, right panel). With increasing carbon-dioxide-induced ocean acidification, the energetic costs of calcification go up. While some organisms are able to compensate for this, others find it increasingly difficult to produce their carbonate shells and skeletons (courtesy Ulf Riebesell, GEOMAR, Kiel)).



Field studies show dissolved oxygen is strongly depleted in some coastal areas and marginal seas, such as the Black Sea and Baltic Sea, as well as at poorly ventilated and highly productive continental margins. Observational data show the volume of these depleted water masses has expanded significantly in recent decades (Stramma *et al.* 2008). Models predict the ongoing oxygen loss at continental margins will be amplified over the coming century in response to anthropogenic carbon dioxide emissions (Oschlies *et al.* 2008). Most fauna living at the sea floor depend on oxygen

and will vanish when dissolved oxygen concentrations in ambient bottom waters fall below a critical threshold value. The spread of low-oxygen conditions is, therefore, a serious threat to fauna living at the sea floor of the affected continental margin areas. Although field studies have not yet demonstrated significant pH decreases or oxygen depletions in the vicinity of methane seeps, it is possible these effects may take a long time to become apparent. Baseline studies might be needed in order to understand these slow environmental degradation issues.



2.3 A GAS HYDRATE CAPACITOR IN THE GLOBAL CARBON CYCLE?

Methane is a dynamic component not just of the sub-sea-floor environment, but the global environment as a whole. The role of gas hydrate in the movement of methane through the global carbon cycle can be visualized by characterizing the gas hydrates as a methane “capacitor” (Dickens 2001; Dickens 2003; Dickens 2011). Like a capacitor in an electrical network, gas hydrates can become charged with methane over time and also discharge, releasing a significant quantity of methane.

Under steady-state conditions, methane slowly enters the gas hydrate stability zone through organic carbon degradation, methane production, and methane migration. Methane slowly leaves this volume through gas hydrate dissociation, gas hydrate dissolution, AOM, venting, and burial. If methane inputs to gas hydrate exceed methane outputs, gas hydrate volumes grow as long as pore water is available; otherwise, they shrink. Gas hydrates, therefore, can act as a

BOX 2.2 Can gas hydrate breakdown trigger submarine slides?

The presence of gas hydrates generally strengthens the host sediment. When gas hydrates break down into water and free methane gas, however, what are the consequences for sediment stability?

When gas hydrate dissociates, the released gas and water occupy a greater volume than they do in the solid hydrate structure. This expansion means gas hydrate dissociation in sediment can increase pressure in the pore space (McIver 1982; Kayen and Lee 1991; Xu and Germanovich 2006), weakening the sediment by pushing sediment grains apart. It has been suggested that dissociated gas hydrate could form a fluid- and gas-rich glide plane, upon which the overlying sediment might be able to slide (see Fig. TB-2.2) (McIver 1982). The slide-triggering, gas-hydrate dissociation might itself be brought on by a pressure decrease due to an earthquake (Bugge *et al.* 1987), a drop in sea level (Maslin *et al.* 2004), or a temperature increase due to rising bottom-water temperatures (Dickens *et al.* 1995).

Gas hydrates have been tied to submarine slides the world over, including the colossal Storegga slide offshore Norway (Bugge *et al.* 1987), along the western Atlantic Margin (Booth *et al.* 1993; Lee 2009), offshore Brunei (Gee *et al.* 2007), and on many other continental slopes around the world. While gas

hydrates may have played a role in some isolated slides (Lopez *et al.* 2010), definitive proof of gas hydrate dissociation substantially contributing to major submarine slides remains elusive, even for the heavily-studied Storegga slide (Mienert, 2008). There are two drawbacks to the gas-hydrate triggering mechanism theory:

1. Because sediments are generally permeable (meaning fluid can flow through them to some extent), gas hydrate dissociation may simply push fluid and gas away from the dissociation site without generating any significant pressure increase. Bouriak *et al.* (2000) suggest that, for the Storegga slide, gas hydrate dissociation would only have increased the pore pressure by 0.2 per cent, not enough to trigger a slide.
2. The distribution of gas hydrates seldom coincides with the initial slide failure location or the glide plane along which the sediment subsequently slides. The Storegga slide, for example, began at the toe of the slide (Kvalstad *et al.* 2005). Gas hydrates were likely to be dissociating in much shallower water, landward toward the slide headwall (Mienert *et al.* 2005). Moreover, the non-uniform distribution of gas hydrates does not coincide with the slide surface, so gas hydrate dissociation did not provide a glide plane for the Storegga slide (Bryn *et al.* 2005; Kvalstad *et al.* 2005).

An alternative gas hydrate breakdown mechanism, in which the topmost gas hydrates dissolve in response to sea-floor warming, has

sink, sequestering methane as the hydrate forms, or act as a source, releasing methane as the hydrate breaks down.

Currently, the global methane hydrate capacitor is thought to be relatively stable – with balanced methane inputs and emissions from natural gas-hydrate reservoirs. Local variations are possible, with gas hydrates in some areas of the globe acting as methane sinks, while others in different environments

may be acting as methane sources (one potential source being methane released from hydrate in submarine slides, as discussed in Text Box 2.2). The relatively simple gas hydrate capacitor concept is not intended to capture the complete, interconnected system of controls on gas hydrate formation, but it does provide a useful analogy for discussing how gas hydrate volumes change over time in response to natural environmental conditions (see Volume 1, Chapter 3).

been proposed by Sultan *et al.* (2004) as a method of weakening the sediment to the point where a slide, such as Storegga, would initially fail near its toe. However, other recognized geologic phenomena are often sufficient to explain large slides, including earthquakes in areas where rapid sediment deposition creates vulnerable slopes (Bryn *et al.* 2005) and over-steepening of slopes due to localized tectonic

uplift (Hornbach *et al.* 2007). Although gas hydrate dissociation may not trigger major submarine slides, it might contribute to the slide's shape. In the Storegga slide scar, for example, the slide headwall coincides with the location at which gas hydrates are thought to have been susceptible to environmental change about 8 200 years ago, when the slide occurred, (Mienert *et al.* 2005).

Schematic of a submarine slide triggered by gas hydrate dissociation

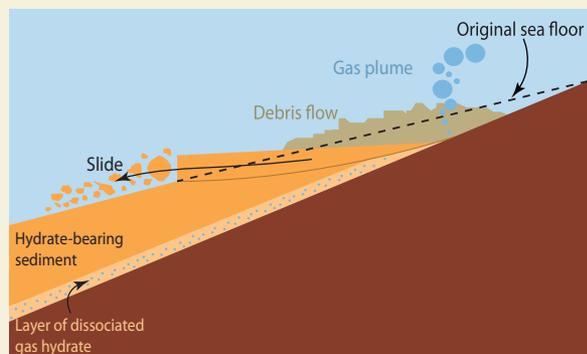


Figure TB-2.2: Schematic of a submarine slide triggered by gas hydrate dissociation. In theory, gas pressure generated by methane released during gas hydrate dissociation weakens the sediment and provides a glide plane for sediment failure. In practice, gas hydrates are rarely located at sites where slides initially fail, nor are gas hydrates generally distributed uniformly over large enough spatial scales or in the proper orientation to provide effective glide planes for submarine slides. (Figure modified from Mclver (1982)).

2.4 LIFE AT MARINE METHANE SEEPS

Sea floor cold seeps emit methane and sometimes other gases into the overlying water column. Some cold seeps are associated with gas hydrates, while others occur at water depths too shallow for gas hydrate to be stable. At these seeps, methane and other fluids are transported to the sea floor through conduits created by over pressurization, leakage of deep gas reservoirs, salt dome accommodation, mud volcano emplacement, and tectonic processes (Judd *et al.* 2002; Suess 2010). Methane seeps are often characterized by specialized life forms whose metabolism is based on chemosynthesis (Levin 2005; Suess 2010) (see Text Box 2.3), and these cold-seep environments are distinct from those associated with hydrothermal vents at mid-ocean ridges.

The presence of near-surface hydrates at a methane seep tends to spread the methane release over a larger sea floor area, while also increasing the amount of methane dissolved in the pore water. This dissolved methane is more easily consumed by the chemosynthetic community than is the gaseous methane that can bypass chemosynthetic communities by venting through focused gas channels outside the hydrate stability

zone (Treude and Ziebis 2010). Near-surface gas hydrates may also enhance the formation of carbonate pavements in the sediment, produced by anaerobic oxidation of methane (AOM) (Bohrmann *et al.* 1998). These carbonates, after erosion and exposure, become secondary habitats for deep-sea organisms (e.g. Paull *et al.* 1984). In this chapter, we will not discriminate between methane-seep life forms found in the presence or absence of near-surface gas hydrates, because their adaptations and survival strategies are almost identical.

Because methane seeps associated with gas hydrates were discovered 30 years ago (Paull *et al.* 1984), their investigation is still in its infancy. Our knowledge of these systems – especially those located on continental margins – is slowly increasing with the advance of deep-sea technologies. Nevertheless, we know these ecosystems can be relatively common features along certain continental margins and in tectonically active areas of the sea floor. Investigations of terrestrial seep fossils (i.e., authigenic carbonates that are now exposed on land and believed to have formed along the sea floor at



Figure 2.4: Bacterial mats associated with gas hydrates. White and orange mats of sulphur-oxidizing bacteria cover sediments with near-surface gas hydrates at Hydrate Ridge, Northeast Pacific Ocean (Courtesy of Lisa Levin, Scripps Institution of Oceanography).

Box 2.3 What is chemosynthesis?

The term chemosynthesis refers to metabolisms that obtain energy to create biomass by using chemical energy through reduction-oxidation reactions. If the carbon source used to form the biomass is inorganic (carbon dioxide), the organisms are called chemoautotrophs. Chemoautotrophs are different from photoautotrophs, organisms that use light energy through photosynthesis to obtain energy for growth from carbon dioxide. Chemoautotrophs are bacteria, exclusively. Animals that live symbiotically with chemoautotrophs are called chemosymbiotic organisms. Animals (including humans) that feed on algae, plants, or other animals are called heterotrophs.

Famous examples of chemosymbiotic animals are the giant tubeworms, clams, and mussels thriving on chemical energy in the permanent darkness of hydrothermal vent systems and methane seeps (Corliss *et al.* 1979; Felbeck 1981; Levin 2005). These ecosystems are often described as functioning completely independent of sunlight, especially when located in the deep sea. At first glance, this statement appears correct, because primary producers at the basis of these ecosystems gain energy and carbon from inorganic compounds, even in the absence of light. However, the chemicals needed to oxidize energy-rich molecules such as hydrogen sulphide, are oxygen and nitrate. Both were rare in ancient oceans. Only through photosynthesis did oxygen accumulate and react with reduced nitrogen compounds to form nitrate.

Hence, modern complex chemosynthetic ecosystems, especially those with higher organisms, are not completely independent of sunlight. They depend on compounds produced directly or indirectly through photosynthesis. This dependence is even

stronger at seeps, where methane, and sometimes petroleum, form the basis for chemosynthetic food chains. Both are often fossil-transformation products of photosynthetically produced organic matter.



Figure TB-2.3: Near the sea floor above active methane seeps, gas hydrate can form mounds such as that pictured above in the Gulf of Mexico. The gas hydrate mound is tinted orange by small amounts of oil, and is partially covered by a thin sediment drape (grey material). (Courtesy of Ian MacDonald).

methane seeps) imply that such sea-floor ecosystems have been occurring for millions of years (Goedert and Benham 2003; Peckmann and Thiel 2004).

2.4.1 OVERVIEW OF CHEMOSYNTHETIC COMMUNITIES AT METHANE SEEPS

Chemosynthetic communities found at methane seeps include both microorganisms and animals that depend on

hydrogen sulphide, which is a by-product of AOM (Paull *et al.* 1984; Sibuet and Olu 1998; Levin 2005), as well as animals that directly consume methane (Childress *et al.* 1986; Schmaljohann and Flugel 1987). Free-living chemosynthetic bacteria include sulphur bacteria such as *Beggiatoa*, *Thiopoloca*, or *Thiomargarita* (Jørgensen and Nelson 2004), as well as aerobic methane-oxidizing bacteria. Filamentous sulphur bacteria can sometimes form extensive white or orange mats on the sediment surface (Fig. 2.4).

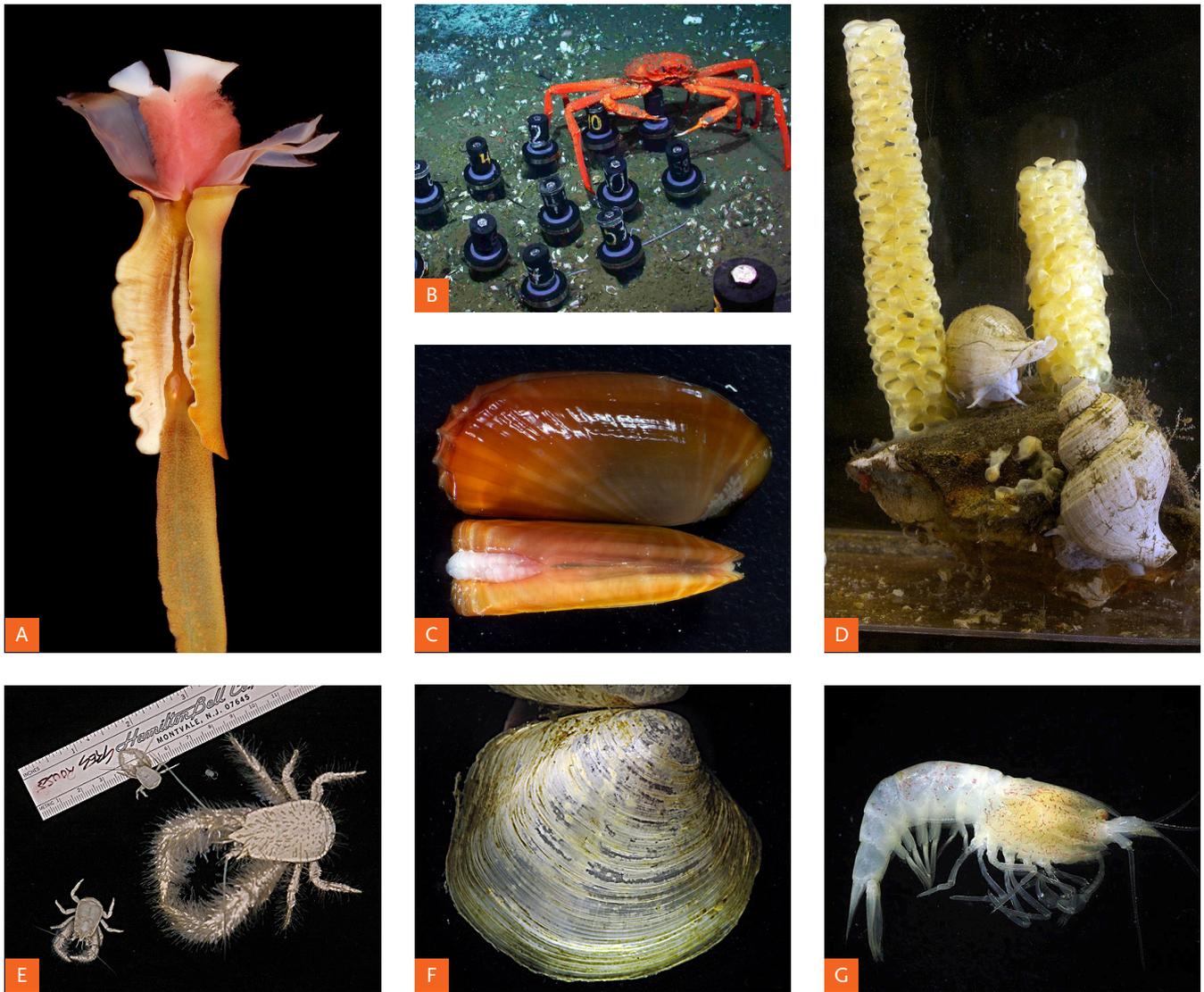


Figure 2.5: Cold-seep organisms. Examples from the methane seep ecosystem. A, C, E and F are chemosymbiotic animals whose energy source is hydrogen sulfide produced by methane-degrading microorganisms in the sediment. A: vestimentiferan tubeworm – *Lamellibrachia barhami*, B: lithodid crab embracing tube cores placed in a field of vesicomyid clams and bacterial mat C: solemyid clam – *Acharax* sp. D: Snail – *Neptunea amianta* and their egg towers attached to rock. E: Yeti crabs – *Kiwa puravida*, the ‘fur’ on their claws is filamentous symbiotic bacteria which they nourish by waving in sulphide-rich fluids, and then consume F: Thyasiridae, Quepos Seep (400 m water depth), Costa Rica margin G: Alvinocarid shrimp, Mound 12, Costa Rica margin (1 000 m water depth) (Photos courtesy of Greg Rouse and Lisa Levin, Scripps Institution of Oceanography).

Chemosymbiotic animals at methane seeps can be large or small, form bushes, dense beds, reefs, or live alone, and they can grow very quickly or exceptionally slowly. Animal communities at methane seeps include single-celled organisms (protozoans) and multi-celled animals (metazoans). Most of the metazoans are invertebrates. Many are sustained, one way or another, by microbial activity linked to methane. Common examples include vestimentiferan tubeworms (Fig. 2.5, A), crabs (Fig. 2.5 B, E), and a diversity of clams (Fig. 2.5, C, F).

All of these taxa are relatively large compared to non-seep, deep-sea fauna. Many seep-endemic organisms have reduced or absent digestive systems. Instead, they provide homes to symbiotic chemoautotrophic bacteria that provide the host with nutrition through aerobic sulphide and/or methane oxidation (Fig. 2.6).

The seeps and seep organisms support a wealth of grazing, predatory, and deposit-feeding taxa by providing substrate for attachment, access to reduced compounds, entrainment of organic-rich particles, and access to microbial protozoan or metazoan prey (Carney 1994; Cordes *et al.* 2010). Additionally, the carbonates (limestone is a type of carbonate) precipitated by microbial AOM consortia form crusts, rocks, boulders, and even vast landscapes at seeps (Teichert *et al.* 2005). These seeps can support high densities of mussels, tubeworms, and grazing gastropods (Olu-Le Roy *et al.* 1996; Levin *et al.* 2010).

Because the chemosynthetic life forms described here require different chemical balances and concentrations of methane and sulphide (Sibuet and Olu-Le Roy 1998; 2003; Levin 2005), distinct habitat patches form in response to the fluid chemistry and fluid flow rate (flux). Generally, sediments covered with mats of sulphur-oxidizing bacteria are associated with the strongest fluid and methane fluxes or near-surface gas hydrates. Mussel and vesicomyid clam beds are associated with high to moderate fluxes. Solemyid clam beds, as well as vestimentiferan frenulate tubeworm fields, are associated with lower oscillating fluxes or deeper gas hydrates (Fig. 2.7) (Sahling *et al.* 2002; Sibuet and Olu-Le Roy 2003; Levin 2005; Sommer *et al.* 2006). Such connections have been documented in several methane-seep environments (e.g. Van Dover *et al.* 2003; Olu-Le Roy *et al.* 2007; 2009). The combination of microbial mats, the beds, bushes, and

Morphology of a tube worm hosting sulphide-oxidizing symbionts

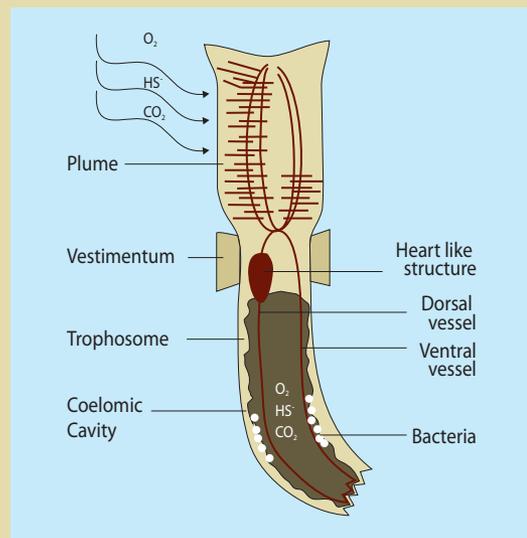


Figure 2.6: Symbiotic relationships for obtaining energy from sulphide. Morphology of a tube worm (top) and photo of a clam hosting sulphide-oxidizing symbionts (bottom, photo courtesy of Greg Rouse, Scripps Institution of Oceanography). Tube worms host their symbionts in the trophosome, a specialized organ. Oxygen (O_2), sulphide (HS^-), and carbon dioxide (CO_2) are taken up from the surrounding water through the animal's plume and delivered via the blood stream to the symbionts. Clams harbour their symbionts in their gills. Oxygen and carbon dioxide are available from the surrounding water, and sulphide is taken up from the sediment through the clam's foot.

fields formed by the engineering/foundation species and the microbially-precipitated carbonates, creates a heterogeneous, highly patchy habitat structure that contributes significantly to the overall biodiversity of seep ecosystems and continental margins (Cordes *et al.* 2010; Vanreusel *et al.* 2010).

The animals present at cold seeps are rarely in direct contact with gas hydrates. Only a single large taxon, the ice worm *Hesiocaeca methanicola* (See Chapter 1, Fig. 1.2) (Desbruyeres and Toulmond 1998; Fisher *et al.* 2000), has been documented to live directly in or on methane hydrates. This species attains relatively large size (2–4 centimetres) and occurs at high densities (2 500 to 3 000 individuals per square metre)

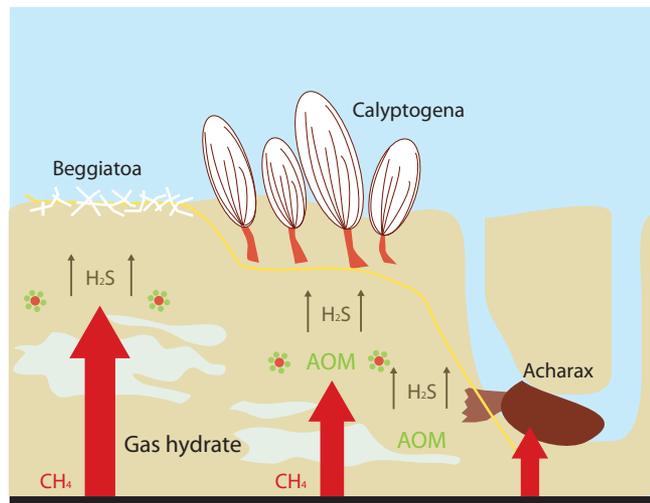


Figure 2.7: Chemosynthetic habitats. Chemosynthetic habitats generated by different fluid flow rates, including transport of methane, as well as the sulphide resulting from anaerobic oxidation of methane (AOM), are colonized by different fauna. Left: free-living, sulphur-oxidizing bacteria mats (e.g., *Beggiatoa* spp.) in sediments with highest fluxes. Centre: vesicomyid clams (e.g., *Calyptogena* spp.) in sediments with high-to-moderate fluxes. Right: solemyid clams (e.g., *Acharax* spp.) in sediments with low flux.

on gas hydrates in the Gulf of Mexico. Studies suggest the ice worm consumes free-living microbes associated with the hydrate and that the worm's activities, which involve forming depressions and creating small-scale water currents at the hydrate surface, may promote microbial growth and speed hydrate decomposition. The association of the ice worm with gas hydrates occurs both at the sediment-water interface and at least 10 centimetres below the surface.

Aside from the Gulf of Mexico, there has been limited direct sampling of massive methane hydrates to assess metazoan associations. Exposed methane hydrate at Hydrate Ridge does not appear to be directly colonized by metazoans (Boetius and Suess 2004), although the presence of gas hydrates supports dense, colourful bacterial mats that can lead to high densities of infauna (animals living inside the sediment) in the near vicinity (Sahling *et al.* 2002; Levin *et al.* 2010; Vanreusel *et al.* 2010). The gas hydrates just below bacterial mats at Hydrate Ridge may actually act as a barrier, blocking some of the digging clams, tubeworms, and other species (Sahling *et al.* 2002).

2.4.2 SENSITIVITIES OF METHANE-SEEP COMMUNITIES TO CLIMATE CHANGE AND GEOLOGICAL VARIATIONS

There are indications in the geological record that warming/cooling trends and oscillations in eustatic sea level could influence methane hydrate stability, authigenic carbonate formation, slope stability, and, in turn, the abundance of seep habitats (Jiang *et al.* 2006; Archer 2007; Kiel 2009). Undersea earthquakes, such as the Grand Banks earthquake, can also produce methane seeps and chemosynthetic habitats (Mayer *et al.* 1988). It is, so far, unknown how the gas-hydrate response to ongoing climate change (Discussed in Volume 1, Chapter 3) will affect chemosynthetic communities. Dissociation could create completely new habitats by increasing methane seepage, or rapid gas hydrate dissociation and disappearance might decrease the horizontal extent of existing seep habitats.

REFERENCES

- Archer, D. (2007). Methane hydrate stability and anthropogenic climate change. *Biogeosciences Discuss.*, 4, 993-1057
- Barnes, R.O. and Goldberg, E.D. (1976). Methane production and consumption in anoxic marine sediments. *Geology*, 4, 297-300
- Biastoch, A., Treude, T., Rüpke, L.H., Riebesell, U., Roth, C., Burwicz, E.B., Park, W., Latif, M., Böhning, C.W., Madec, G. and Wallmann, K. (2011). Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification. *Geophys. Res. Lett.*, 38, L08602, doi:08610.01029/02011GL047222
- Blasing, T.J. (2013). "Recent greenhouse gas concentrations". Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory. http://cdiac.ornl.gov/pns/current_ghg.html
- Boetius, A. and Suess, E. (2004). Hydrate Ridge: A natural laboratory for the study of microbial life fueled by methane from near-surface gas hydrates. *Chem. Geol.*, 205, 291-310
- Bohrmann, G., Greinert, J., Suess, E. and Torres, M. (1998). Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. *Geology*, 26, 647-650. doi: 10.1130/0091-7613(1998)026<0647:acftcs>2.3.co;2
- Booth, J.S., O'Leary, D.W., Popenoe, P. and Danforth, W.W. (1993). U.S. Atlantic continental slope landslides: their distribution, general attributes, and implications. In *Submarine landslides: Selected studies in the U.S. Exclusive Economic Zone* (eds. W.C. Schwab, H.J. Lee and D.C. Twichell). pp. 14-22. U.S. Geological Survey Bulletin no. 2002
- Borowski, W.S., Paull, C.K. and Ussler, W., III (1999). Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates. *Mar. Geol.*, 159, 131-154
- Boswell, R., Collett, T., Frye, M., Shedd, B., McConnell, D. and Shelander, D. (2012). Subsurface gas hydrates in the northern Gulf of Mexico. *J. Mar. Pet. Geol.*, 34, 4-30.
- Boucher, O., Friedlingstein, P., Collins, B. and Shine, K.P. (2009). The indirect global warming potential and global temperature change potential due to methane oxidation. *Environ. Res. Lett.*, 4, 044007
- Bourriak, S., Vanneste, M. and Saoutkine, A. (2000). Inferred gas hydrates and clay diapirs near the Storegga Slide on the southern edge of the Voring Plateau, offshore Norway. *Mar. Geol.*, 163, 125-148
- Bryn, P., Berg, K., Forsberg, C.F., Solheim, A. and Kvalstad, T.J. (2005). Explaining the Storegga Slide. *Mar. Petrol. Geol.*, 22, 11-19. doi: 10.1016/J.Marpetgeo.2004.12.003
- Buffett, B. and Archer, D. (2004). Global inventory of methane clathrate: Sensitivity to changes in the deep ocean. *Earth Planet Sc. Lett.*, 227, 185-199
- Bugge, T., Befring, S., Belderson, R.H., Eidvin, T., Jansen, E., Kenyon, N.H., Holtedahl, H. and Sejrup, H.P. (1987). A giant 3-stage submarine slide off Norway. *Geo-Mar. Lett.*, 7, 191-198
- Carney, R.S. (1994). Consideration of the oasis analogy for chemosynthetic communities at Gulf-of-Mexico hydrocarbon vents. *Geo-Mar. Lett.*, 14, 149-159
- Childress, J.J., Fisher, C.R., Brooks, J.M., Kennicutt, M.C., Bidigare, R. and Anderson, A.E. (1986). A methanotrophic marine molluscan (*Bivalvia*, Mytilidae) symbiosis - Mussels fueled by gas. *Science*, 233, 1306-1308
- Colwell, F.S. and Ussler III, W. (2010). Global scale consequences of biological methane production. In *Handbook of hydrocarbon and lipid microbiology* (ed. K.N. Timmis). pp. 3056-3065. Springer-Verlag, Berlin
- Cordes, E.E., Cunha, M.R., Galéron, J., Mora, C., Roy, K.O.-L., Sibuet, M., Gaever, S.V., Vanreusel, A. and Levin, L.A. (2010). The influence of geological, geochemical, and biogenic habitat heterogeneity on seep biodiversity. *Mar. Ecol.*, 31, 51-65
- Corliss, J.B., Dymond, J., Gordon, L.I., Edmond, J.M., Herzen von, R.P., Ballard, R.D., Green, K., Williams, D., Brainbridge, A., Crane, K. and Andel van, T.H. (1979). Submarine thermal springs on the Galápagos Rift. *Science*, 203, 1073-1083
- Davie, M.K. and Buffett, B.A. (2003). A steady state model for marine hydrate formation: Constraints on methane supply from pore water sulfate profiles. *J. Geophys. Res.*, 108, 2495, doi:2410.1029/2002JB002300
- Desbruyeres, D. and Toulmond, A. (1998). A new species of hesionid worm, *Hesioeca methanicola* sp. nov. (Polychaeta: Hesionidae), living in ice-like methane hydrates in the deep Gulf of Mexico. *Cah. Biol. Mar.*, 39, 93-98
- Dickens, G. (2001). On the fate of past gas: What happens to methane released from a bacterially mediated gas hydrate capacitor? *Geochem. Geophys. Geosy.*, 2, art. no.-2000GC000131
- Dickens, G. (2011). Down the rabbit hole: toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events. *Past*, 7, 831-846
- Dickens, G.R. (2003). Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. *Earth Planet Sc. Lett.*, 213, 169-183. doi: 10.1016/S0012-821X(03)00325-X
- Dickens, G.R., O'Neil, J.R., Rea, D.K. and Owen, R.M. (1995). Dissociation of oceanic methane hydrates as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, 10(6), 965-972
- Ding, H. and Valentine, D.L. (2008). Methanotrophic bacteria occupy benthic microbial mats in shallow marine hydrocarbon seeps, Coal Oil Point, California. *J. Geophys. Res.-Biogeo.*, 113. doi: 10.1029/2007jg000537

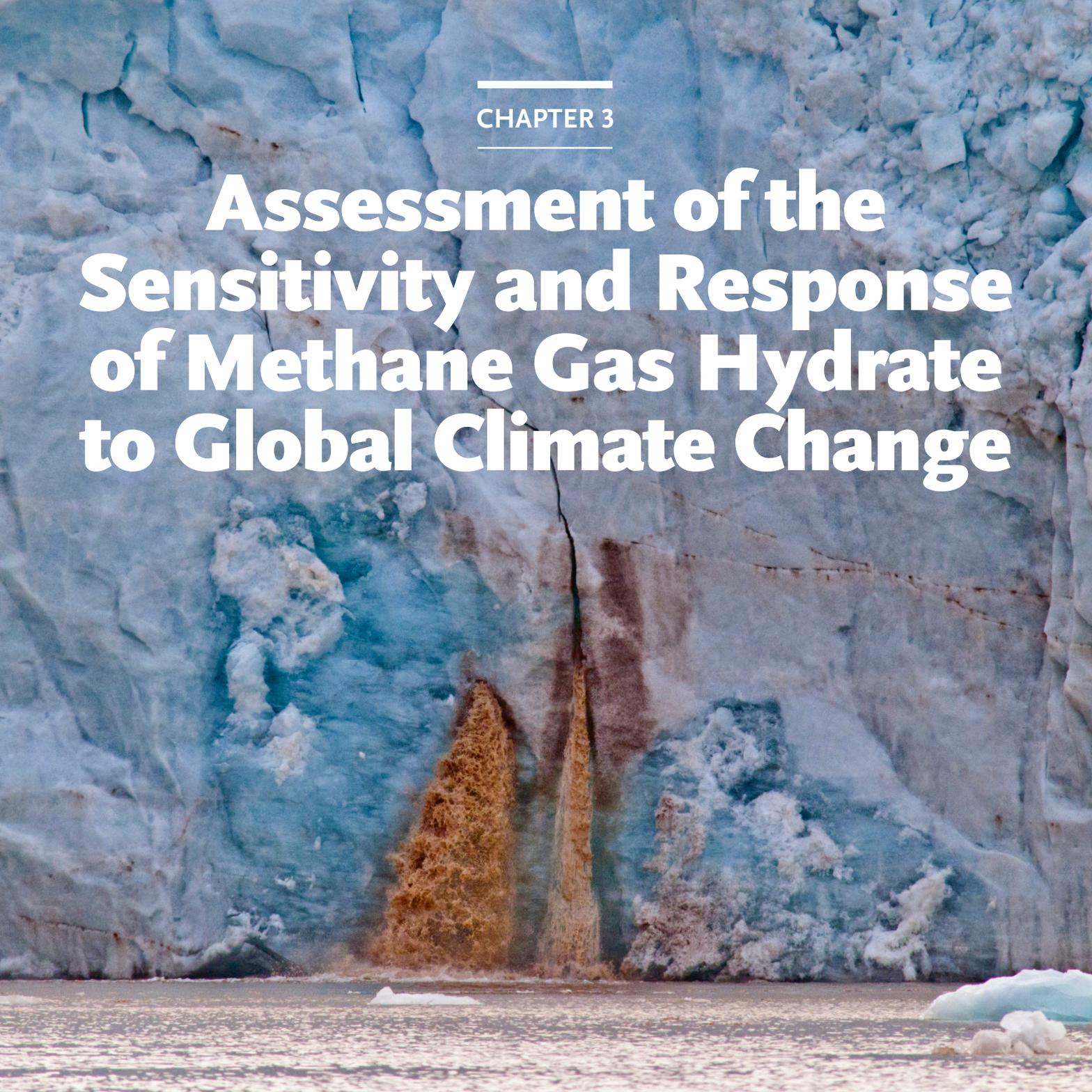
- Felbeck, H. (1981). Chemoautotrophic potential of the hydrothermal vent tube worm, *Riftia pacijptila* Jones (Vestimentifera). *Science*, 213, 336-338
- Fisher, C.R., MacDonald, I.R., Sassen, R., Young, C.M., Macko, S.A., Hourdez, S., Carney, R.S., Joye, S.B. and McMullin, E. (2000). Methane ice worms: *Hesiocaeca methanicola* colonizing fossil fuel reserves. *Naturwissenschaften*, 87, 184-187
- Gee, M.J.R., Uy, H.S., Warren, J., Morley, C.K. and Lambiase, J.J. (2007). The Brunei slide: A giant submarine landslide on the North West Borneo Margin revealed by 3D seismic data. *Mar. Geol.*, 246, 9-23. doi: Doi 10.1016/J.Margeo.2007.07.009
- Goedert, J.L. and Benham, S.R. (2003). Biogeochemical processes at ancient methane seeps: the Bear River site in southwestern Washington. In *Western Cordillera and adjacent areas: Boulder, Colorado* (ed. T.W. Swanson). pp. 201-208. Geological Society of America
- Hansen, J., Funck, A., Lacis, A., Rind, D. and Lebedeff, S. (1988). Global climate changes as forecast by Goddard Institute for Space Studies 3-D Model. *J. Geophys. Res.*, 93, 9341-9364
- Hanson, R.S. and Hanson, T.E. (1996). Methanotrophic bacteria. *Microbiol. Rev.*, 60, 439-471
- Hedges, J.I. and Keil, R.G. (1995). Sedimentary organic-matter preservation – An assessment and speculative synthesis. *Mar. Chem.*, 49, 81-115
- Hornbach, M.J., Lavier, L.L. and Ruppel, C.D. (2007). Triggering mechanism and tsunamogenic potential of the Cape Fear Slide complex, U.S. Atlantic margin. *Geochem. Geophys. Geosy.*, 8, Q12008, doi: 10.1029/2007GC001722, 001716 p.
- Houghton, R. A. (2007). Balancing the global carbon budget, *Annu. Rev. Earth Planet. Sci.*, 35, 313-347
- Hu, L., Yvon-Lewis, S.A., Kessler, J.D. and MacDonald, I.R. (2012). Methane fluxes to the atmosphere from deepwater hydrocarbon seeps in the northern Gulf of Mexico. *J. Geophys. Res.*, 117. doi: 10.1029/2011jc007208
- IPCC (2007). *Climate Change 2007: The physical science basis. Contribution of Working Group I to the fourth assessment report of the Intergovernmental Panel on Climate Change* 996 p. IPCC, Cambridge, United Kingdom and New York, NY, USA
- Jiang, G., Shi, X. and Zhang, S. (2006). Methane seeps, methane hydrate destabilization, and the late Neoproterozoic postglacial cap carbonates. *Chin. Sci. Bull.*, 51, 1152-1173
- Jørgensen, B.B. and Nelson, D.C. (2004). Sulfide oxidation in marine sediments: Geochemistry meets microbiology. *Geol. Soc. Am., Special Paper* 379, 63-81
- Joye, S.B., Samarkin, V.A., Orcutt, B.N., MacDonald, I.R., Hinrichs, K.U., Elvert, M., Teske, A.P., Lloyd, K.G., Lever, M.A., Montoya, J.P. and Meile, C.D. (2009). Metabolic variability in seafloor brines revealed by carbon and sulphur dynamics. *Nat. Geosci.*, 2, 349-354. doi: Doi 10.1038/Ngeo0475
- Judd, A.G., Hovland, M., Dimitrov, L.I., García Gil, S. and Jukes, V. (2002). The geological methane budget at continental margins and its influence on climate change. *Geofluids*, 2, 109-126
- Kastner, M., Torres, M., Solomon, E. and Spivack, A. (2008). Marine pore fluid profiles of dissolved sulfate; do they reflect in situ methane fluxes. *Fire in the Ice, NETL Methane Hydrate Newsletter*, Summer, 6-8
- Kayen, R.E. and Lee, H.J. (1991). Pleistocene slope instability of gas hydrate-laden sediment on the Beaufort Sea Margin. *Mar. Geotechnol.*, 10, 125-141
- Kiel, S. (2009). Global hydrocarbon seep-carbonate precipitation correlates with deep-water temperatures and eustatic sea-level fluctuations since the Late Jurassic. *Terra Nova*, 21, 279-284
- Knittel, K. and Boetius, A. (2009). Anaerobic oxidation of methane: progress with an unknown process. *Annu. Rev. Microbiol.*, 63, 311-334
- Kvalstad, T.J., Andresen, L., Forsberg, C.F., Berg, K., Bryn, P. and Wangen, M. (2005). The Storegga slide: evaluation of triggering sources and slide mechanics. *Mar. Petrol. Geol.*, 22, 245-256. doi: 10.1016/J.Marpetgeo.2004.10.019
- Lacis, A., Hansen, J., Lee, P., Mitchell, T. and Lebederr, S. (1981). Greenhouse effects of trace gases. *Geophys. Res. Lett.*, 8, 1035-1038
- Lee, H.J. (2009). Timing of occurrence of large submarine landslides on the Atlantic Ocean margin. *Mar. Geol.*, 264, 53-64. doi: 10.1016/J.Margeo.2008.09.009
- Levin, L.A. (2005). Ecology of cold seep sediments: interactions of fauna with flow, chemistry and microbes. *Oceanogr. and Mar. Biol.: Ann. Rev.*, 43, 1-46
- Levin, L.A., Mendoza, G.F., Gonzalez, J.P., Thurber, A.R. and Cordes, E.E. (2010). Diversity of bathyal macrofauna on the northeastern Pacific margin: the influence of methane seeps and oxygen minimum zones. *Mar. Ecol.-Prog. Ser.*, 31, 94-110
- Liu, X. and Flemings, P.B. (2006). Passing gas through the hydrate stability zone at southern Hydrate Ridge, offshore Oregon. *Earth Planet Sc. Lett.*, 241, 211-226
- Lopez, C., Spence, G., Hyndman, R. and Kelley, D. (2010). Frontal ridge slope failure at the northern Cascadia margin: Margin-normal fault and gas hydrate control. *Geology*, 38, 967-970. doi: Doi 10.1130/G31136.1
- Macdonald, I., Bender, L., Vardaro, M., Bernard, B. and Brooks, J. (2005). Thermal and visual time-series at a seafloor gas hydrate deposit on the Gulf of Mexico slope, *Earth and Planetary Science Letters*, 233(1-2), 45-59
- MacDonald, I.R., Leifer, I., Sassen, R., Stine, P., Mitchell, R. and Guinasso, N., Jr. (2002). Transfer of hydrocarbons from natural seeps to the water column and atmosphere. *Geofluids*, 2, 95-107
- Maslin, M., Owen, M., Day, S. and Long, D. (2004). Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis. *Geology*, 32, 53-56. doi: 10.1130/G20114.1

- Mau, S., D. L. Valentine, J. F. Clark, J. Reed, R. Camilli, and L. Washburn (2007). Dissolved methane distributions and air-sea flux in the plume of a massive seep field, Coal Oil Point, California, *Geophysical Research Letters*, 34(22).
- Mayer, L.A., Shor, A.N., Clarke, H. and Piper, D.J.W. (1988). Dense biological communities at 3850 m on the Laurentian Fan and their relationship to the deposits of the 1929 Grand Banks earthquake. *Deep-Sea Res. I*, 35, 1235-1246
- McGinnis, D.F., Greinert, J., Artemov, Y., Beaubien, S.E. and Wüst, A. (2006). Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere? *J. Geophys. Res.*, 111, C09007. doi: 10.1029/2005JC003183
- McIver, R.D. (1982). Role of naturally occurring gas hydrates in sediment transport. *AAPG Bull.*, 66, 789-792
- Mienert, J., 2008. Methane hydrate and submarine slides, p. 790-798, In: *Encyclopedia of Ocean Sciences* (2nd edition), Editors-in-chief: John H. Steele, Karl K. Turekian, and Steve A. Thorpe.
- Mienert, J., Vanneste, M., Bünz, S., Andreassen, K., Hafliðason, H. and Sejrup, H.P. (2005). Ocean warming and gas hydrate stability on the mid-Norwegian margin at the Storegga Slide. *Mar. Petrol. Geol.*, 22, 233-244
- Niemann, H., Lösekann, T., De Beer, D., Elvert, M., Nadalig, T., Knittel, K., Aman, A., Sauter, E.J., Schlüter, M., Klages, M., Foucher, J.-P. and Boetius, A. (2006). Novel microbial communities of the Haakon Mosby mud volcano and their role as a methane sink. *Nature*, 443, 854-858
- Olu-Le Roy, K., Caprais, J.C., Fifis, A., Fabri, M.C., Galéron, J., Budzinsky, H., Le Ménach, K., Khrpounoff, A., Ondréas, H. and Sibuet, M. (2007). Cold-seep assemblages on a giant pockmark off West Africa: spatial patterns and environmental control. *Mar. Ecol.*, 28, 115-130
- Olu-Le Roy, K., Caprais, J.C., Galéron, J., Causse, R., Cosel, R.v., Budzinsky, H., Le Ménach, K., Le Roux, C., Levanchél, D., Khrpounoff, A. and Sibuet, M. (2009). Influence of seep emission on the non symbiont-bearing fauna and vagrant species at an active giant pockmark in the Gulf of Guinea (Congo-Angola margin). *Deep-Sea Res. II*, 56, 2380-2393
- Olu-Le Roy, K., Duperré, A., Sibuet, M., Foucher, J.-P. and Fiala-Médioni, A. (1996). Structure and distribution of cold seep communities along the Peruvian active margin: relationship to geological and fluid patterns. *Mar. Ecol.-Prog. Ser.*, 132, 109-125
- Oschlies, A., Schulz, H.D. and Riebesell, U. (2008). Simulated 21st century's increase in oceanic suboxia by CO₂-enhanced biotic carbon export. *Global Biogeochem. Cy.*, 22, 01-36. doi: 10.1029/2007GB004008
- Paull, C.K., Hecker, B., Commeau, R., Freeman-Lynde, R.P., Neumann, C., Corso, W.P., Golubic, S., Hook, J.E., Sikes, E. and Curray, J. (1984). Biological communities at the Florida escarpment resemble hydrothermal vent taxa. *Science*, 226, 965-967
- Peckmann, J. and Thiel, V. (2004). Carbon cycling at ancient methane-seeps. *Chem. Geol.*, 205, 443-467
- Pelejero, C., Calvo, E. and Hoegh-Guldberg, O. (2010). Paleo-perspectives on ocean acidification. *Trends Ecol. Evol.*, 25, 332-344
- Reeburgh, W.S. (1996). "Soft spots" in the global methane budget. In *Microbial growth on C1 compounds* (eds. L. M.E. and F.R. Tabita). pp. 334-342. Kluwer Academic Publishers, Intercept, Andover, UK
- Reeburgh, W.S. (2003). Global methane biogeochemistry. In *Treatise on geochemistry* (ed. R.F. Keeling). pp. 65-89. Elsevier
- Reeburgh, W.S. (2007). Oceanic methane biogeochemistry. *Chem. Rev.*, 107, 486-513
- Sahling, H., Rickert, D., Raymond, W.L., Linke, P. and Suess, E. (2002). Macrofaunal community structure and sulfide flux at gas hydrate deposits from the Cascadia convergent margin, NE Pacific. *Mar. Ecol.-Prog. Ser.*, 231, 121-138
- Sassen, R., Sweet, S.T., Milkov, A.V., DeFreitas, D.A. and Kennicutt, M.C., II (2001). Thermogenic vent gas and gas hydrate in the Gulf of Mexico slope: Is gas hydrate decomposition significant? *Geology*, 29, 107-110
- Schmaljohann, R. and Flugel, H.J. (1987). Methane-oxidizing bacteria in Pogonophora. *Sarsia*, 72, 91-99
- Shakhova, N., Semiletov, I., Salyuk, A., Yusupov, V., Kosmach, D. and Gustafsson, O. (2010). Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science*, 327, 1246-1250
- Sibuet, M. and Olu, K. (1998). Biogeography, biodiversity and fluid dependence of deep-sea cold-seep communities at active and passive margins. *Deep-Sea Res. II*, 45, 517-567
- Sibuet, M. and Roy, K.O.-L. (2003). Cold seep communities on continental margins: Structure and quantitative distribution relative to geological and fluid venting patterns. In *Ocean margin systems* (eds. G. Wefer, D. Billett and D. Hebbeln). pp. 235-251. Springer, Berlin
- Solomon, E.A., Kastner, M., Jannasch, H., Robertson, G. and Weinstein, Y. (2008). Dynamic fluid flow and chemical fluxes associated with a seafloor gas hydrate deposit on the northern Gulf of Mexico slope. *Earth Planet Sc. Lett.*, 270, 95-105. doi: 10.1016/J.Epsl.2008.03.024
- Sommer, S., Pfannkuche, O., Linke, P., Luff, R., Greinert, J., Drews, M., Gubsch, S., Pieper, M., Poser, M. and Viergutz, T. (2006). Efficiency of the benthic filter: Biological control of the emission of dissolved methane from sediments containing shallow gas hydrates at Hydrate Ridge. *Global Biogeochem. Cy.*, 20. doi: 10.1029/2004gb002389
- Stramma, L., Johnson, G., Sprintall, J. and Morholz, V. (2008). Expanding oxygen-minimum zones in the tropical oceans. *Science* 320, 4
- Suess, E. (2010). Marine cold seeps. In *Handbook of hydrocarbon and lipid microbiology* (ed. K.N. Timmis). pp. 187-203. Springer-Verlag, Berlin Heidelberg
- Sultan, N., Cochonat, P., Foucher, J.P. and Mienert, J. (2004). Effect of gas hydrates melting on seafloor slope instability. *Mar. Geol.*, 213, 379-401

- Sundquist, E. T., and K. Visser (2003), The geologic history of the carbon cycle, in *Biochemistry: Treatise on Geochemistry*, edited by W. Schlesinger, exec. eds. Holland, H.D., Turekian, K.K., pp. 425-472, Elsevier, New York.
- Teichert, B.M.A., Borhmann, G. and Suess, E. (2005). Chemoherms on Hydrate Ridge - unique microbally-mediated carbonate build-ups growing into the water column. *Palaeogeogr., Paleoclimatol., Palaecol.*, 227
- Treude, T., Boetius, A., Knittel, K., Wallmann, K. and Barker Joergensen, B. (2003). Anaerobic oxidation of methane above gas hydrates at Hydrate Ridge, NE Pacific Ocean. *Mar. Ecol.-Prog. Ser.*, 264, 1-14
- Treude, T., Krüger, M., Boetius, A. and Jørgensen, B.B. (2005b). Environmental control on anaerobic oxidation of methane in the gassy sediments of Eckernförde Bay (German Baltic). *Limnol. Oceanogr.*, 50, 1771-1786
- Treude, T. and Ziebis, W. (2010). Methane oxidation in permeable sediments at hydrocarbon seeps in the Santa Barbara Channel, California. *Biogeosciences*, 7, 1-14
- Van Dover, C. L., Aharon, P., Bernhard, J. M., Caylor, E., Doerries, M., Flickinger, W., Gilhooly, W., Goffredi, S. K., Knick, K. E., Macko, S. A., Rapoport, S., Raulfs, E. C., Ruppel, C., Salerno, J. L., Seitz, R. D., Sen Gupta, B. K., Shank, T., Turnipseed, M., Vrijenhoek, R. (2003), Blake Ridge methane seeps: characterization of a soft-sediment, chemo synthetically based ecosystem, *Deep-Sea Research Part I*, 50(2), 281-300.
- Vanreusel, A., Fonseca, G., Danovaro, R., Da Silva, M.C., Esteves, A.M., Ferrero, T., Gad, G., Galtsova, V., Gambi, C. and da Fonsêca Genevois, V. (2010). The contribution of deep sea macrohabitat heterogeneity to global nematode diversity. *Mar. Ecol.*, 31, 6-20
- Xu, W. and Germanovich, L.N. (2006). Excess pore pressure resulting from methane hydrate dissociation in marine sediments: A theoretical approach. *J. Geophys. Res.*, 111, B01104, doi:10.1029/2004JB003600
- Zachos, J.C., Röhl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E., Nicolo, M., Raffi, I., Lourens, L.J., McCarren, H. and Kroon, D. (2005). Rapid acidification of the ocean during the Paleocene-Eocene Thermal Maximum. *Science*, 308, 1611-1615

CHAPTER 3

Assessment of the Sensitivity and Response of Methane Gas Hydrate to Global Climate Change



3.1 INTRODUCTION

As discussed earlier in this report, methane in the atmosphere is a potent greenhouse gas. Methane's radiative forcing value, a measure of how it changes Earth's balance between incoming and lost solar energy, is about 0.5 watts per square metre, second only to the 1.66 watts per square metre of carbon dioxide (IPCC 2007).

The atmosphere contains about 3.7 Gt of methane carbon (IPCC 2007). This value is reasonably constant because of a delicate balance between atmospheric methane input and removal rates, both in the range of 0.45 Gt of methane carbon per year (IPCC 2007). Taking the midrange estimate of 5 000 Gt of carbon held as methane sequestered in gas hydrates (see Volume 1 Chapter 1), an instantaneous release of just a tenth of a per cent of Earth's gas hydrates to the

atmosphere would more than double the IPCC's estimated atmospheric methane concentration.

Methane's greenhouse potency, combined with the amount of methane stored in gas hydrates, has led researchers to suggest methane released from dissociating gas hydrates played a significant role in past climate changes, and could be an important factor in future climate change. This chapter presents an example of how gas hydrates have been connected to past climate change and discusses key factors in establishing the role of gas hydrates in future climate change. Future climate change scenarios and the possible response of marine and permafrost gas hydrate deposits are then considered. The chapter concludes with a summarized assessment of the deposits that are most susceptible to change.

3.2 THE ROLE OF GAS HYDRATE IN PAST CLIMATE CHANGE

An extreme global warming event in the geological record began at the Paleocene-Eocene Boundary, about 56 million years ago (Dunkley-Jones *et al.* 2010; McNerney and Wing 2011). During this event, now called the Palaeocene-Eocene thermal maximum (PETM), global surface temperatures, including in the deep-sea, rose by 5 to 6 °C over a 1 to 10 thousand year period (Dunkley-Jones *et al.* 2010). Potential global-scale triggers for a temperature rise include a change in ocean circulation patterns (Lunt *et al.* 2010), or a change in snow, ice and vegetation coverage that altered the amount of sunlight absorbed by the Earth (Adams *et al.* 1999). Triggers for warming at a local or regional scale might include cometary impact (Kent *et al.* 2003) or large-scale magma eruptions (Storey *et al.* 2007; Cohen *et al.* 2007).

Triggering mechanisms themselves may not be capable of generating the full global-scale temperature increase, however, so many researchers invoke a process proposed by Dickens *et al.* (1995) in which the warming trigger destabilizes a significant volume of gas hydrate. This link to gas hydrate dissociation is suggested by the numerous stable isotope records across Earth indicating the PETM warming coincided with at least 2 000 Gt of isotopically light (¹³C-depleted) carbon to the ocean and atmosphere (Zeebe *et al.* 2009; Cui *et al.* 2011), as well as oxygen depletion in the oceans and widespread carbonate dissolution on the sea floor (Dickens *et al.* 1997). Isotopically light carbon can be an indication of biogenic methane that has been released from dissociating hydrate. Moreover, as discussed in Volume 1, Chapter 2, methane released into the ocean can be oxidized to CO₂, a process that consumes oxygen and can also cause carbonate dissolution by making the water more acidic (see Volume 1 Chapter 2, Text Box 2.1).

Irrespective of the fate of methane, atmospheric carbon concentrations would increase over relatively short-time scales, and contribute to the dramatic PETM warming (e.g. Dickens *et al.* 1997; Zeebe *et al.* 2009). Gas hydrate's role during the PETM continues to be debated, however, because there are several possible sources for massive and rapid carbon input to the ocean and atmosphere unrelated to gas hydrates. Other suggested carbon sources during the PETM include: oxidation or burning of peat (Kurtz *et al.* 2003), impact of a carbonaceous comet (Kent *et al.* 2003), intrusion of volcanic sills into organic-rich sediment (Svensen *et al.* 2004), or carbon dioxide and methane release from degrading permafrost (DeConto *et al.* 2010).

For the PETM and other past warming events, a few examples being the Permian-Triassic boundary (Krull and Retallack, 2000), in the early Toarcian (Hesselbo *et al.* 2000; Cohen *et al.* 2007), in the Cretaceous (Jenkyns and Wilson, 1999), and in the Quaternary (Hill *et al.* 2006), one general conclusion is that if methane hydrate dissociation was important, it exacerbated, but did not initially trigger, rapid global warming (Dickens *et al.* 1995; Dickens 2003; Zachos *et al.* 2005; Sluijs *et al.* 2007; Dunkley-Jones *et al.* 2010; Maslin *et al.* 2010). Another important conclusion is that a large fraction of the methane released from the sea floor may be oxidized in the water column, such that a primary consequence of hydrate dissociation is ocean acidification and loss of dissolved oxygen (Dickens 2003). These past-climate studies help guide our expectations for what role gas hydrates might play in the future, given current climate trends.

3.3 KEY ISSUES FOR LINKING GAS HYDRATE WITH CLIMATE CHANGE

Establishing the importance of methane from gas hydrates in ongoing and future climate change remains a challenge. Part of the challenge is the considerable uncertainty about the total amount of methane involved, as well as the timing and nature of gas hydrates' response to future change (Kerr 2010). To establish quantifiable connections between gas hydrates, ongoing climate change, and future climate change, four main questions must be answered:

How much warming will there be, and where? Surface temperature changes must be linked to global processes, such as fluctuations in ocean circulation, sea level, and glacier mass balance, in order to provide information about temperature changes at the sea floor or in coastal permafrost regions. Predictive models of heat transfer through sediment can then be applied to forecast the temperature evolution for the buried gas hydrates themselves.

How much gas hydrate breakdown will result from that warming? Answering this question requires knowing the

spatial distribution and concentration of gas hydrates in relation to regions of enhanced warming, as well as verifying the depth of hydrate occurrence in these locations to determine whether a given surface temperature change will cause any or all of the buried gas hydrates to break down.

How long will the warming take to destabilize those gas hydrates? Heat transfer down through sediment can be slow. The process is further slowed by the heat absorbed in thawing overlying permafrost or dissociating gas hydrates themselves. There can be delays of 3 000 years or more between ground-surface or sea-floor warming and the ensuing gas hydrate dissociation at depth (Ruppel 2011).

How much of the methane released from the destabilized gas hydrates will be transferred to the atmosphere? To increase atmospheric methane concentrations, methane liberated from gas hydrates must migrate through the sediment and/or water column without being consumed or dissolved. Consumption rates are not well-constrained and vary by location.

3.4 GLOBAL CLIMATE CHANGE PROJECTIONS

Future trends in global climate change have been subjected to intense scientific investigation, with major efforts being mounted by the Intergovernmental Panel on Climate Change (IPCC). Their fourth assessment report, published in 2007,

documents the growing impact of human activities on global climate and reviews the challenges of undertaking forward predictions (IPCC 2007).

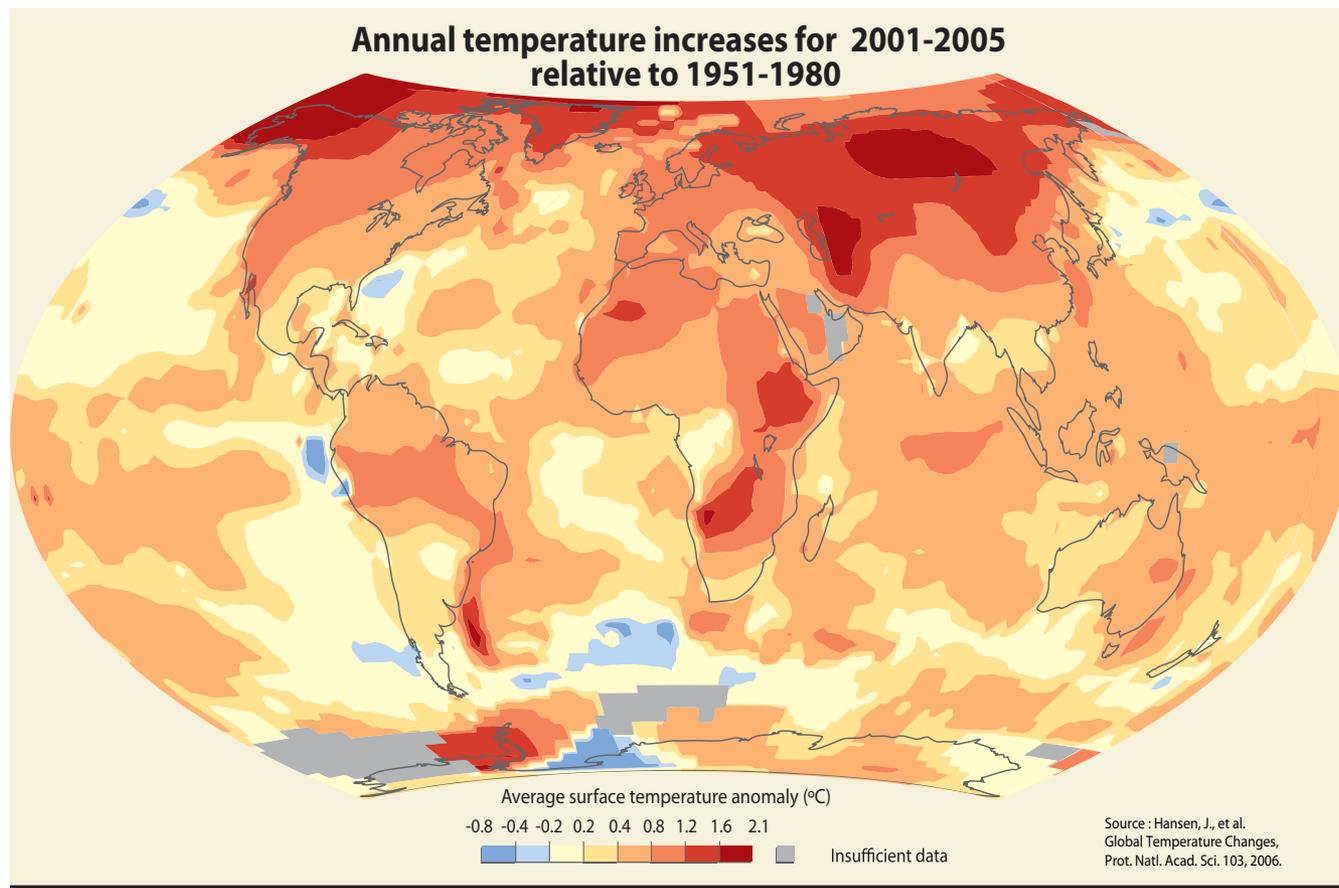


Figure 3.1: Sea-surface and land-surface temperature changes. Change in ocean sea-surface temperature and temperature over land from 2001 to 2005, relative to the 1951-1980 mean (Hansen *et al.* 2006). The Arctic is experiencing some of the Earth's most significant warming.

Predicted increase in global mean surface-air temperatures

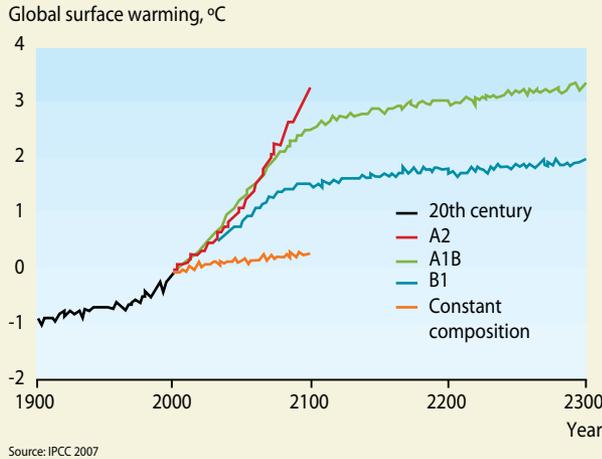


Figure 3.2: Predicted increase in global mean surface-air temperatures. Increases are relative to 1980–1999 for different emission scenarios (IPCC 2007). The partial pressure of carbon dioxide in the atmosphere ($p\text{CO}_2$) is assumed to attain a value of 800 to 1 000 parts per million (ppm) at the end of this century for scenario A2. It increases to about 700 ppm in scenario A1B and reaches approximately 500 ppm in scenario B1. The current $p\text{CO}_2$ value of about 390 ppm is maintained until the end of the century in the constant composition scenario. (See IPCC (2007) for further information.)

According to the IPCC assessments, surface temperatures rose significantly over the last century, with the strongest warming signal in the Arctic (Fig. 3.1).

Future trends in climate change have been estimated by the IPCC for different greenhouse gas emission scenarios (Fig. 3.2). Predictions of global surface-air-temperature increases over the next century range from 1.5 to >3 °C. As observed in the historical data, the most substantial warming is anticipated at high northern latitudes (Fig. 3.3) where surface

Arctic surface air-temperature change

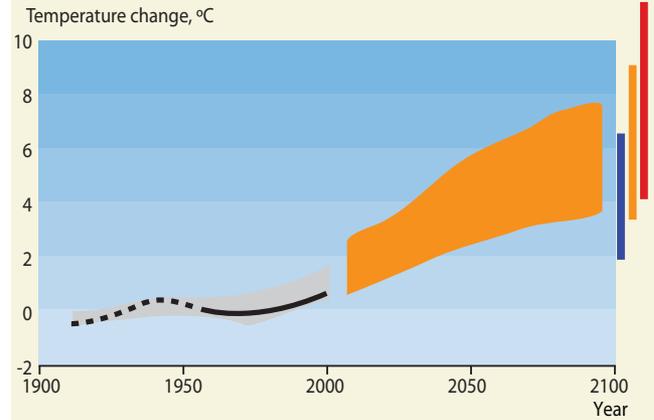


Figure 3.3: Arctic surface air-temperature change. Change is measured relative to measurements from 1901 to 1950 (black curve). Orange region is the 2001–2100 prediction given the A1B scenario ($p\text{CO}_2$ increase to 700 ppm by 2100). Bars to the right indicate the predictions for 2091–2100 for the scenarios B1 (blue bar, $p\text{CO}_2$ increases to 500 ppm by 2100), A1B (orange bar, $p\text{CO}_2$ increases to 700 ppm by 2100), and A2 (red bar, $p\text{CO}_2$ increases to 800–1 000 ppm by 2100) (IPCC 2007).

air temperatures may increase by up to 8 °C by the end of this century.

Methane release from dissociating gas hydrates is not included in the IPCC climate predictions, in part because the magnitude and timing of the induced emissions are poorly constrained and therefore difficult to forecast. Gas hydrate dissociation might nevertheless amplify future warming, ocean acidification, and oxygen loss, as discussed in Volume 1, Chapter 2.

3.5 RESPONSE OF GAS HYDRATES TO CLIMATE CHANGE

3.5.1 OCEANIC RESPONSE TO CLIMATE CHANGE

Marine gas-hydrate deposits occur in sediments under 300-500 metres or more of water and at a significant depth beneath the sea floor. As a result, the most important climate change consideration for hydrate dissociation is the possible warming of bottom waters. Heat conduction is the primary heat transfer process from the atmosphere into the ground in terrestrial settings, but a number of processes can transport heat from the sea surface into the ocean's interior. These include vertical mixing, convection of water masses and changes in ocean circulation.

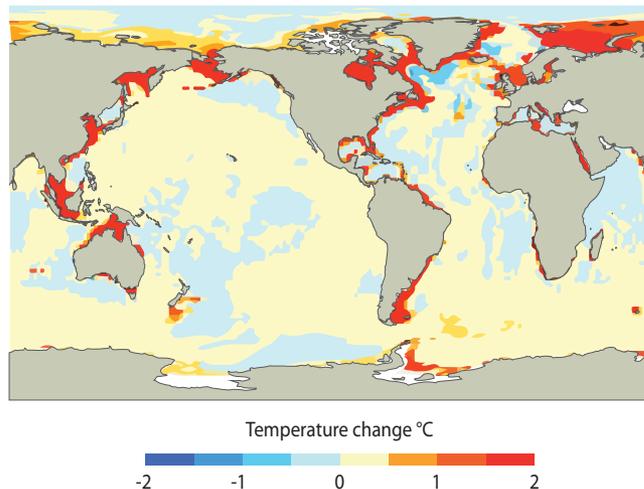
First-order predicted trends in bottom-water temperatures over the next 100 years are shown in Figure 3.4. Bottom-water temperatures could increase by up to 2 °C in shallow water along continental margins by the end of this century, but significantly smaller temperature changes are predicted for deep-sea settings. However, new results show that even during cold stadials, persistent intermediate water warming existed (Ezat *et al.*, 2014) making future scenarios more difficult to predict. Gas hydrates occurring at shallow burial depths or as outcrops around the continental margins could experience significant warming over the coming decades and centuries. The largest bottom-water warming is predicted for the Arctic Ocean, where large areas of sea floor are affected by changes in the relatively warm Atlantic waters flowing into the European Nordic seas and the Arctic Ocean (Biaostoch *et al.* 2011). In some Arctic locations, shallow bottom waters may warm by up to 5 °C by 2100 (Fig. 3.5).

The increase in bottom-water temperatures is slowed by the high heat capacity of seawater and by slow communication between surface waters and the deep ocean. Atmospheric temperature increases will however, over the coming centuries and millennia, raise bottom-water temperatures. The long-term effect of global warming on sea-floor temperatures has been evaluated by Fyke

and Weaver (2006). According to their model, the bottom-water temperature at continental margins will eventually increase by about 4 °C, and as reported by Ruppel (2011), approximately 3.5 per cent of world's gas hydrate could be dissociated over the next century due to bottom-water warming (see Section 3.6).

In addition to changes in ocean temperature, the global sea level will rise in response to global warming. Sea level rise in-

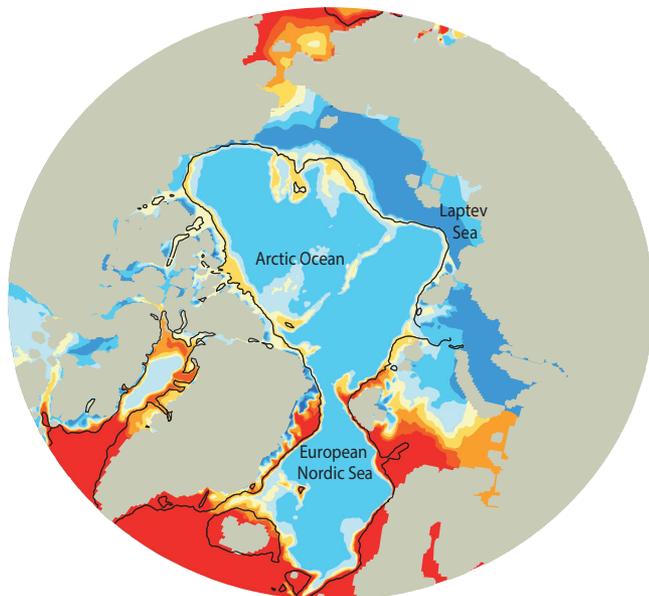
Future change in bottom-water temperatures at the sea floor



Source: adapted from Park *et al.* 2009

Figure 3.4: Future change in bottom-water temperatures at the sea floor. Changes are given in °C per 100 years as predicted by the Kiel Climate Model (KCM) (Park *et al.* 2009), for a pCO₂ increase scenario (1 per cent increase until current-day values are doubled). Values are an ensemble average of eight individual model realizations starting at different initial states.

Arctic bottom water temperature

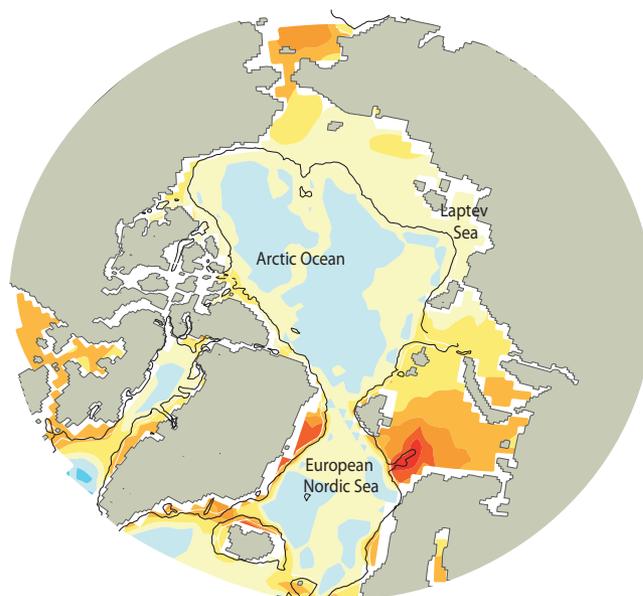


Mean bottom water temperature (1985-2004), °C

— 400 metres isobath

Source: redrawn from Biastoch, A., *et al.*, Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification

Trend in Arctic bottom water temperature



Mean trend per 100 years, °C

— 400 metres isobath

Source: redrawn from Biastoch, A., *et al.*, Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification

Figure 3.5: Current values and future changes in Arctic bottom-water temperatures. Left: Map of the modern bottom-water temperatures in an ocean model at $1/2^\circ$ resolution (1985-2004). Right: Trend in bottom-water warming under elevated $p\text{CO}_2$ as predicted by the Kiel Climate Model (KCM) (in $^\circ\text{C}$ per 100 years). The contour line depicts the 400-metre water-depth contour (From Biastoch *et al.* (2011)).

duces a pressure increase at the sea floor and may help to stabilize marine gas hydrates. However, IPCC projections of eustatic sea-level rise are generally less than two metres by 2100 and not expected to significantly enhance the stability of gas hydrates, which are more sensitive to temperature than pressure (Ruppel 2000, 2011; Reagan and Moridis 2008). For example, modelling by Tishchenko *et al.* (2005) shows how the complete breakdown of the Greenland ice sheet, and the

seven-metre sea level rise it would cause, would only protect gas hydrates from a $\sim 0.2^\circ\text{C}$ temperature increase. In fact, as discussed in Section 3.5.4, sea level rise might actually have accelerated gas hydrate dissociation along Arctic shelves by submerging and warming the sediment. Other changes in the ocean regime, such as sea-ice cover in the Arctic, wave and current regime, or hydrology, are also not expected to have a great influence on gas hydrate stability.

3.5.2 RESPONSE OF MARINE GAS HYDRATES TO SEA-FLOOR WARMING

In deep waters, the upper sediment layers remain within the gas hydrate stability zone upon bottom water warming (Fig. 3.6, left panel). Heat penetrating into the sediment from above may induce gas hydrate dissociation at the base of the GHSZ, where gas hydrates are most sensitive to change. However, heat is transferred slowly into marine sediments via conduction through the sediment and pore-water matrix, because bottom waters cannot penetrate into the sea floor. As such, hydrate dissociation along much of the middle to lower conti-

nental slope can only occur after a prolonged warming period of several thousand years (Xu *et al.* 2001). Moreover, the liberated methane would have a tendency to migrate upwards to shallow sediment, where colder temperatures should induce gas hydrate formation. Depending on the magnitude of warming and time, considerable amounts of methane would remain trapped within sediments with a rise in bottom water temperature (Dickens, 2001). Thus, as reported by a number of authors, fluxes of methane from gas hydrate regions in deep-water settings are likely quite negligible to warming of bottom waters over the coming centuries (Reagan and Moridis 2007; Garg *et al.* 2008; Reagan and Moridis 2008; Ruppel 2011).

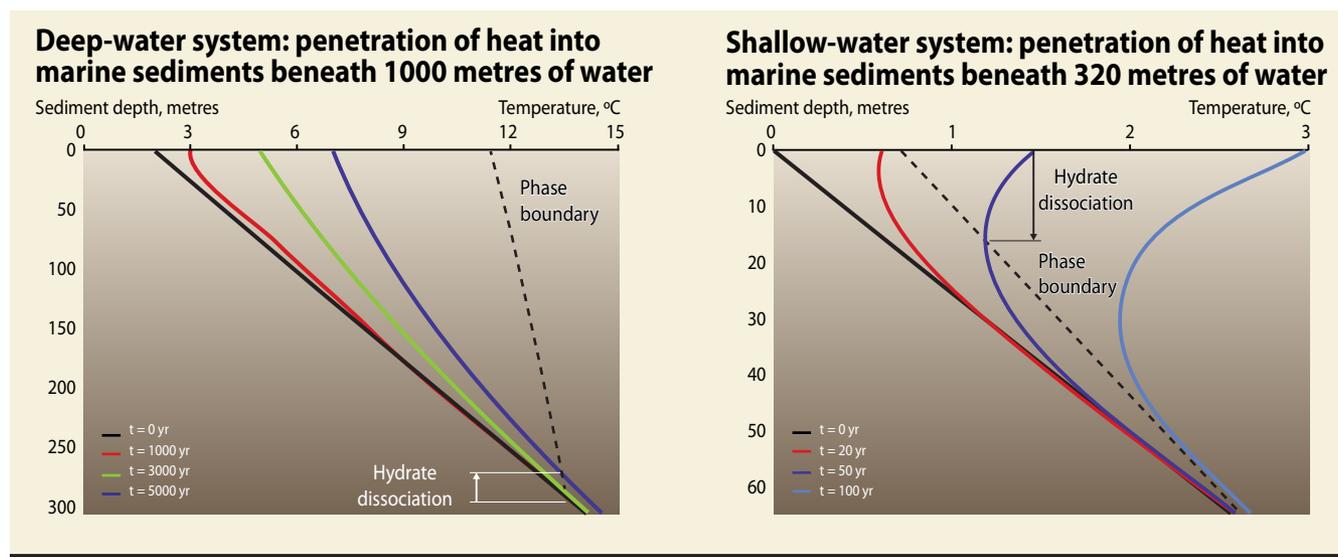


Figure 3.6: Penetration of heat into marine sediments. The left panel shows the increase in temperature with depth for sediments, located at 1 000 metres water depth, that are exposed to linear bottom-water warming of 1 °C per 1 000 years. Only the deepest gas hydrates dissociate, and only after a significant time delay. Methane released in this fashion is likely to migrate to slightly shallower depths and reform gas hydrate. The right panel depicts the response of permafrost-free Arctic upper-slope sediments at 320 metres water depth to a linear increase in bottom-water temperature of 3 °C per 100 years. In contrast to the deep marine setting, gas hydrates in shallow settings can be destabilized more rapidly, and dissociation occurs at the upper hydrate surface, facilitating the methane transport away from the hydrate. Temperature profiles were calculated by applying a thermal conductivity of 1.2 W m⁻¹ K⁻¹ and a volumetric thermal capacity of 5.1 J cm⁻³ K⁻¹. The initial geothermal gradient was implemented as 40 °C km⁻¹. The phase boundary (dotted line) is calculated for methane-gas hydrates in sulphate-depleted pore water with salt content of 35 g per kg of pore water (Tishchenko *et al.* 2005). Methane-gas hydrate is only stable when ambient sediment temperatures are lower than the temperature defined by the phase boundary. Gas hydrates dissociate when ambient temperatures exceed the phase boundary value. Heat absorbed during gas hydrate dissociation is not considered here.

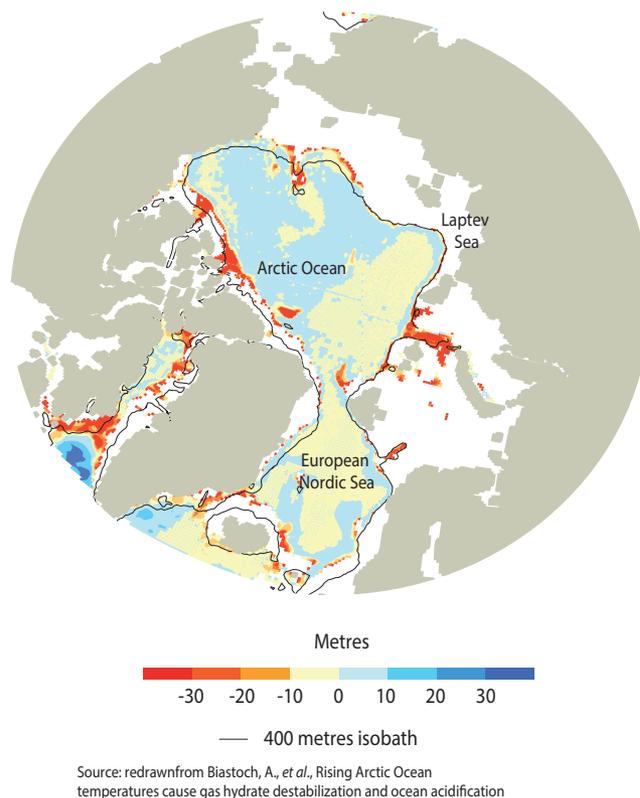
A very different scenario is possible in the shallower settings typical of the upper continental slope. Here, even modest warming can destabilize gas hydrates (Fig. 3.6, right panel). Hydrate dissociation would start at the top of the deposit, and the entire gas hydrate inventory in this setting could theoretically be transformed into water and methane. If the methane release rates were high enough, methane could escape the sediment's methane biofilter and be released into the water column (See also Volume 1, Chapter 2). Gas hydrate outcroppings at the upper-slope sea floor might react instantaneously to sea-floor warming, while gas hydrates situated at greater water and sediment depth would dissociate only after a prolonged heating period of one hundred to several hundred years (Reagan and Moridis 2007; Garg *et al.* 2008; Reagan and Moridis 2008; Ruppel 2011).

The effect on gas hydrate stability of the predicted warming of the Arctic sea floor was estimated by Biastoch *et al.* (2011). According to their model, the GHSZ thickness will be significantly reduced at several continental-slope areas due to global warming (Figs. 3.5 and 3.7). The authors proposed that about 10^{14} Gt of methane carbon might be released from dissociating gas hydrates deposited in Arctic slopes at greater than 60° N over the next 100 years, considering the slow penetration of heat into the sediments (Fig. 3.6, right panel). Their gas hydrate concentration estimates are based on the work of Klauda and Sandler (2005), which are at the high end of the published estimates. If released completely to the atmosphere, even this upper-estimate methane release would be too small to significantly enhance global warming in a 100-year time span. Nonetheless, this quantity of methane has the ability to enhance ocean acidification and oxygen depletion along the continental slope (see Volume 1 Chapter 2, Text Box 2.1). It should also be noted that the estimated amount of methane likely to be released remains uncertain, since the methane release rate depends on the largely unconstrained distribution and inventory of methane gas hydrates in shallow Arctic slope sediments.

3.5.3 FIELD EVIDENCE FOR ONGOING MARINE GAS-HYDRATE DISSOCIATION

Methane release as free-gas venting at the sediment-water interface is observed in many deep-water environments around the world. Some of these active gas seeps are from

Changes in thickness of the GHSZ caused by temperature increase



environments where pressure and temperature settings are conducive to gas hydrate formation (Ginsburg *et al.* 1993; MacDonald *et al.* 1994; Suess *et al.* 1999; Van Dover *et al.* 2003; Tomaru *et al.* 2007). In many cases, it appears this phenomenon is not related to gas hydrate dissociation, but is the result of complex porous-media processes that allow some free gas to pass through the gas hydrate stability zone without forming gas hydrates (Liu and Flemings 2006). Potential links between climate change and sea floor methane release due to dissociating marine gas hydrates have been found along the shallow-water-limit of hydrate stability along the upper continental slope, however (Westbrook *et al.* 2009; Mienert *et al.* 2010; Berndt *et al.* 2014; see also Text Box 3.1).

Effect of arctic bottom-water warming on gas-hydrate stability

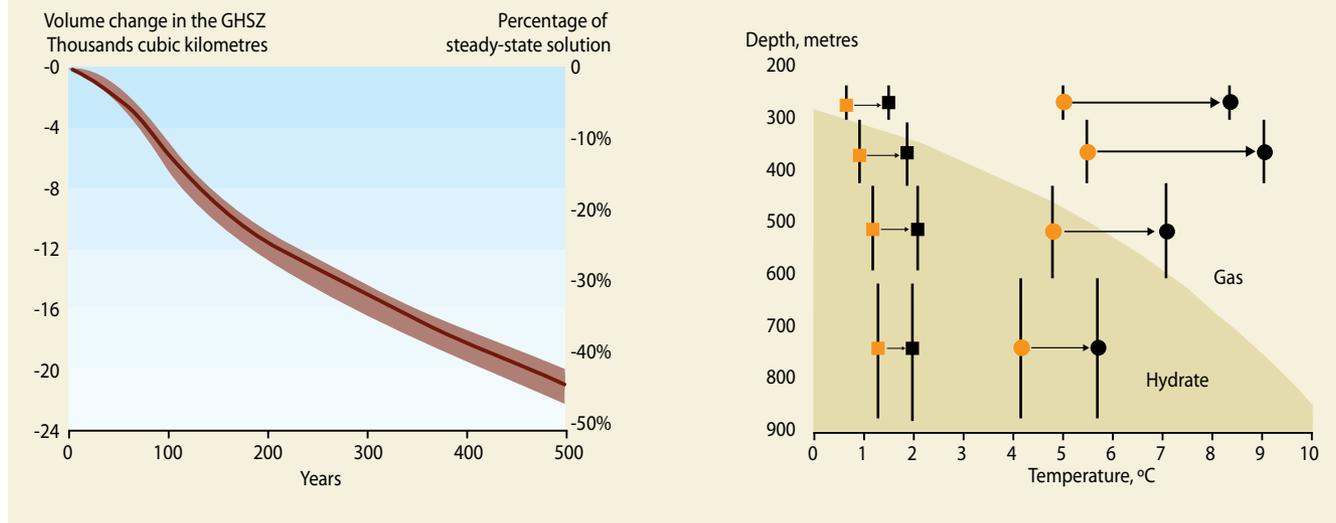


Figure 3.7: Effect of arctic bottom-water warming on gas hydrate stability. Left: Changes in the thickness of the GHSZ caused by the bottom-water temperature increase depicted in Figure 3.5. Above left: Volumetric GHSZ thickness changes north of 60°N as a function of time, given in absolute numbers (left axis) and as percentage of the steady-state solution, neglecting the transient heat intrusion into the sediment (right axis). Above right: Phase diagram of methane-gas hydrates as a function of pressure and temperature (constant salinity of $S = 35$ p.s.u.). Orange symbols mark the current bottom-water temperatures along the European Nordic Sea (circles) and Russian slope along the Laptev and East Siberian Seas (squares), black symbols mark the predicted bottom-water temperatures in 100 years. Vertical bars indicate the vertical resolution of the ocean model (From Biastoch *et al.* (2011)).

3.5.4 RESPONSE OF PERMAFROST GAS HYDRATE TO CLIMATE WARMING

In the Arctic, where thick occurrences of permafrost are found at depth, temperature and pressure conditions in the subsurface create a significant interval where gas hydrates can be stable in and beneath the permafrost (Dallimore and Collett 1995). Permafrost gas hydrates have been described in terrestrial areas where permafrost is more than 250 metres thick in Siberia, Arctic Canada, and northern Alaska. Permafrost gas hydrates are also likely to exist in shallow-shelf settings, associated with relict permafrost that formed while these areas were exposed as dry land by low sea levels during Pleistocene ice ages.

As in permafrost-free sediments (Fig 3.6), heat must first diffuse down into the sediment before gas hydrates can be warmed and destabilized. The presence of permafrost slows this heat transfer (Fig. 3.8). Heat from the sediment surface is consumed over millennial time scales to warm and eventually thaw the permafrost (Lachenbruch and Marshall 1986; Taylor *et al.* 1996a,b; Majorowicz *et al.* 2004; Taylor *et al.* 2006; Ruppel 2011). Forward modelling, with the effects of possible warming over the next century taken into consideration, shows only negligible changes in terrestrial Arctic gas hydrate stability conditions (Taylor *et al.* 2006; Ruppel 2011).

Box 3.1 Methane bubble plumes from the sea floor off West Svalbard

Over 200 methane gas plumes have been observed coming from the seabed offshore West Svalbard (Fig. TB-3.1.1). There are plumes on the continental shelf in relatively shallow water near the shelf edge, on the continental slope in water shallower than the ~400 m water depth required for methane hydrates to be stable, and a few plumes have even been observed in deeper water (Westbrook *et al.* 2009; Sarkar *et al.* 2012; Rajan *et al.* 2012). From a climate-change perspective, it is of interest to know if 1) methane in the plumes reaches the atmosphere to directly increase atmospheric greenhouse gas levels, and 2) if recent climate change is responsible for creating the methane plumes. It does not appear methane in these plumes is reaching the atmosphere (Fisher *et al.* 2011), but there is ongoing debate about whether the plumes are caused by gas hydrates that are dissociating in response to bottom-water warming over the past ~30 years (Thatcher *et al.* 2013; Sarkar *et al.* 2012; Rajan *et al.* 2012; Berndt *et al.* 2014).

Much of the methane feeding into this region appears to be migrating toward the sea floor from below the gas hydrate stability zone, further down the continental slope than where most of the methane flares are found (Hustoft *et al.* 2009, Thatcher *et al.* 2013; Sarkar *et al.* 2012; Rajan *et al.* 2012). As methane migrates upward through sediment, it can occasionally find flow conduits through which it can escape vertically through the gas hydrate stability zone (GHSZ) (Liu and Flemings 2006), but in this region that type of flare is quite rare (Sarkar *et al.* 2012).

More generally, methane either becomes incorporated into the gas hydrate or migrates up the continental slope through permeable sediment layers and conduits, some of which reach all the way to the shelf (Thatcher *et al.* 2013; Sarkar *et al.* 2012; Rajan *et al.* 2012) (Fig. TB-3.1.2). Of particular interest, however, are the plumes located just upslope from the current limit of gas hydrate stability (Fig. TB-

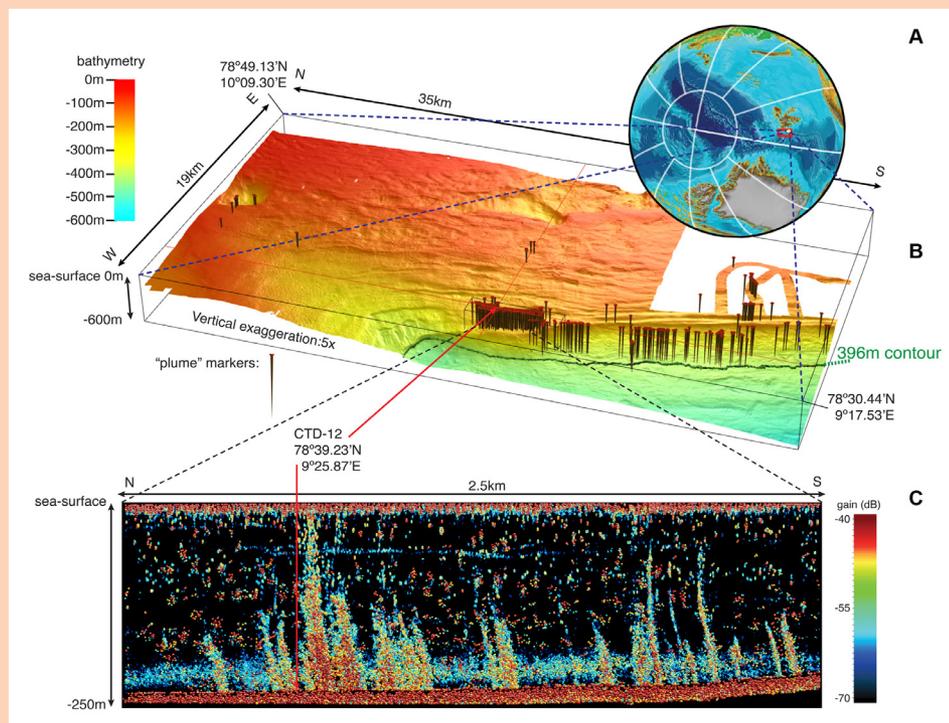


Figure TB-3.1.1: Methane-rich plumes in the water column on the West Svalbard continental margin. A: Location of survey area west of Svalbard; bathymetry (Jakobsson *et al.* 2008). B: Positions of acoustically imaged plumes are depicted by "pins" superimposed on a perspective view of the bathymetry of part of the area of plume occurrence. The 396-metre isobath contour is the expected landward limit of the GHSZ. C: Part of the record from an acoustic survey showing examples of observed plumes. All plumes show a deflection towards the north caused by the West Svalbard Current. The sea floor, at around 240-metre depth, is shown by the strong (red) response (adapted from Westbrook *et al.* 2009).

Sedimentary layers and gas migration pathways for the continental margin and slope offshore Svalbard

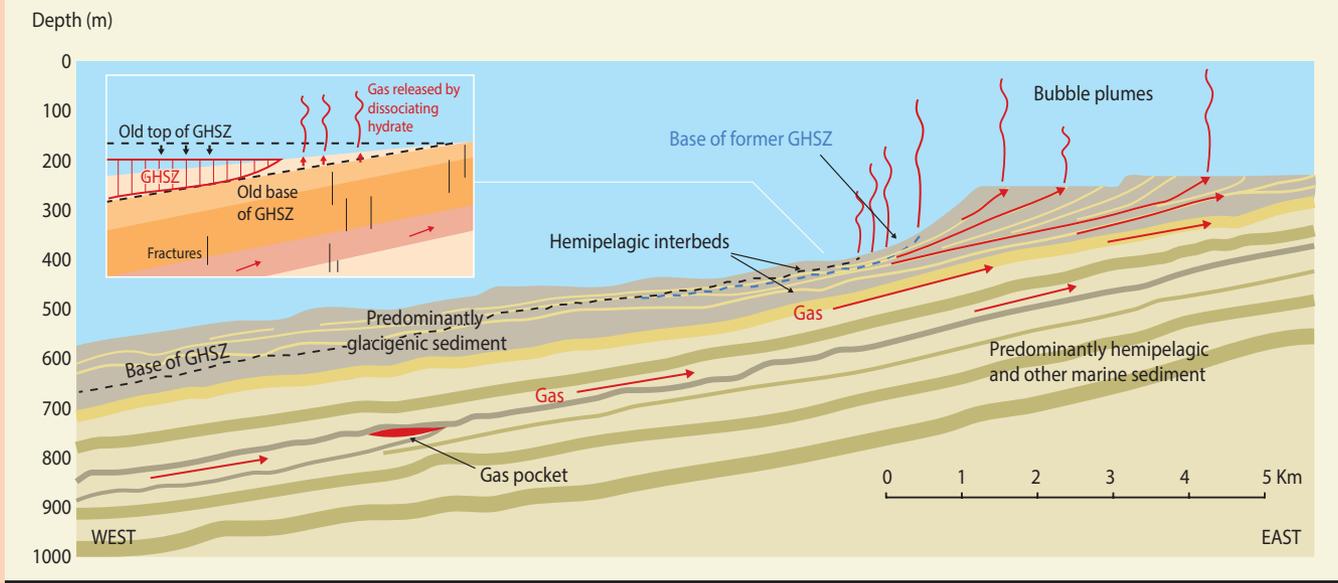


Figure TB-3.1.2: Sedimentary layers and gas migration pathways for the continental margin and slope offshore Svalbard. In this conceptual model, gas cannot easily reach the sediment surface of the continental slope without being transformed to gas hydrates or diverted upslope by impermeable hydrate-bearing sediment or glacial debris flows. Instead, gas migrates up through faulted sediment and upslope through permeable layers before reaching the sediment surface in the gas-flare region near the top of the continental slope (adapted from Thatcher *et al.* 2013).

3.1.2, inset). It has been postulated that hydrate had been stable in shallower waters, but a 1°C bottom water temperature increase over the past ~ 30 years caused that hydrate to begin dissociating and emitting methane from the sea floor (Thatcher and Westbrook 2011; Sarkar *et al.* 2012). Marin-Moreno *et al.* (2013) have extended this idea to predict the regional methane release over the next 300 years. They use two different climate models to estimate the distribution of hydrates in the region, and assuming hydrate dissociation is driven by long-term temperature increases, they estimate anywhere from $\sim 1 - 25 \text{ TgC}$ ($0.001 - 0.025 \text{ GtC}$) could be released per year from the section of sea floor between 400 – 550 metres water depth along the Eurasian Margin over the next 300 years. Recent observations from the MASOX autonomous observatory, however, suggest the methane plumes may be thousands of years old, having already begun hosting

biologic communities that have formed carbonate deposits. Rather than resulting from modern warming trends, the plumes may instead come from methane hydrates that form and dissociate in response to seasonal temperature changes of the bottom water (Berndt *et al.* 2014). In spite of the many observed plumes, the methane released from the sea floor contribute a negligible amount of methane to the atmosphere (Fisher *et al.* 2011), but will instead likely contribute to acidification and oxygen depletion in the ocean.

This region remains an active study area as researchers continue to investigate the origins and fate of methane in this location. Our understanding of this system will evolve rapidly over the next few years as results are released from ongoing studies, as well as from several new research cruises.

The situation is more complex on Arctic shelves, which were frozen as permafrost until being flooded during the sea-level rise that started 7 000 to 15 000 years ago (Shakhova *et al.* 2010b). Flooding warmed the ground surface to above freezing and began thawing the permafrost. An example of the geothermal response of permafrost and the gas hydrate stability zone is illustrated in Figure 3.8 for sites on the Beaufort Shelf.

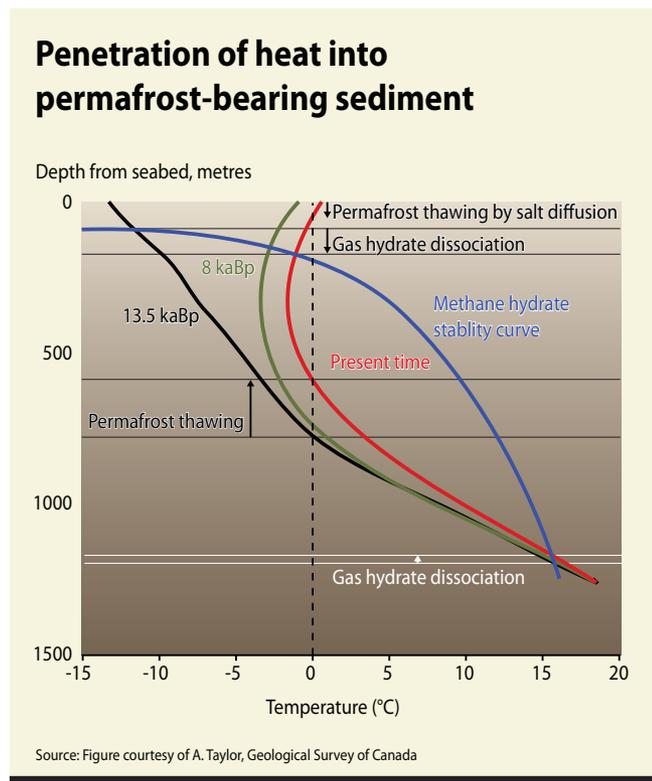


Figure 3.8: Penetration of heat into permafrost-bearing sediment that has been flooded by sea water. Thawing permafrost acts as a thermal buffer, slowing the diffusion of heat into sediment. Once dissociated, however, gas released at the top of the hydrate stability zone can migrate through the sediment without re-entering the gas hydrate stability zone. This case is similar to the shallow marine case illustrated in Figure 3.6. Gas liberated from dissociation at the base of gas hydrate stability will likely reform as gas hydrate as it migrates up through the gas hydrate stability zone (Figure courtesy of A. Taylor, Geological Survey of Canada).

The shift in mean annual sediment-surface temperatures from around -15°C to near 0°C , induced by the marine transgression, is far more significant than current air-temperature increases, and the shelf warming has been going on for approximately 13 500 years. This marine transgression has an on-shore analogy: the emplacement of a thermokarst lake on a terrestrial landscape. As with the shelf transgression, a lake can more quickly transport heat to the depths of gas hydrate stability than could occur in terrestrial systems subjected only to atmospheric warming at the ground surface.

Although sub-sea permafrost destabilizes on time scales of 5 000 to 10 000 years (Shakhova *et al.* 2010a), the roughly 4°C warming predicted for the Arctic (Fig. 3.5) has the potential to perturb or accelerate processes that have been going on for millennia. Without a permafrost cap, underlying methane – either from gas hydrates or other sources – can more easily escape through degrading permafrost to the sediment surface (Shakhova *et al.* 2010a; Brothers *et al.* 2012, Portnov *et al.* 2013). Moreover, as illustrated in Figure 3.8, gas hydrate dissociation in these flooded permafrost environments can occur at the top of the GHSZ, as in the upper-continental-slope case (Section 3.5.2). Methane released at the top the GHSZ will not reform as gas hydrates while migrating to the sediment surface, increasing the likelihood of methane reaching the ocean/atmosphere system and contributing to climate warming.

3.5.5 FIELD EVIDENCE FOR ONGOING DISSOCIATION OF PERMAFROST GAS HYDRATE

Direct evidence for the release of methane from dissociating gas hydrates associated with relict subsea permafrost or terrestrial permafrost is lacking, but Paull *et al.* (2007, 2011) have suggested that some features associated with gas release on the Beaufort shelf may be related to gas hydrate dissociation initiated by marine transgression. Pingo-like features (PLFs) are one example. Based on shallow geologic studies, geothermal modelling, and the geochemistry of sediment pore waters/gases, it has been proposed that PLFs on the Canadian Beaufort Shelf may be formed by sediment, water, and gas movement from depth, resulting from permafrost gas hydrate dissociation, as shown in Figure 3.9.

On the U.S. Beaufort shelf/slope area, recent measurements suggest there is no measurable difference in the surface water's methane content across the zone where methane hydrate may currently be dissociating, meaning that while the surface waters are methane rich, widespread gas bubbling in the water column that can be attributed to hydrate dissociation is not observed (Pohlman *et al.* 2012).

The Laptev Sea and the surrounding Siberian shelf areas are also quite rich in methane (Shakhova *et al.* 2010b) and bubble plumes have been observed, but there are many methane sources in that system and it is not yet known the extent to which dissociating hydrates are contributing to the observed methane concentrations (Text Box 3.2).

Evolution of a pingo-like feature (PLF)

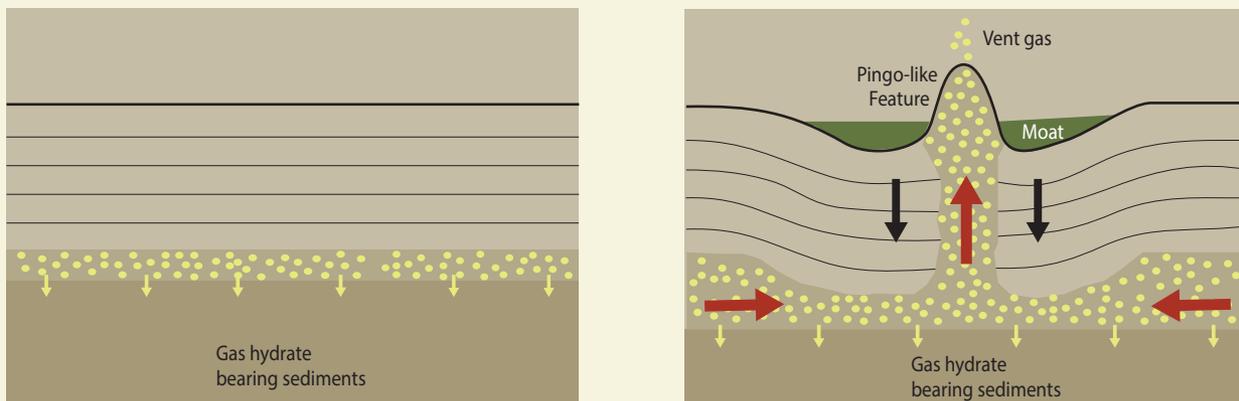


Figure 3.9: Evolution of a pingo-like feature (PLF). As the subsurface warms, the top of the gas hydrate stability zone moves downward (yellow arrows in the left panel). Warming results in gas hydrate dissociation in a gradually thickening zone (brown), releasing gaseous methane into the sediments (yellow bubbles). Bubble formation associated with this phase change creates overpressured conditions. The right-hand panel shows how material may flow (red arrows) both laterally and vertically in response to overpressure. Displaced sediments rise upward to form the PLF and allow the gas to vent. As the pressure is dissipated through both the transfer of solids and degassing, subsidence in the area immediately surrounding the PLF (black arrows) creates the moat.

Box 3.2 Methane release along the East Siberian Arctic Shelf

In the East Siberian Arctic Shelf (ESAS, Fig. TB-3.2.1), methane concentrations in the surface waters exceed typical seawater values and far exceed the atmosphere's equilibrium methane concentrations (Shakhova *et al.* 2010a). Shakhova *et al.* (2010b) suggest methane is released into the atmosphere at an annual rate of about 8 Tg of carbon (.008 GtC) for the ESAS alone,

comparable to the rate expected for the rest of Earth's oceans combined. The present-day ESAS methane release rate is nearly 2 per cent of the nearly 450 Tg of methane carbon (.45 GtC) annually released to the atmosphere from all sources globally (IPCC, 2007). A current research challenge is to predict whether methane release rates will increase significantly in response to ongoing climate change.

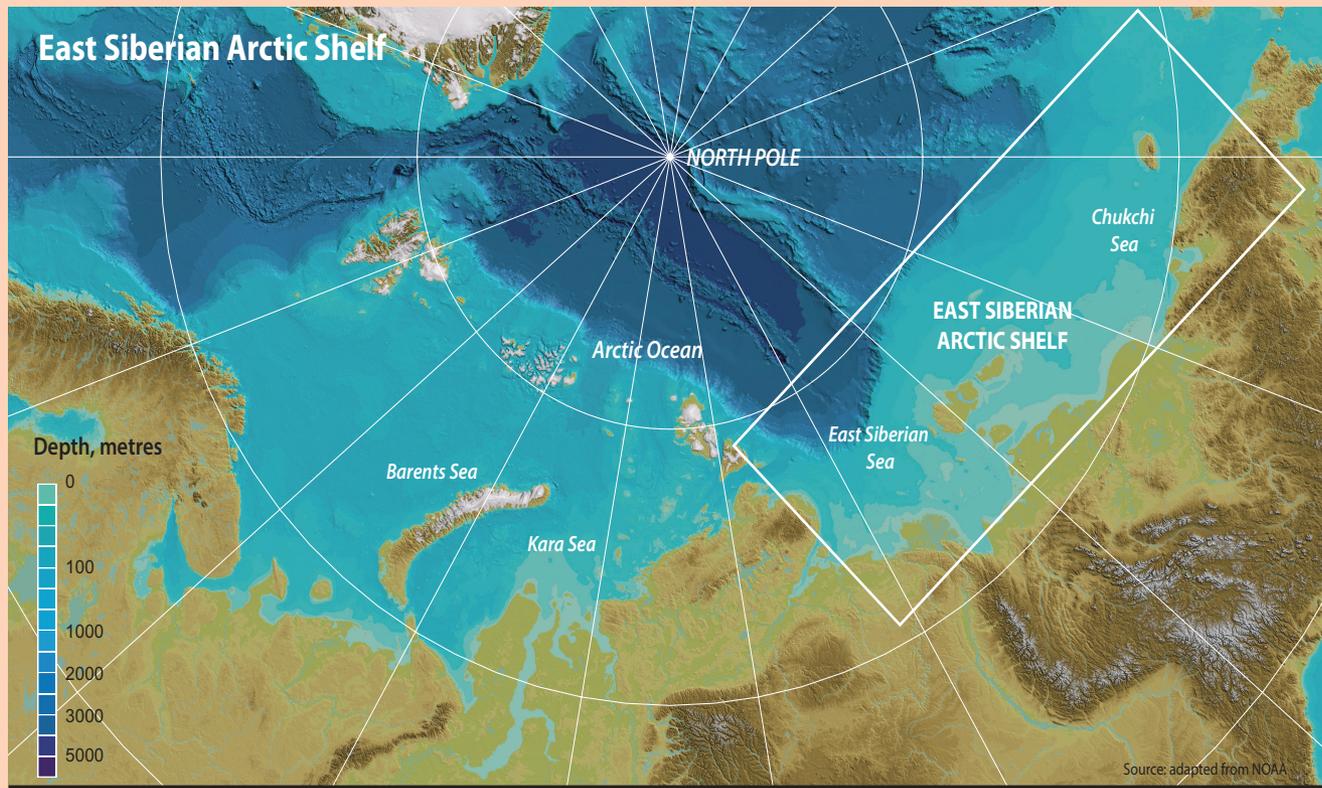


Figure TB-3.2.1: East Siberian Arctic Shelf (ESAS). The ESAS makes up a quarter of the Arctic shelf area (Shakhova *et al.* 2010a), with an average depth of only 58 metres (Jakobsson 2002) and significant riverine input.

Two key questions are:

- What are the methane sources?
- How effective are the methane sinks that consume methane before it reaches the atmosphere?

Knowing the sources can reveal whether the system has been steadily releasing methane at these rates in response to long-term climate change and/or whether the methane release rates are likely to accelerate as the system responds to short-term warming.

One possible source is methane brought in by the six largest Eurasian rivers, although Shakhova *et al.* (2010a) suggest most of the riverine methane is oxidized in the rivers prior to reaching the ESAS. Given the geologic history of the ESAS, it is more likely that methane is coming out of the ESAS sediment (Fig. TB-3.2.2). The sediment drape on the ESAS is organic-rich (Vetrov and Romankevich 2004; Shakhova *et al.* 2010a). The upper layers were frozen as permafrost until increasing sea levels, starting 7 000 to 15 000 years ago, flooded the region (Shakhova *et al.* 2010b) and raised the ground-surface temperature above freezing. The permafrost has been thawing ever since as heat and salt from overlying sea water penetrate deeper into the sediment. Shakhova *et al.* (2010a) summarize four methane sources in this thawing, organic-rich system:

1. Methane can be produced via microbial breakdown of organic material in the shallow, modern ESAS sediment, which was never frozen.
2. As permafrost thaws, the newly unfrozen, older organic material also becomes available for microbes to consume, producing methane as a by-product of that consumption.
3. Gas hydrates, thought to exist across a significant portion of the ESAS (Soloviev 2002; Shakhova *et al.* 2010a), may be dissociating and releasing methane in response to heat transferred down from the sea floor.
4. Methane may be leaking up through the thinning or thawed permafrost from a deeper petroleum system.

The present-day methane release from ESAS sediments is thought to be occurring in response to long-term sediment warming resulting from seawater flooding the ESAS region (Shakhova *et al.* 2010a), rather than to recent atmospheric warming trends. However, it is not yet certain which sources contribute to the observed seawater-methane concentrations. Methane consumption efficiency, the combined removal of methane due to dissolution and to microbial processes in the soil and water column (see Volume 1 Chapter 2), is also not well-constrained in the ESAS region. Quantifying methane sources and sinks remains a requirement for establishing the long-term climatic impact of methane released to the atmosphere.

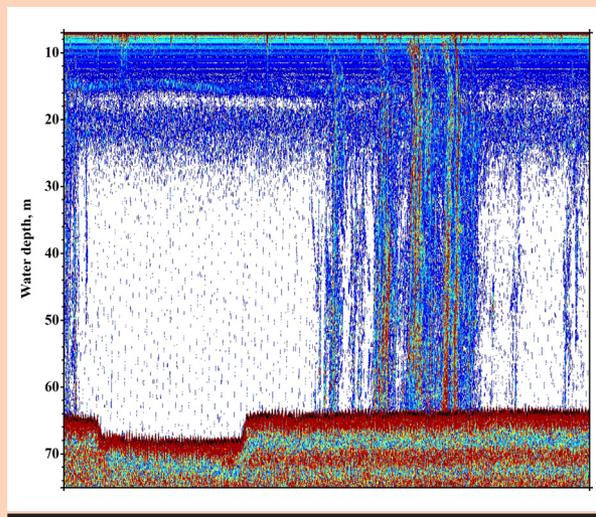


Figure TB-3.2.2: Methane plumes in the East Siberian Arctic Shelf (ESAS). The extremely shallow ESAS environment allows gas-bubble plumes to reach the water surface, facilitating the transfer of methane from the sediment to the atmosphere (Image courtesy of I. Semiletov, unpublished data from cruise-2011).

3.6 REVIEW OF SENSITIVITY OF GLOBAL GAS HYDRATE INVENTORY TO CLIMATE CHANGE

How long a warming event takes to affect gas hydrate stability and whether methane released from gas hydrates is transported to the atmosphere depend, to a large extent, on where gas hydrates are located. Based on published distribution estimates, Ruppel (2011) summarizes five general categories or “zones” of gas hydrate occurrence and the extent to which predicted climate change would result in the transport of methane from gas hydrates to the atmosphere (Figure 3.10). Following the work of Ruppel (2011), estimates of gas hydrate sensitivity to warming are given as percentages of the global gas hydrate store, assuming 99 per cent of the world’s gas hydrates are located in deep-water marine environments (zones 3-5 in Figure 3.10), and 1 per cent are associated with permafrost, either on land or submerged in shallow Arctic shelf regions (zones 1 and 2 in Figure 3.10) (McIver 1981). The percentages given by Ruppel (2011) depend on whether future studies uphold the assumed balance between marine and permafrost-associated gas hydrate volumes. For a sense of scale, even 1 per cent of the estimated global supply of methane in gas hydrates (5 000 GtC) is equivalent to 25 times the estimated global consumption of methane in 2020 (2.15 GtC), based on consumption estimates from the (U.S. Energy Information Administration, 2010).

1: Terrestrial Arctic environments

Less than 1 per cent of the world’s gas hydrates are likely to exist in this environment (Zone 1 in Fig. 3.10). Because the presence of permafrost dramatically slows the transfer of heat to the depths at which gas hydrates exist, time scales in excess of 1 000 years are necessary for atmospheric warming to begin dissociating gas hydrates at the top of the gas hydrate stability zone (Ruppel 2011). On an extremely localized scale, thermokarst lakes may provide a conduit for more rapid delivery of heat into the subsurface to dissociate gas

hydrates. Gas-venting pockmark features beneath delta lakes and channels at the edge of the Mackenzie Delta have been attributed to gas hydrate dissociation (Bowen *et al.* 2008). As noted in Ruppel (2011), however, methane seeps in terrestrial Arctic environments may be carrying methane from deeper hydrocarbon reservoirs, rather than from gas hydrates breaking down due to warming. Identifying the methane source in this sector is an important research focus.

2: Flooded permafrost environments (<100 metres water depth)

Given the assumption that 1 per cent of the world’s gas hydrates exist in polar regions, and much of that 1 per cent exists below terrestrial permafrost, Ruppel (2011) estimates less than 0.25 per cent of the global gas hydrate volume is found in flooded permafrost regions (Zone 2 in Fig. 3.10). Gas hydrates in Zone 2 are also buried beneath about 200 metres of sediment, and it is not likely that human-activity-related warming trends are affecting them significantly. However, this sector has experienced significant warming, because coastal flooding that occurred about 13 500 years ago generated up to 17 °C of warming (Shakhova *et al.* 2010b) at the sediment surface. This warming continues to thaw and degrade both permafrost and underlying gas hydrates (Semiletov *et al.* 2004). In these shallow environments, methane gas released from the sea floor can pass through the water column and enter the atmosphere (McGinnis *et al.* 2006). This sector is a likely location for gas hydrates to impact the atmospheric methane concentration over the next few hundred years. However, identifying how much of the methane release is caused by anthropogenic warming of gas hydrates requires first distinguishing between methane produced by gas hydrate dissociation and methane from other sources, such as organic matter decay or migration from deeper methane sources.

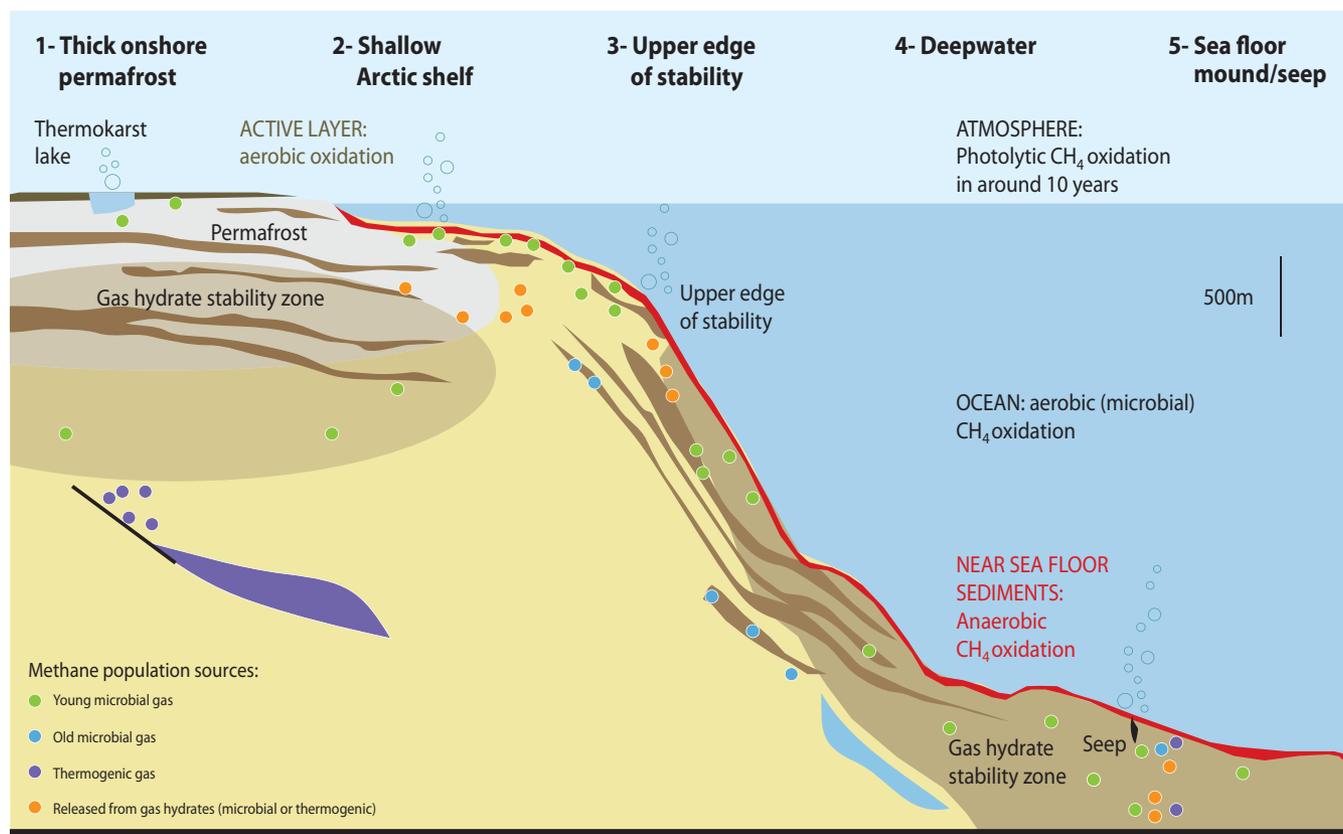


Figure 3.10: Pathways for methane release from sediment. This schematic cross-section of a high-latitude ocean margin, broken into five distinct zones, contains four potential methane sources. Methane is released from sediment along much of the cross-section, but over the next few hundred years, methane released from gas hydrates, in particular, is likely to reach the atmosphere only from Zone 2, the shallow Arctic shelf (From Ruppel (2011)).

3: Upper continental slope environments (about 300-500 metres water depth)

Ruppel (2011) calculates that about 3.5 per cent of the world's gas hydrates exist in this environment (Zone 3 in Fig. 3.10). At this feather-edge of stability, bottom-water warming could destabilize the entire thickness of gas hydrates in the shallow subsurface. Reagan and Moridis (2007) estimate gas hydrates in these shallow systems extending nearly 50 metres into the sediment could dissociate within 100 years. If gas hydrates have not already begun dissociating along the Arctic slope, the process could begin within the next century (Biastoch *et al.*

2011, Marin-Moreno *et al.* 2013) and progress rapidly to lower latitudes (Reagan *et al.* 2011). However, as noted by Ruppel (2011), methane gas released from sediments at these water depths would likely be oxidized prior to reaching the atmosphere (see also Text Box 3.1 for a discussion of evidence of climate-related hydrate dissociation in this zone).

4: Deepwater marine environments (greater than 500 metres water depth)

These gas hydrate deposits (Zone 4 of Fig. 3.10) probably account for about 95 per cent of all gas hydrates on Earth. In spite

of their abundance, they would contribute little to no methane to the ocean, even over a 3 000-year period after imposing a 1.25°C bottom-water temperature increase over present conditions (Ruppel 2011). A heat pulse entering the sediment would require millennia to reach the vulnerable gas hydrates at the base of the gas hydrate stability zone. In addition, the methane would likely remain trapped below the GHSZ or be converted back into gas hydrate as it migrated up through the sediment. An exception to this recycling model could occur if overpressuring associated with methane gas release generated highly permeable pathways that facilitated the transit of the gas through the overlying gas hydrate stability zone. Once released from the sea floor at these depths, methane would likely be consumed in the water column prior to reaching the atmosphere (McGinnis *et al.* 2006). However, as discussed in Chapter 2, bubbles released at these depths could form hydrate shells that would limit the rate at which methane in the bubble dissolved and allow methane to reach shallower depths.

5. Gas hydrate mounds on the sea floor

In the presence of seeps, gas hydrate mounds can occur in Zones 2 to 5 (see Fig. 3.10). Whether methane from mounds and seeps is being transferred to the atmosphere is a current topic of debate (Solomon *et al.* 2009; Hu *et al.* 2012). The direct exposure of gas hydrate mounds to sea water means they are constantly dissolving, and their breakdown increases with increasing temperature. As with the upper-continental-slope gas hydrates, methane released from mounds will be subject to dissolution and oxidation in the water column. If gas hydrate mounds break apart or dislodge from the sediment surface, however, the gas hydrate can rise through the water column and allow methane to reach the mixed layer near the sea surface and enter the atmosphere (Brewer *et al.* 2002; Paull *et al.* 2003). As noted by Ruppel (2011), however, mounds represent only a trace fraction of the global gas hydrate reservoir.

3.7 CONCLUSIONS

Even in response to present-day warming rates, the vast majority of the world's gas hydrates will not contribute methane to the atmosphere over the next century (Archer, 2007). The roughly 3.5 per cent of the world's gas hydrates existing at the feather-edge of stability on the upper continental slope could break down over the next 100 years, but the released methane would likely be consumed in the sediment or water column before entering the atmosphere. Only the approximately 0.25 per cent of the world's gas hydrates located in flooded permafrost environments (Ruppel, 2011), which have been subjected to warming over the past 7 000 to 15 000 years, are likely to release, or are releasing, methane that can reach the atmosphere.

Because a significant increase in atmospheric methane concentrations can result from transferring even a very small fraction of the methane in gas hydrates to the atmosphere, quantifying the climatic impact of gas hydrate breakdown will require reducing substantial uncertainties in estimates of methane transfer to the atmosphere. Three key research goals are:

1. Constrain the gas hydrate volumes that currently exist in the most sensitive environments through in situ sampling, remote sensing and modelling;
2. Establish water-column methane-consumption rates to constrain estimates of how much methane from gas hy-

drates could transfer directly to the atmosphere. Since water-column methane oxidation consumes oxygen as well as methane, quantifying methane oxidation rates is also necessary for establishing the biologic repercussions of reduced oxygen levels in marine systems; and,

3. Identify or fingerprint methane entering the atmosphere from gas hydrates in order to distinguish gas hydrates from other active methane sources. The release rates and the volume scales of methane from the decomposition of organic material or from deeper hydrocarbon reservoirs can be quite different from the methane-release patterns associated with gas hydrates.

So far, contemporary anthropogenic climate change does not appear to have triggered significant gas hydrate dissociation. However, the potential climate and environmental impact of even a limited dissociation of the world's gas hydrates continues to fuel multidisciplinary research in this area (see Text Boxes 3.1 and 3.2). In addition to the climatic impact of methane release to the atmosphere, methane release can affect other aspects of the environment. Methane oxidation within the ocean contributes to ocean acidification and will also affect the budget of dissolved oxygen, carbon dioxide, and other compounds in the ocean (as discussed in Volume 1, Chapter 2).

REFERENCES

- Adams, J., Maslin, M. and Thomas, E. (1999). Sudden climate transitions during the Quaternary. *Prog. Phys. Geog.*, 23, 1-36
- Anderson, B., Bartlett, K., Frolking, S., Hayhoe, K., Jenkins, J. and Salas, W. (2010). Methane and nitrous oxide emissions from natural sources. Report No. EPA 430-R-10-001. 194 p. United States Environmental Protection Agency, Office of Atmospheric Programs (6207J), Washington, D.C.
- Archer, D. (2007). Methane hydrate stability and anthropogenic climate change. *Biogeosciences*, 4, 521-544
- Bains, S., R. M. Corfield, and R. D. Norris (1999). Mechanisms of climate warming at the end of the Paleocene, *Science*, 285(5428), 724-727
- Berndt, C., T. Feseker, T. Treude, S. Krastel, V. Liebetrau, H. Niemann, V. J. Bertics, I. Dumke, K. Dunnbier, B. Ferre, C. Graves, F. Gross, K. Hissmann, V. Huhnerbach, S. Krause, K. Lieser, J. Schauer, and L. Steinle (2014). Temporal constraints on hydrate-controlled methane seepage off Svalbard, *Science*, 343(6168), 284-287
- Biaostoch, A., Treude, T., Rüpke, L.H., Riebesell, U., Roth, C., Burwicz, E.B., Park, W., Böning, C.W., Latif, M., Madec, G. and Wallmann, K. (2011). Evolution of Arctic Ocean temperatures and the fate of marine gas hydrates under global warming. *Geophys. Res. Lett.*, 38, doi:10.1029/2011GL047222
- Bowen, R.G., Dallimore, S.R., Côté, M.M., Wright, J.F. and T.D., L. (2008). Geomorphology and gas release from pockmark features in the Mackenzie Delta, Northwest Territories, Canada. In: *Permafrost on a warming planet: Implications for ecosystems, infrastructure and climate. Proceedings of the 9th International Conference on Permafrost* (eds. D.L. Kane and K.M. Hinkel). University of Fairbanks Alaska, Fairbanks Alaska
- Brewer, P.G., Paull, C.K., Peltzer, E.T., Ussler, W., Rehder, G. and Friederich, G. (2002). Measurements of the fate of gas hydrates during transit through the ocean water column. *Geophys. Res. Lett.*, 29, 2081, doi:10.1029/2002GL014727
- Brook, E. J., S. Harder, J. Severinghaus, E. J. Steig, and C. M. Sucher (2000). On the origin and timing of rapid changes in atmospheric methane during the last glacial period, *Global Biogeochemical Cycles*, 14(2), 559-572
- Brothers, L. L., P. E. Hart, and C. D. Ruppel (2012). Minimum distribution of subsea ice-bearing permafrost on the US Beaufort Sea continental shelf, *Geophysical Research Letters*, 39, doi 10.1029/2012gl052222, 6p.
- Cohen, A. S., A. L. Coe, and D. B. Kemp (2007). The late Palaeocene-Early Eocene and Toarcian (Early Jurassic) carbon isotope excursions: a comparison of their time scales, associated environmental changes, causes and consequences, *J Geol Soc London*, 164, 1093-1108
- Cui, Y., L. R. Kump, A. J. Ridgwell, A. J. Charles, C. K. Junium, A. F. Diefendorf, K. H. Freeman, N. M. Urban, and I. C. Harding (2011). Slow release of fossil carbon during the Palaeocene-Eocene Thermal Maximum, *Nature Geoscience*, 4(7), 481-485.
- Dallimore, S.R. and Collett, T.S. (1995). Intrapermafrost gas hydrates from a deep core in the Mackenzie Delta, Northwest Territories, Canada. *Geology*, 23, 527-530
- DeConto, R. M., S. Galeotti, M. Pagani, D. Tracy, K. Schaefer, T. J. Zhang, D. Pollard, and D. J. Beerling (2012). Past extreme warming events linked to massive carbon release from thawing permafrost, *Nature*, 484, 87-91
- Dickens, G. R. (2001). The potential volume of oceanic methane hydrates with variable external conditions, *Organic Geochemistry*, 32(10), 1179-1193
- Dickens, G.R. (2003). Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor. *Earth Planet Sc. Lett.*, 213, 169-183. doi: 10.1016/S0012-821X(03)00325-X
- Dickens, G.R., Castillo, M.M. and Walker, J.C.G. (1997). A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology*, 25, 259-262
- Dickens, G.R., O'Neil, J.R., Rea, D.K. and Owen, R.M. (1995). Dissociation of oceanic methane hydrates as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, 10(6), 965-972
- Dunkley-Jones, T.D., Ridgwell, A., Lunt, D., Maslin, M., Schmidt, D. and Valdes, P. (2010). A Palaeogene perspective on climate sensitivity and methane hydrate instability. *Philos. T. R. Soc. Lond.*, 368, 2395-2415
- Ezat, M. M., Rasmussen, T. L. and Groeneveld, J., (2014). Persisten intermediate water warming during cold stadials in the southeastern Nordic seas during the past 65 k.y., *Geology*, v. 42 no 8, o. 663-666.
- Fisher, R., Sriskantharajah, S., Lowry, D., Lanoisellé, M., Fowler, C., James, R., Hermansen, O., Myhre, C.L., Stohl, A. and Greinert, J. (2011). Arctic methane sources: Isotopic evidence for atmospheric inputs. *Geophys. Res. Lett.*, 38, L21803
- Fyke, J.G. and Weaver, A.J. (2006). The effect of potential future climate change on the marine methane hydrate stability zone. *Bull. Am. Meteorol. Soc.*, 19, 5903-5917
- Garg, S.K., Pritchett, J.W., Katoh, A., Baba, K. and Fujii, T. (2008). A mathematical model for the formation and dissociation of methane hydrates in the marine environment *J. Geophys. Res.*, 113, 1-32. doi: 10.1029/2006JB004768, 2008
- Ginsburg, G.D., Soloviev, Cranston, R.E., Lorenson, T.D. and Kvenvolden, K.A. (1993). Gas hydrates from the continental slope, offshore Sakhalin Island, Okhotsk Sea. *Geo-Mar. Lett.*, 13, 41-48

- Hesselbo, S. P., D. R. Grocke, H. C. Jenkyns, C. J. Bjerrum, P. Farrimond, H. S. M. Bell, and O. R. Green (2000), Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event, *Nature*, 406(6794), 392-395.
- Hill, T. M., J. P. Kennett, D. L. Valentine, Z. Yang, C. M. Reddy, R. K. Nelson, R. J. Behl, C. Robert, and L. Beaufort (2006), Climatically driven emissions of hydrocarbons from marine sediments during deglaciation, *Proceedings of the National Academy of Sciences of the United States of America*, 103(37), 13570-13574
- Hu, L., Yvon-Lewis, S.A., Kessler, J.D. and MacDonald, I.R. (2012). Methane fluxes to the atmosphere from deepwater hydrocarbon seeps in the northern Gulf of Mexico. *J. Geophys. Res.*, 117. doi: 10.1029/2011jco007208
- Hustoft, S., Büinz, S., Mienert, J. and Chand, S. (2009). Gas hydrate reservoir and active methane-venting province in sediments on <20 Ma young oceanic crust in the Fram Strait, offshore NW-Svalbard. *Earth Planet Sc. Lett.*, 284, 12-24. doi: 10.1016/j.epsl.2009.03.038
- IPCC (2007). *Climate Change 2007: The physical science basis. Contribution of Working Group I to the fourth assessment report of the Intergovernmental Panel on Climate Change* 996 p. IPCC, Cambridge, United Kingdom and New York, NY, USA
- Jakobsson, M. (2002), Hypsometry and volume of the Arctic Ocean and its constituent seas, *Geochemistry Geophysics Geosystems*, 3, 18p.
- Jakobsson, M., R. Macnab, L. Mayer, R. Anderson, M. Edwards, J. Hatzky, H. W. Schenke, and P. Johnson (2008), An improved bathymetric portrayal of the Arctic Ocean: Implications for ocean modeling and geological, geophysical and oceanographic analyses, *Geophysical Research Letters*, 35(7), 5p.
- Jenkyns, H. C., and P. A. Wilson (1999), Stratigraphy, paleoceanography, and evolution of Cretaceous Pacific guyots: Relics from a greenhouse earth, *American Journal of Science*, 299(5), 341-392
- Kerr, R.A. (2010). 'Arctic Armageddon' needs more science, less hype. *Science*, 329, 620-621
- Kent, D. V., B. S. Cramer, L. Lanci, D. Wang, J. D. Wright, and R. Van der Voo (2003). A case for a comet impact trigger for the Paleocene/Eocene thermal maximum and carbon isotope excursion, *Earth and Planetary Science Letters*, 211(1-2), 13-26
- Klauda, J.B. and Sandler, S.I. (2005). Global distribution of methane hydrate in ocean sediment. *Energy Fuels*, 19, 459-470
- Krull, E. S., and G. J. Retallack (2000), delta C-13 depth profiles from paleosols across the Permian-Triassic boundary: Evidence for methane release, *Geological Society of America Bulletin*, 112(9), 1459-1472
- Kurtz, A. C., L. R. Kump, M. A. Arthur, J. C. Zachos, and A. Paytan (2003), Early Cenozoic decoupling of the global carbon and sulfur cycles, *Paleoceanography*, 18(4), doi 10.1029/2003pa000908, 14 p.
- Lachenbruch, A.H. and Marshall, B.V. (1986). Changing climate: Geothermal evidence from permafrost in the Alaskan Arctic. *Science*, 234, 689-696
- Liu, X. and Flemings, P.B. (2006). Passing gas through the hydrate stability zone at southern Hydrate Ridge, offshore Oregon. *Earth Planet Sc. Lett.*, 241, 211-226
- Lunt DJ, Valdes PJ, Dunkley-Jones T, Ridgwell A, Haywood AM, Schmidt DN, Marsh R, and Maslin M, (2010), CO₂ driven ocean circulation changes as an amplifier of Paleocene-Eocene thermal maximum hydrate destabilization, *Geology*, 38, p. 875-878.
- MacDonald, I.R., Guinasson, N.L., Sassen, R., Brooks, J.M., Lee, L. and Scott, K.T. (1994). Gas hydrate that breaches the sea floor on the continental slope of the Gulf of Mexico. *Geology*, 22, 699-702
- Majorowicz, J.A., Skinner, W.R. and Safanda, J. (2004). Large ground warming in the Canadian Arctic inferred from inversion of temperature logs. *Earth Planet Sc. Lett.*, 221, 15-25
- Marin-Moreno, H., T. A. Minshull, G. K. Westbrook, B. Sinha, and S. Sarkar (2013), The response of methane hydrate beneath the seabed offshore Svalbard to ocean warming during the next three centuries, *Geophysical Research Letters*, 40(19), 5159-5163.
- Maslin, M., Owen, M., Betts, R., Day, S., Jones, T.D. and Ridgwell, A. (2010). Gas hydrates: past and future geohazard? *Philos. T. R. Soc. Lond.*, 368, 2369-2393
- McGinnis, D.F., Greinert, J., Artemov, Y., Beaubien, S.E. and Wüst, A. (2006). Fate of rising methane bubbles in stratified waters: How much methane reaches the atmosphere? *J. Geophys. Res.*, 111, C09007. doi: 10.1029/2005JC003183
- McInerney, F. A., and S. L. Wing (2011), The Paleocene-Eocene Thermal Maximum: A Perturbation of Carbon Cycle, Climate, and Biosphere with Implications for the Future, *Annual Review of Earth and Planetary Science*, 39, 489-516.
- McIver, R.D. (1981). Gas hydrates. In *Long term energy resources* (eds. R.F. Meyer and J.C. Olson). pp. 713-726. Pitman, Boston
- Mienert, J., M. Vanneste, H. Haflidason, and S. Bunz (2010), Norwegian margin outer shelf cracking: a consequence of climate-induced gas hydrate dissociation?, *International Journal of Earth Sciences*, 99, S207-S225
- Miller, G. H., R. B. Alley, J. Brigham-Grette, J. J. Fitzpatrick, L. Polyak, M. C. Serreze, and J. W. C. White (2010). Arctic amplification: can the past constrain the future?, *Quat. Sci. Rev.*, 29(15-16), 1779-1790
- Park, W., N. Keenlyside, M. Latif, A. Stroh, R. Redler, E. Roeckner, and G. Madec (2009), Tropical Pacific Climate and Its Response to Global Warming in the Kiel Climate Model, *J Climate*, 22(1), 71-92.

- Paull, C., Dallimore, S., Hughes-Clarke, J., Blasco, S., Lundsten, E., Ussler, W., Graves, D., Sherman, A., Conway, K., Melling, M., Vagle, S. and Collett, T.S. (2011). Tracking the decomposition of submarine permafrost and gas hydrate under the shelf and slope of the Beaufort Sea. 8th International Conference on Gas Hydrates. Edinburg, Scotland, U.K.
- Paull, C.K., Brewer, P.G., Ussler III, W., Peltzer, E.T., Rehder, G. and Clague, D. (2003). An experiment demonstrating that marine slumping is a mechanism to transfer methane from seafloor gas-hydrate deposits into the upper ocean and atmosphere. *Geo-Mar. Lett.*, 22 198-203
- Paull, C.K., Ussler, W.I., Dallimore, S.R., Blasco, S.M., Lorenson, T.D., Melling, H., Medioli, B.E., Nixon, F.M. and McLaughlin, F.A. (2007). Origin of pingo-like features on the Beaufort Sea shelf and their possible relationship to decomposing methane gas hydrates. *Geophys. Res. Lett.*, 34
- Pohlman, J. Ruppel, C., Maue, C., Brothers, L., Kessler, J. (2012). Real-time mapping of seawater and atmospheric methane concentrations offshore Alaska's North Slope. *Sound Waves*, a U.S. Geological Survey Newsletter, Vol. FY2012(140) May/June, 2012, p. 4-5. <http://soundwaves.usgs.gov/2012/06/research2.html>
- Portnov, A., A. J. Smith, J. Mienert, G. Cherkashov, P. Rekant, P. Semenov, P. Serov, and B. Vanshtein (2013), Offshore permafrost decay and massive seabed methane escape in water depths > 20m at the South Kara Sea shelf, *Geophysical Research Letters*, 40(15), 3962-3967
- Rajan, A., Mienert, J. and Bünz, S. (2012). Acoustic evidence for a gas migration and release system in Arctic glaciated continental margins offshore NW-Svalbard. *Mar. Petrol. Geol.*, 32, 36-49
- Reagan, M.T. and Moridis, G.J. (2007). Oceanic gas hydrate instability and dissociation under climate change scenarios. *Geophys. Res. Lett.*, 34, doi:10.1029/2007GL031671
- Reagan, M.T. and Moridis, G.J. (2008). Dynamic response of oceanic hydrate deposits to ocean temperature change. *J. Geophys. Res.-Oceans*, 113. doi: 10.1029/2008JC004938
- Reagan, M.T., Moridis, G.J., Elliott, S.M. and Maltrud, M. (2011). Contribution of oceanic gas hydrate dissociation to the formation of Arctic Ocean methane plumes. *J. Geophys. Res.-Oceans*, 116. doi: 10.1029/2011JC007189
- Ruppel, C. (2000). Thermal state of the gas hydrate reservoir. In *Natural gas hydrate in oceanic and permafrost environments* (ed. M.D. Max). pp. 29-42. Kluwer Academic Publishers, Dordrecht, Netherlands
- Ruppel, C.D. (2011). Methane hydrates and contemporary climate change. *Nature Education Knowledge*, 2, 12
- Sarkar, S., C. Berndt, T. A. Minshull, G. K. Westbrook, D. Klaeschen, D. G. Masson, A. Chabert, and K. E. Thatcher (2012), Seismic evidence for shallow gas-escape features associated with a retreating gas hydrate zone offshore west Svalbard, *Journal of Geophysical Research*, 117(B9), doi: 10.1029/2011JB009126, 18p.
- Semiletov, I., Shakhova, N. and Romanovsky, V. (2004). Methan climate forcing and methane observations in the Siberian Arctic Land-Shelf system. *World Resource Review*, 16, 505-543
- Shakhova, N., Semiletov, I., Leifer, I., Salyuk, A., Rekant, P. and Kosmach, D. (2010a). Geochemical and geophysical evidence of methane release over the East Siberian Arctic Shelf. *J. Geophys. Res.*, 115, doi:10.1029/2009JC005602
- Shakhova, N., Semiletov, I., Salyuk, A., Yusupov, V., Kosmach, D. and Gustafsson, O. (2010b). Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf. *Science*, 327, 1246-1250
- Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S.M., John, C.M., Zachos, J.C., Reichert, G.J., Damste, J.S.S., Crouch, E.M. and Dickens, G.R. (2007). Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature*, 450, 1218-1215. doi: 10.1038/nature06400
- Solomon, E.A., Kastner, M., MacDonald, I.R. and Leifer, I. (2009). Considerable methane fluxes to the atmosphere from hydrocarbon seeps in the Gulf of Mexico. *Nat. Geosci.*, 2, 561-565. doi: 10.1038/Ngeo574
- Soloviev, V.A. (2002). Gas-hydrate-prone areas of the ocean and gas hydrate accumulations. the Sixth International Conference on Gas in Marine Sediments, pp. 158. St. Petersburg, Russia, *Journal of the Conference*, 6(1), p. 158
- Storey, M., R. A. Duncan, and C. C. Swisher (2007). Paleocene-Eocene thermal maximum and the opening of the northeast Atlantic, *Science*, 316(5824), 587-589
- Suess, E., Torres, M., Bohrmann, G., Collier, R.W., Greinert, J., Linke, P., Rheder, G., Trehu, A., Wallmann, K., Winckler, G. and Zuleger, E. (1999). Gas hydrate destabilization: Enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin. *Earth Planet Sc. Lett.*, 170, 1-15
- Svensen, H., S. Planke, A. Malthe-Sorensen, B. Jamtveit, R. Myklebust, T. R. Eidem, and S. S. Rey (2004), Release of methane from a volcanic basin as a mechanism for initial Eocene global warming, *Nature*, 429(6991), 542-545
- Thatcher, K.E., Westbrook, G.K., Sarkar, S. and Minshull, T.A. (2013). Methane release from warming-induced hydrate dissociation in the West Svalbard continental margin: timing, rates and geological controls, *Journal of Geophysical Research*, doi: 10.1029/2012JB009605.
- Taylor, A.E., Dallimore, S.R. and Judge, A.S. (1996a). Late Quaternary history of the Mackenzie-Beaufort region, Arctic Canada, from modelling of permafrost temperatures: 2. The Mackenzie Delta-Tuktoyaktuk Coastlands. *Can. J. Earth Sci.*, 33, 62-71
- Taylor, A.E., Dallimore, S.R. and Outcalt, S. (1996b). Geothermal analysis of permafrost temperatures in the Mackenzie-Beaufort region, Arctic Canada: 1. An onshore-offshore transect. *Can. J. Earth Sci.*, 33, 52-61
- Taylor, A.E., Wang, K., Smith, S.L., Burgess, M.M. and Judge, A.S. (2006).

- Canadian Arctic permafrost observatories: Detecting contemporary climate change through inversion of subsurface temperature time series. *J. Geophys. Res.*, 111, doi:10.1029/2004JB003208
- Thatcher, K. and Westbrook, G.K. (2011). Timing of methane release from hydrate dissociation on the west Svalbard margin. *Proceedings of the 7th International Conference on Gas Hydrates*, pp. 12. Edinburgh
- Tishchenko, P., Hensen, C., Wallmann, K. and Wong, C.S. (2005). Calculation of the stability and solubility of methane hydrate in seawater. *Chem. Geol.*, 219, 37-52
- Tomaru, H., Lu, Z., Snyder, G., Fehn, U., Hiruta, A. and Matsumoto (2007). Origin and age of pore water in an actively venting gas hydrate field near Sado Island, Japan Sea: Interpretation of halogen and $\delta^{19}\text{I}$ distributions. *Chem. Geol.*, 236, 350-366
- U.S. Energy Information Administration (2010). International energy outlook 2010. Report No. DOE/EIA-0484(2010). Department of Energy, Washington, D.C.
- Van Dover, C. L., P. Aharon, J. M. Bernhard, E. Caylor, M. Doerries, W. Flickinger, W. Gilhooly, S. K. Goffredi, K. E. Knick, S. A. Macko, S. Rapoport, E. C. Raulfs, C. Ruppel, J. L. Salerno, R. D. Seitz, B. K. Sen Gupta, T. Shank, M. Turnipseed, and R. Vrijenhoek (2003), Blake Ridge methane seeps: characterization of a soft-sediment, chemo synthetically based ecosystem, *Deep-Sea Res. Part I-Oceanogr. Res. Pap.*, 50(2), 281-300.
- Vetrov, A.A. and Romankevich, E.A. (2004). Carbon cycle in the Russian Arctic seas. 331 p. Springer-Verlag, Berlin
- Westbrook, G.K., Thatcher, K.E., Rohling, E.J., Piotrowski, A.M., Pälike, H., Osborne, A.H., Nisbet, E.G., Minshull, T.A., Lanoiselle, M., James, R.H., Hühnerbach, V., Green, D., Fisher, R.E., Crocker, A.J., Chabert, A., Bolton, C., Beszczynaska-Möller, A., Berndt, C. and Aquilina, A. (2009). Escape of methane gas from the seabed along the West Spitsbergen continental margin. *Geophys. Res. Lett.*, 36, doi:10.1029/2009GL039191
- Xu, W., R. P. Lowell, and E. T. Peltzer (2001), Effect of seafloor temperature and pressure variations on methane flux from a gas hydrate layer: Comparison between current and Late Paleocene climate conditions, *Journal of Geophysical Research*, 106(B11), 26413-26423
- Zachos, J.C., Röhl, U., Schellenberg, S.A., Sluijs, A., Hodell, D.A., Kelly, D.C., Thomas, E., Nicolo, M., Raffi, I., Lourens, L.J., McCarren, H. and Kroon, D. (2005). Rapid acidification of the ocean during the Paleocene-Eocene Thermal Maximum. *Science*, 308, 1611-1615
- Zeebe, R. E., J. C. Zachos, and G. R. Dickens (2009). Carbon dioxide forcing alone insufficient to explain Palaeocene-Eocene Thermal Maximum warming, *Nature Geoscience*, 2(8), 576-580

EDITORIAL TEAM AND AUTHORS

EDITOR

Yannick Beaudoin

GUEST EDITORS

William F. Waite, U.S. Geological Survey

Ray Boswell, U.S. Department of Energy

Scott Dallimore, Geological Survey of Canada – Natural Resources Canada

TECHNICAL EDITORS

Claire Eamer

Patrick Daley

REVIEWER

Carolyn Ruppel, U.S. Geological Survey

AUTHORS

Chapter 1

Ray Boswell, U.S. Department of Energy

William F. Waite, U.S. Geological Survey

Keith Kvenvolden, U.S. Geological Survey

Carolyn A. Koh, Colorado School of Mines

Jeffery B. Klauda, University of Maryland

Bruce A. Buffett, University of California, Berkeley

Matthew Frye, U.S. Bureau of Ocean Energy Management

Mark Maslin, University College London

Chapter 2

Tina Treude, GEOMAR

Kelly Rose, U.S. Department of Energy

Samantha B. Joye, University of Georgia

Lisa A. Levin, Scripps Institution of Oceanography

Gerald Dickens, Rice University

Craig Shipp, Shell

Espen S. Andersen, Statoil

George Claypool, Independent Research Geochemist

Miriam Kastner, Scripps Institution of Oceanography

Craig Smith, University of Hawaii

Andrew Thurber, Oregon State University

Chapter 3

Klaus Wallmann, GEOMAR

Scott Dallimore, Geological Survey of Canada – Natural Resources Canada

Arne Biastoch, GEOMAR

Graham Westbrook, University of Birmingham

Natalia Shakova, University of Alaska-Fairbanks

Jeffrey Severinghaus, Scripps Institution of Oceanography

Gerald Dickens, Rice University

Jürgen Mienert, University of Tromsø

STEERING COMMITTEE

Espen Sletten Andersen, Statoil

Yannick Beaudoin, GRID-Arendal

Jean-Marie Beaulieu, Canadian Polar Commission

Ray Boswell, U.S. Department of Energy

Tim Collett, U.S. Geological Survey

Scott Dallimore, Geological Survey of Canada – Natural Resources Canada

Rolando di Primio, GFZ-Potsdam

Nader C. Dutta, Schlumberger

James Goodman, Forum for the Future

Haffidi Haflidason, University of Bergen

Berit Oline Blihovde Hjelstuen, University of Bergen

Jarle Husebø, Statoil

MV Lall, Directorate General for Hydrocarbon, India

Joo Yong Lee, Korea Institute of Geoscience and Mineral Resources

Yoshihiro Nakatsuka, Japan Oil, Gas and Metals National Corporation (JOGMEC)

Kelly Rose, U.S. Department of Energy

Tatsuo Saeki, Japan Oil, Gas and Metals National Corporation (JOGMEC)

Paul Siegel, retired, World Wide Fund for Nature

Anne Solgaard, GRID-Arendal

Jan Stenløkk, Norwegian Petroleum Directorate

Bruce Alastair Tocher, Statoil

Tina Treude, Helmholtz Centre for Ocean Research Kiel (GEOMAR)

William F. Waite, U.S. Geological Survey

Klaus Wallmann, Helmholtz Centre for Ocean Research Kiel (GEOMAR)

Koji Yamamoto, Japan Oil, Gas and Metals National Corporation (JOGMEC)

CONTRIBUTORS

We would also like to acknowledge content support provided by:

Chapter 1

Katherine V. Ackerman, U.S. Geological Survey
Timothy S. Collett, U.S. Geological Survey
Tomas D. Lorenson, U.S. Geological Survey
Katherine Y. McMullen, U.S. Geological Survey
John Pohlman, U.S. Geological Survey
John Ripmeester, National Research Council of Canada
Pieter Tans, National Oceanic and Atmospheric Administration
William J. Winters, U.S. Geological Survey
Fred Wright, Geological Survey of Canada

Chapter 2

Shana K. Goffredi, California Institute of Technology
John Pohlman, U.S. Geological Survey
David Valentine, University of California, Santa Barbara

Chapter 3

Inez Fung, University of California, Berkeley
Matthew Reagan, Lawrence Berkeley National Laboratory



www.unep.org

United Nations Environment Programme
P.O. Box 30552 - 00100 Nairobi, Kenya
Tel.: +254 20 762 1234
Fax: +254 20 762 3927
e-mail: unepub@unep.org
www.unep.org



ISBN: 978-92-807-3429-4
Job No: DEW/1866/NO