CHAPTER 5

# Potential for Abrupt Changes in Atmospheric Methane

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## KEY FINDINGS

- The main concerns about abrupt changes in atmospheric methane ($CH_4$) stem from (1) the large quantity of methane believed to be stored as methane hydrate in the sea floor and permafrost soils and (2) climate-driven changes in methane emissions from northern high-latitude and tropical wetlands.
- The size of the methane hydrate reservoir is uncertain, perhaps by up to a factor of 10. Because the size of the reservoir is directly related to the perceived risks, it is difficult to make certain judgment about those risks.
- There are a number of suggestions in the scientific literature about the possibility of catastrophic release of methane to the atmosphere based on both the size of the hydrate reservoir and indirect evidence from paleoclimatological studies. However, modeling and detailed studies of ice core methane so far do not support catastrophic methane releases to the atmosphere in the last 650,000 years or in the near future. A very large release of methane may have occurred at the Paleocene-Eocene boundary (about 55 million years ago), but other explanations for the evidence have been offered.
- The current network of atmospheric methane monitoring sites is sufficient for capturing large-scale changes in emissions, but it is insufficient for attributing changes in emissions to one specific type of source.
- Observations show that there have not yet been significant increases in methane emissions from northern terrestrial high-latitude hydrates and wetlands resulting from increasing Arctic temperatures.
- Catastrophic release of methane to the atmosphere appears very unlikely in the near term (*e.g.,* this century). However, it is very likely that climate change will accelerate the pace of chronic emissions from both hydrate sources and wetlands. The magnitude of these releases is difficult to estimate with existing data. Methane release from the hydrate reservoir will likely have a significant influence on global warming over the next 1,000 to 100,000 years.

## CHAPTER 5. RECOMMENDATIONS

- Monitoring of the abundance of atmospheric methane and its isotopic composition sufficient to allow detection of change in emissions from northern and tropical wetland regions should be prioritized. Specifically, systematic measurements of $CH_4$ from tall towers and aircraft in the Arctic and subarctic regions and expanded surface flux measurements and continued observation of $CH_4$ abundance in the tropics and subtropics would allow detection of changes in emissions from sparsely monitored but important regions.
- The feasibility of monitoring methane in the ocean water column near marine hydrate deposits, or in the atmosphere near terrestrial hydrate deposits, to detect changes in emissions from those sources, should be investigated, and if feasible, this monitoring should be implemented.
- Efforts should be made to increase certainty in the size of the global methane hydrate reservoirs. The level of concern about catastrophic release of methane to the atmosphere is directly linked to the size of these reservoirs.
- The size and location of hydrate reservoirs that are most vulnerable to climate change (for example, shallow-water deposits, shallow subsurface deposits on land, or regions of potential large submarine landslides) should be identified accurately and their potential impact on future methane concentrations should be evaluated.
- Improvement in process-based modeling of methane release from marine hydrates is needed. The transport of bubbles is particularly important, as are the migration of gas through the stability zone and the mechanisms controlling methane release from submarine landslides.
- Modeling efforts should establish the current and future climate-driven acceleration of chronic release of methane from wetlands and terrestrial hydrate deposits. These efforts should include development of improved representations of wetland hydrology and biogeochemistry, and permafrost dynamics, in earth system and global climate models.
- Further work on the ice core record of atmospheric methane is needed to fully understand the implications of past abrupt changes in atmospheric methane. This work should include high-resolution and high-precision measurements of methane mixing ratios and isotopic ratios, and biogeochemical modeling of past methane emissions and relevant atmospheric chemical cycles. Further understanding of the history of wetland regions is also needed.

## 1. BACKGROUND: WHY ARE ABRUPT CHANGES IN METHANE OF POTENTIAL CONCERN?

### 1.1 Introduction

Methane ($CH_4$) is the second most important greenhouse gas that humans directly influence, carbon dioxide ($CO_2$) being first. Concerns about methane's role in abrupt climate change stem primarily from (1) the large quantities of methane stored as solid methane hydrate on the sea floor and to a lesser degree in terrestrial sediments, and the possibility that these reservoirs could become unstable in the face of future global warming, and (2) the possibility of large-scale conversion of frozen soil in the high-latitude Northern Hemisphere to methane-producing wetland, due to accelerated warming at high latitudes. This chapter summarizes the current state of knowledge about these reservoirs and their potential for forcing abrupt climate change.

### 1.2 Methane and Climate

A spectral window exists between ~7 and 12 micrometers (µm) where the atmosphere is somewhat transparent to terrestrial infrared (IR) radiation. Increases in the atmospheric abundance of molecules that absorb IR radiation in this spectral region contribute to the greenhouse effect. Methane is a potent greenhouse gas because it strongly absorbs terrestrial IR radiation near 7.66 µm, and its atmospheric abundance has more than doubled since the start of the Industrial Revolution. Radiative forcing (RF) is used to assess the contribution of a perturbation (in this case, the increase in $CH_4$ since 1750 *A.D.*) to the net irradiance at the top of the tropopause (that area of the atmosphere between the troposphere and the stratosphere) after allowing the stratosphere to adjust to radiative equilibrium. The direct radiative forcing of atmospheric methane determined from an increase in its abundance from its pre-industrial value of 700 parts per billion (ppb) (Etheridge *et al.,* 1998; MacFarling Meure *et al.,* 2006) to its globally averaged abundance of 1,775 ppb in 2006 is 0.49±0.05 watts per square meter (W $m^{-2}$) (Hofmann *et al.,* 2006). Methane oxidation products, stratospheric water ($H_2O$) vapor and tropospheric ozone ($O_3$), contribute indirectly to radiative forcing, increasing methane's total contribution to ~0.7 W $m^{-2}$ (*e.g.,* Hansen and Sato, 2001), nearly half of that for carbon dioxide ($CO_2$). Increases in methane emissions can also increase the methane lifetime and the lifetimes of other gases oxidized by the hydroxyl radical (OH). Assuming the abundances of all other parameters that affect OH stay the same, the lifetime for an additional pulse of $CH_4$ (*e.g.,* 1 teragram, Tg; 1 Tg = $10^{12}$ g = 0.001 Gt, gigaton) added to the atmosphere would be ~40% larger than the current value. Additionally, $CH_4$ is oxidized to $CO_2$; $CO_2$ produced by $CH_4$ oxidation is equivalent to ~6% of $CO_2$ emissions from fossil fuel combustion. Over a 100-year time horizon, the direct and indirect effects on RF of emission of 1 kilogram (kg) $CH_4$ are 25 times greater than for emission of 1 kg $CO_2$ (Forster *et al.,* 2007).

Methane ($CH_4$) is the second most important greenhouse gas that humans directly influence, carbon dioxide ($CO_2$) being first.

The atmospheric abundance of $CH_4$ increased with human population because of increased demand for energy and food. Beginning in the 1970s, as $CH_4$ emissions from natural gas venting and flaring at oil production sites declined and rice agriculture stabilized, the growth rate of atmospheric $CH_4$ decoupled from population growth. Since 1999, the global atmospheric $CH_4$ abundance has been nearly stable; globally averaged $CH_4$ in 1999 was only 3 ppb less than the 2006 global average of 1,775 ppb. Potential contributors to this stability are decreased emissions from the Former Soviet Union after their economy collapsed in 1992 (Dlugokencky *et al.,* 2003), decreased emissions from natural wetlands because of widespread drought (Bousquet *et al.,* 2006), decreased emissions from rice paddies due to changes in water management (Li *et al.,* 2002), and an increase in the chemical sink (removal terms in the methane budget are referred to as "sinks") because of changing climate (Fiore *et al.,* 2006). Despite attempts to explain the plateau in methane levels, the exact causes remain unknown, making predictions of future methane levels difficult. Hansen *et al.* (2000) have suggested that, because methane has a relatively short atmospheric lifetime (see below) and reductions in emissions are often cost effective, it is an excellent gas to target to counter increasing RF of $CO_2$ in the short term.

Given the short $CH_4$ lifetime (~9 yr), short-term changes in methane emissions from climatically sensitive sources such as biomass burning and wetlands, or in sinks, are seen immediately in surface observations of atmospheric methane.

### 1.3 The Modern Methane Budget

The largest individual term in the global methane budget is removal from the atmosphere by oxidation of methane initiated by reaction with hydroxyl radical (OH; $OH + CH_4 \rightarrow CH_3 + H_2O$) in the troposphere.

Approximately 90% of atmospheric $CH_4$ is removed by this reaction, so estimates of OH concentrations as a function of time can be used to establish how much methane is removed from the atmosphere. When combined with measurements of the current trends in atmospheric methane concentrations, these estimates provide a powerful constraint on the total source. OH is too variable for its large-scale, time-averaged concentration to be determined by direct measurements, so measurements of 1,1,1-trichloroethane (methyl chloroform), an anthropogenic compound with relatively well-known emissions and predominant OH sink, are most commonly used as a proxy. As assessed by the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (Forster *et al.,* 2007), the globally averaged OH concentration is ~$10^6$ per cubic centimeter ($cm^{-3}$), and there was no detectable change from 1979 to 2004. Reaction with OH is also the major $CH_4$ loss process in the stratosphere. Smaller atmospheric sinks include oxidation by chlorine in the troposphere and stratosphere, and oxidation by electronically excited oxygen atoms [O(1D)] in the stratosphere. Atmospheric $CH_4$ is also oxidized by bacteria (methanotrophs) in soils, a term which is usually included in budgets as a negative source. These sink terms result in an atmospheric $CH_4$ lifetime of ~9 years (±10%). In other words, at steady state, each year one ninth of the total amount of methane in the atmosphere is removed by oxidation, and replaced by emissions to the atmosphere.

When an estimate of the lifetime is combined with global observations in a one-box mass balance model of the atmosphere (that is, considering the entire atmosphere to be a well-mixed uniform box), total global emissions can be calculated with reasonable certainty. Using a lifetime of 8.9 years and National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) global observations of $CH_4$ and its trend gives average emissions of 556±10 Tg $CH_4$ per year ($yr^{-1}$), with no significant trend for 1984–2006 (Figs. 5.1 and 5.7). The uncertainty on total emissions is 1 standard deviation (s.d.) of the interannual variability; total uncertainty is on order of ±10%. The total amount of methane in the atmosphere (often referred to as the atmospheric "burden") is ~5,000 Tg, or 5 Gt $CH_4$.

Methane is produced by a variety of natural and anthropogenic sources. Estimates of emissions from individual sources are made using bottom-up and top-down methods. Bottom-up inventories use emission factors (*e.g.,* average emissions of $CH_4$ per unit area for a specific wetland type) and activity levels (*e.g.,* total area of that wetland type) to calculate emissions. Because the relatively few measurements of emission factors are typically extrapolated to large spatial scales, uncertainties in emissions estimated with the bottom-up approach are typically quite large. An example of the top-down method applied to the global scale using a simple one-box model is shown in Figure 5.1 and

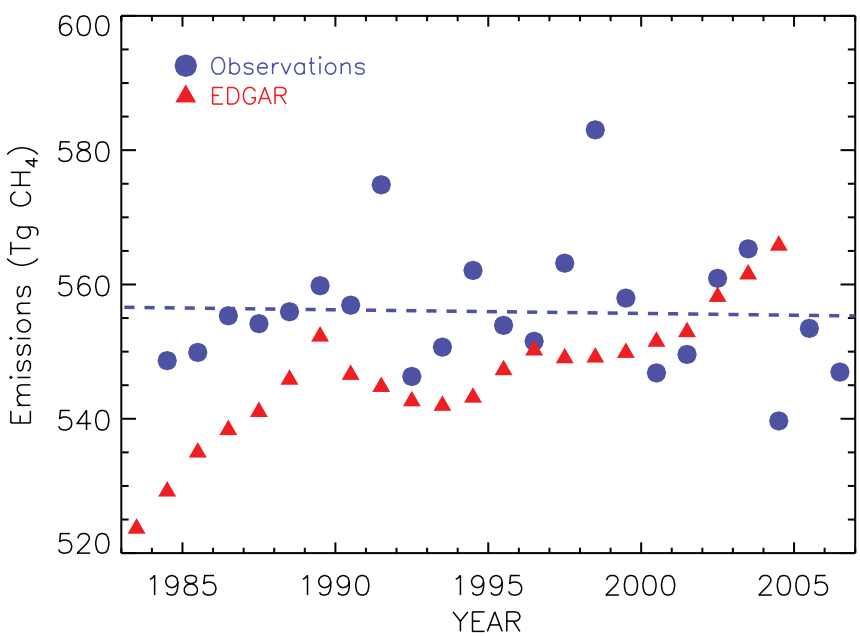


**Figure 5.1.** Methane emissions as function of time calculated with constant lifetime; emissions from EDGAR inventory with constant natural emissions shown as red triangles. The dashed line is a linear least-squares fit to the calculated emissions; its slope is –0.05+/–0.31 Tg $CH_4$ $yr^{-2}$. EDGAR is Emission Database for Global Atmospheric Research (described in Olivier and Berdowski, 2001); 2001 to 2004 emissions are preliminary (source: http://www.milieuennatuurcompendium.nl/indicatoren/nl0167-Broeikasgasemissies%2C-mondiaal.html?i=9-20). Tg, teragrams; 1 Tg = $10^{12}$ g.

described above, but the method can also be applied using a three-dimensional chemical transport model to optimize emissions from regional to continental scales based on a comparison between model-derived mixing ratios and observations. Bottom-up inventories are normally used as initial guesses in this approach. This approach is used to estimate emissions by source and region. Table 5.1 shows optimized $CH_4$ emissions calculated from an inverse modeling study (Bergamaschi *et al.,* 2007, scenario 3) that was constrained by *in situ* surface observations and satellite-based estimates of column-averaged $CH_4$ mixing ratios. It should be noted that optimized emissions from inverse model studies depend on the *a priori* estimates of emissions and the observational constraints, and realistic estimates of uncertainties are still a challenge. For example, despite the small uncertainties given in the table for termite emissions, emissions from this sector varied from ~31 to 67 Tg $yr^{-1}$ over the range of scenarios tested, which is a larger range than the uncertainties in the table would imply. While total global emissions are fairly well constrained by this combination of measurements and lifetime, individual source terms still have relatively large uncertainties.

**Table 5.1.** Annual $CH_4$ emissions for 2003 by source type (from scenario 3 of Bergamaschi *et al.,* 2007); chemical sinks are scaled to total emissions based on Lelieveld *et al.* (1998). Tg/yr, teragrams per year; 1 Tg = $10^{12}$ g.

| Source | Emissions (Tg/yr) | Fraction of total (%) |
|---|---|---|
| Coal | 35.6±4.4 | 6.7 |
| Oil and gas | 41.8±5.5 | 7.9 |
| Enteric fermentation | 82.0±9.6 | 15.4 |
| Rice agriculture | 48.7±5.1 | 9.2 |
| Biomass burning | 21.9±2.6 | 4.1 |
| Waste | 67.0±10.7 | 12.6 |
| Wetlands | 208.5±7.6 | 39.2 |
| Wild animals | 6.8±2.0 | 1.3 |
| Termites | 42.0±6.7 | 7.9 |
| Soil | –21.3±5.8 | –4.0 |
| Oceans | –1.3±2.9 | –0.2 |
| **Total** | **531.6±3.7** | |
| | | |
| **Chemical Sinks** | **Loss (Tg/yr)** | |
| Troposphere | 490±50 | 92.5 |
| Stratosphere | 40±10 | 7.5 |
| **Total** | **530** | |

The constraint on the total modern source strength is important because any new proposed source (for example, a larger than previously identified steady-state marine hydrate source) would have to be balanced by a decrease in the estimated magnitude of another source. The budget presented in Table 5.1 refers to net fluxes to the atmosphere only. The gross production of methane is very likely to be significantly larger, but substantial quantities of methane are consumed in soils, oxic freshwater, and the ocean before reaching the atmosphere (Reeburgh, 2004). (The soil sink in Table 5.1 refers only to removal of atmospheric methane by oxidation in soils.)

Given the short $CH_4$ lifetime (~9 yr), short-term changes in methane emissions from climatically sensitive sources such as biomass burning and wetlands, or in sinks, are seen immediately in surface observations of atmospheric methane. As implied above, reaction with methane is one of the major sinks for the OH radical (the main methane sink), and therefore increases in methane levels should cause an increase in the lifetimes of methane and other long-lived greenhouse gases consumed by OH. Higher methane emissions therefore mean increased methane lifetimes, which in turn means that the impact of any short-term increase in methane emissions will last longer.

### 1.4 Observational Network and Its Current Limitations, Particularly Relative to the Hydrate, Permafrost, and Arctic Wetland Sources

The network of air sampling sites where atmospheric methane mixing ratios are measured can be viewed on the World Meteorological Organization (WMO) World Data Centre for Greenhouse Gases (WDCGG) Web site (http://gaw.kishou.go.jp/wdcgg/) and is reproduced in Figure 5.2. Methane data have been reported to the WDCGG for ~130 sites. Relatively few measurements are reported for the Arctic, and sites are typically far from potential permafrost, hydrate, and wetland sources. Existing Arctic sites have been used to infer decreased emissions from the fossil-fuel sector of the Former Soviet Union (Dlugokencky *et al.,* 2003) and provide boundary conditions for model studies of emissions, but they are too remote from source regions to accurately quantify emissions, so uncertainties on northern emissions will remain large until more continuous measurement sites are added close to sources. The optimal strategy would include continuous measurements from tall towers and vertical profiles collected from aircraft. Measurements from tall towers are influenced by emissions from much larger areas than those derived from eddy-correlation flux techniques, which have footprints on the order of 1 square kilometer ($km^2$). When combined with global- or regional-scale models, these measurements can be used to quantify fluxes; the vertical profiles would be used to assess the quality of the model results through the troposphere. To properly constrain $CH_4$ emissions in the tropics, retrievals of $CH_4$ column-averaged mixing ratios must be continued to complement surface observations.

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### 1.5 Abrupt Changes in Atmospheric Methane?

Concern about abrupt changes in atmospheric methane stems largely from the large amounts of methane present as solid methane hydrate in ocean sediments and terrestrial sediments, which may become unstable in the face of future warming. Methane hydrate is a solid substance that forms at low temperatures and high pressures in the presence of sufficient methane, and is found primarily in marine continental margin sediments and some arctic terrestrial sedimentary deposits (see Box 5.1). Warming or release of pressure can destabilize methane hydrate, forming free gas that may ultimately be released to the atmosphere. The processes controlling hydrate stability and gas transport are complex and only partly understood. Estimates of the total amount of methane hydrate vary widely, from 500 to 10,000 gigatons of carbon (GtC) stored as methane in hydrates in marine sediments, and 7.5 to 400 GtC in permafrost (both figures are uncertain, see Sec. 4 ). The total amount of carbon in the modern atmosphere

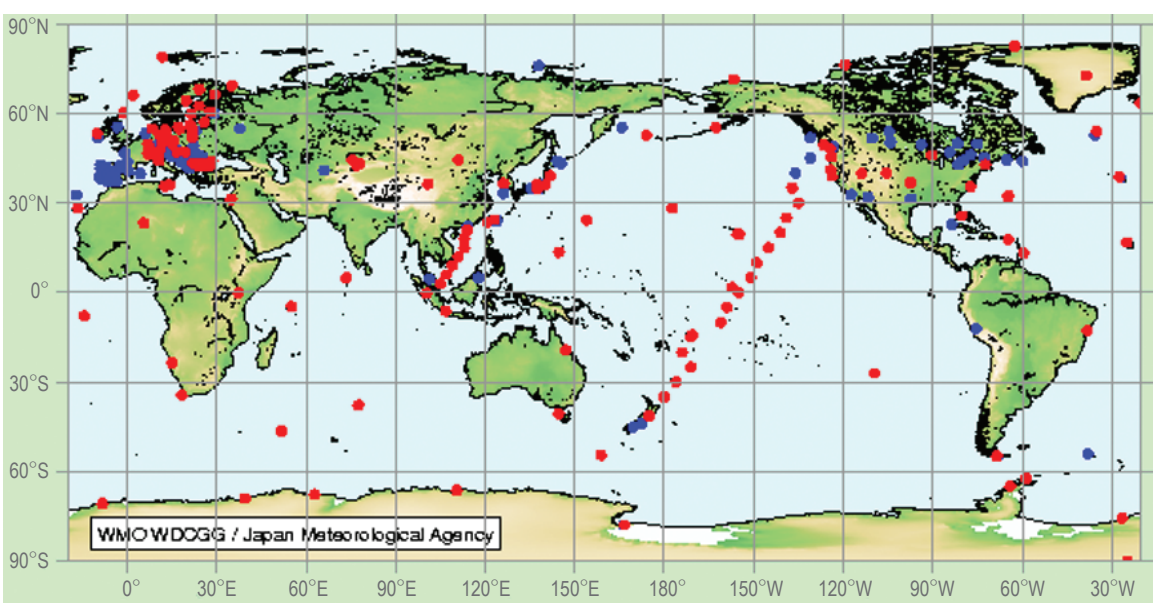



**Figure 5.2.** World Meteorological Organization global network of monitoring sites (red and blue dots) for long-term observation of atmospheric methane as of this date. Source: World Data Centre for Greenhouse Gases (WDCGG; http://gaw.kishou.go.jp/wdcgg/).

## Box 5.1. Chemistry, Physics, and Occurrence of Methane Hydrate

A clathrate is a substance in which a chemical lattice or cage of one type of molecule traps another type of molecule. Gas hydrates are substances in which gas molecules are trapped in a lattice of water molecules (Fig. 5.3). The potential importance of methane hydrate to abrupt climate change results from the fact that large amounts of methane can be stored in a relatively small volume of solid hydrate. For example, 1 cubic meter ($m^3$) of methane hydrate is equivalent to 164 $m^3$ of free gas (and 0.8 $m^3$ of water) at standard temperature and pressure (Kvenvolden, 1993). Naturally occurring gas hydrate on Earth is primarily methane hydrate and forms under high pressure–low temperature conditions in the presence of sufficient methane. These conditions are most often found in relatively shallow marine sediments on continental margins, but also in some high-latitude terrestrial sediments (Fig. 5.4). Although the amount of methane stored as hydrate in geological reservoirs is not well quantified, it is very likely that very large amounts are sequestered in comparison to the present total atmospheric methane burden.

The right combination of pressure and temperature conditions forms what is known as the hydrate stability zone, shown schematically in Figure 5.5. In marine sediments, pressure and temperature both increase with depth, creating a relatively narrow region where methane hydrate is stable. Whether or not methane hydrate forms depends not only on temperature and pressure but also on the amount of methane present. The latter constraint limits methane hydrate formation to locations of significant biogenic or thermogenic methane (Kvenvolden, 1993). When ocean bottom water temperatures are near 0 °C, hydrates can form at shallow depths, below ~200 m water depth, if sufficient methane is present. The upper limit of the hydrate stability zone can therefore be at the sediment surface, or deeper in the sediment, depending on pressure and temperature. The thickness of the stability zone increases with water depth in typical ocean sediments. It is important to note, however, that most marine methane hydrates are found in shallow water near continental margins, in areas where the organic carbon content of the sediment is sufficient to fuel methanogenesis. In terrestrial sediments, hydrate can form at depths of ~200 m and deeper, in regions where surface temperatures are cold enough that temperatures at 200 m are within the hydrate stability zone.

**Figure 5.3.** Photographs of methane hydrate as nodules, veins, and laminae in sediment. Courtesy of USGS (http://geology.usgs.gov/connections/mms/joint_projects/methane.htm).

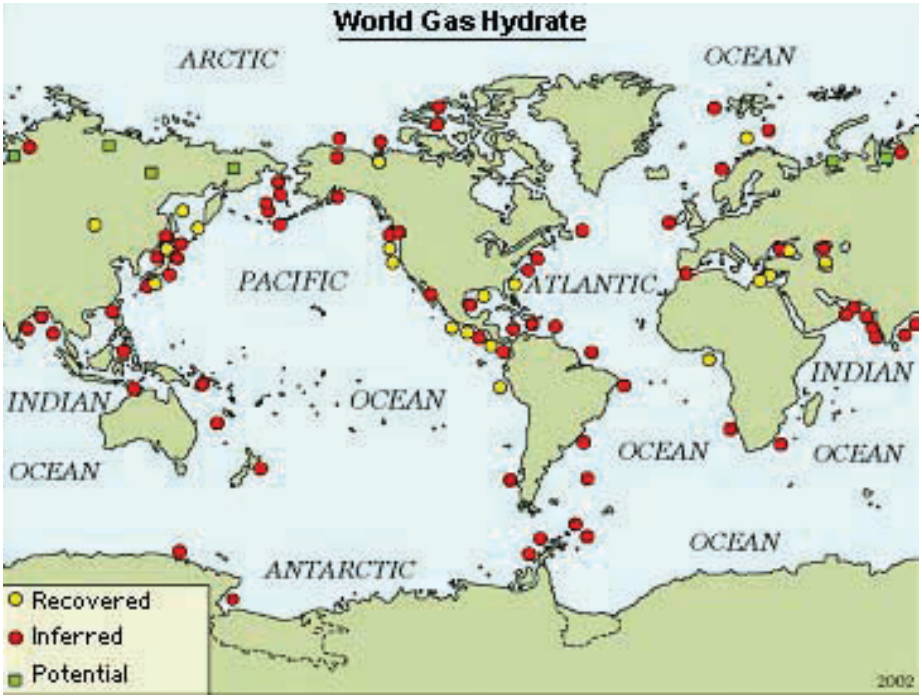



**Figure 5.4.** Map of methane hydrate deposit locations. Courtesy of USGS (http://geology.usgs.gov/connections/mms/joint_projects/methane.htm).

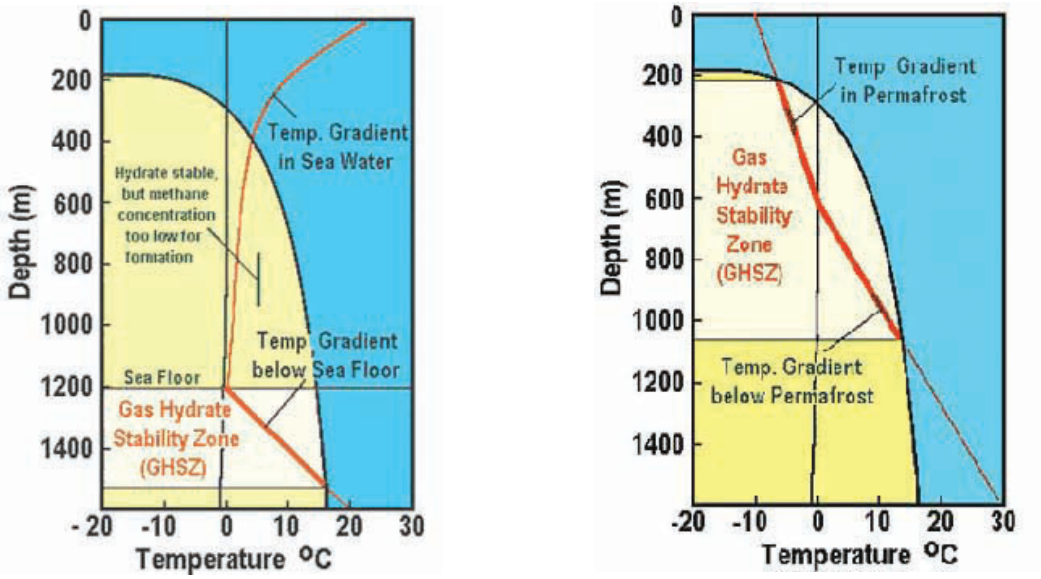



**Figure 5.5.** Schematic diagram of hydrate stability zone for typical continental margin (left) and permafrost (right) settings. The red line shows the temperature gradient with depth. The hydrate stability zone is technically the depth interval where the *in situ* temperature is lower than the temperature of the phase transition between hydrate and free gas. In the ocean this can occur above the sea floor, but generally there is not sufficient methane in the water column for methane hydrate to form. For this reason the stability zone in the left figure terminates at the sea floor. From National Energy Technology Laboratory (http://204.154.137.14/technologies/oil-gas/FutureSupply/MethaneHydrates/about-hydrates/conditions.htm).

is ~810 GtC, but the total methane content of the atmosphere is only ~4 GtC (Dlugokencky *et al.,* 1998). Therefore, even a release of a small portion of the methane hydrate reservoir to the atmosphere could have a substantial impact on radiative forcing.

Massive releases of methane from marine or terrestrial hydrates have not been observed. Evidence from the ice core record indicates that abrupt shifts in methane concentration have occurred in the past 110,000 years (Chappellaz *et al.,* 1993a; Brook *et al.,* 1996, 2000), although the concentration changes during these events were relatively small. Farther back in geologic time, an abrupt warming at the Paleocene-Eocene boundary (about 55 million years ago) has been attributed to a large release of methane to the atmosphere, although alternate carbon sources such as oxidation of sedimentary organic carbon or peats have also been proposed (see discussion in Sec. 4). These past abrupt changes are discussed in detail below, and their existence provides further motivation for considering the potential for future abrupt changes in methane.

The large impact of a substantial release of methane hydrates to the atmosphere, if it were to occur, coupled with the potential for a more steady increase in methane production from melting hydrates and from wetlands in a warming climate, motivates several questions this chapter attempts to address:

1. What is the volume of methane in terrestrial and marine sources and how much of it is likely to be released if the climate warms in the near future?
2. What is the impact on the climate system of the release of varying quantities of methane over varying intervals of time?
3. What is the evidence in the past for abrupt climate change caused by massive methane release?
4. What conditions (in terms of sea-level rise and warming of bottom waters) would allow methane release from hydrates locked up in sea-floor sediments?
5. How much methane is likely to be released by warming of northern high-latitude soils, sea-level rise, and other climate-driven changes in wetlands?
6. What are the observational and modeling requirements necessary to understand methane storage and its release under various future scenarios of abrupt climate change?

## 2. HISTORY OF ATMOSPHERIC METHANE

Current levels of methane are anomalous with respect to the long-term ice core record, which now extends back to 800,000 years.

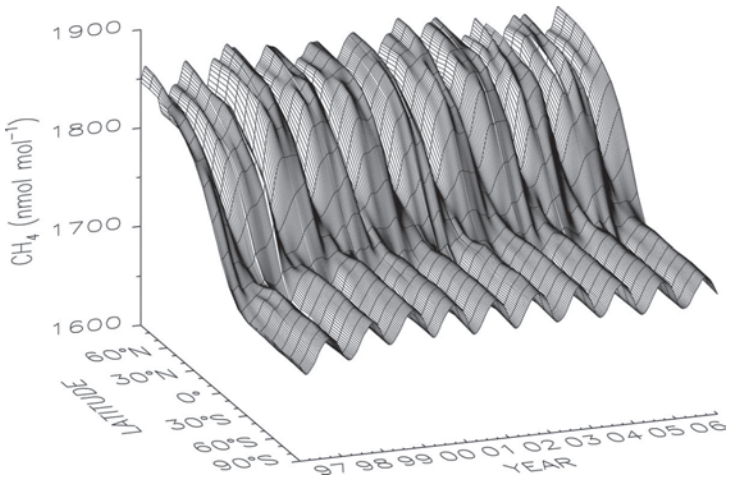
Over the last ~300 years the atmospheric methane mixing ratio increased from ~700–750 ppb in 1700 *A.D.* to a global average of ~1,775 ppb in 2006. Direct atmospheric monitoring has been conducted in a systematic way only since the late 1970s, and data for previous times come primarily from ice cores (Fig. 5.6). Current levels of methane are anomalous with respect to the long-term ice core record, which now extends back to 800,000 years (Spahni *et al.,* 2005; Loulergue *et al.,* 2008). New international plans to drill at a site of very low accumulation rate in Antarctica may in the future extend the record to 1.5 million years (Brook and Wolff, 2005).

### 2.1 Direct Observations

Early systematic measurements of the global distribution of atmospheric $CH_4$ established a rate of increase of ~16 ppb $yr^{-1}$ in the late 1970s and early 1980s and a strong gradient between high northern and high southern latitudes of ~150 ppb (Blake and Rowland, 1988). By the early 1990s it was clear that the $CH_4$ growth rate was decreasing (Steele *et al.,* 1992) and that, if the $CH_4$ lifetime were constant, atmospheric $CH_4$ was approaching steady state where emissions were approximately constant (Dlugokencky *et al.,* 1998). Significant variations are superimposed on this declining growth rate and have been attributed to climate-induced variations in emissions from biomass burning (van der Werf *et al.,* 2004) and wetlands (Walter *et al.,* 2001), and changes in the chemical sink after the eruption of Mount Pinatubo (Dlugokencky *et al.,* 1996). Recent measurements show that the global atmospheric $CH_4$ burden has been nearly constant since 1999 (Fig. 5.7). This observation is not well understood, underscoring our lack of understanding of how individual methane sources are changing.

Recently published column-averaged $CH_4$ mixing ratios determined from a satellite sensor greatly enhance the spatial coverage of $CH_4$ ob-

**A.**


1900
1800
1700
1600
$CH_4$ (nmol mol$^{-1}$)
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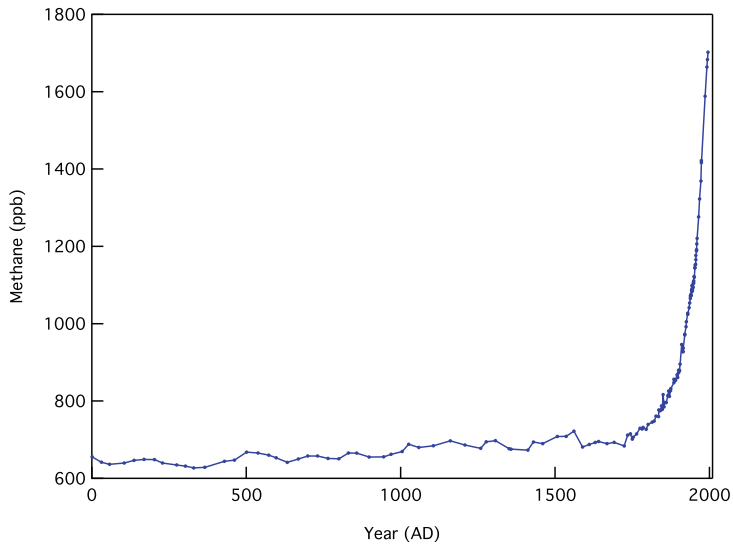
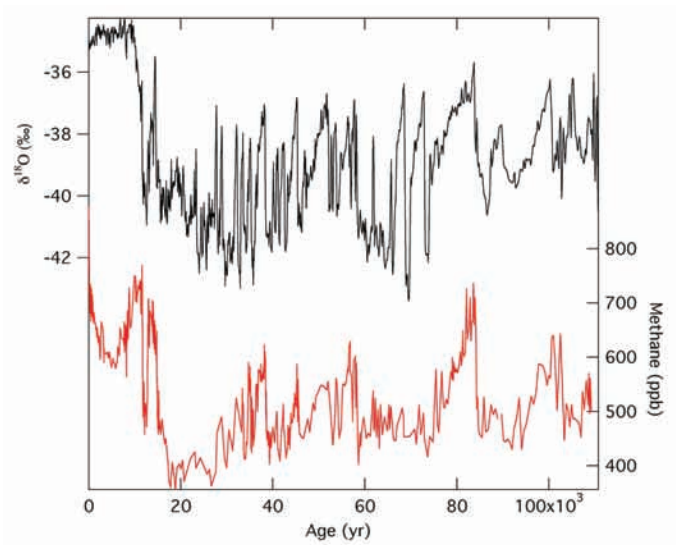
YEAR

**B.**


1800
1600
1400
1200
1000
800
600
Methane (ppb)
0
500
1000
1500
2000
Year (AD)

**C.**


-36
-38
-40
-42
$\delta^{18}O$ (‰)
800
700
600
500
400
Methane (ppb)
0
20
40
60
80
100x10$^3$
Age (yr)

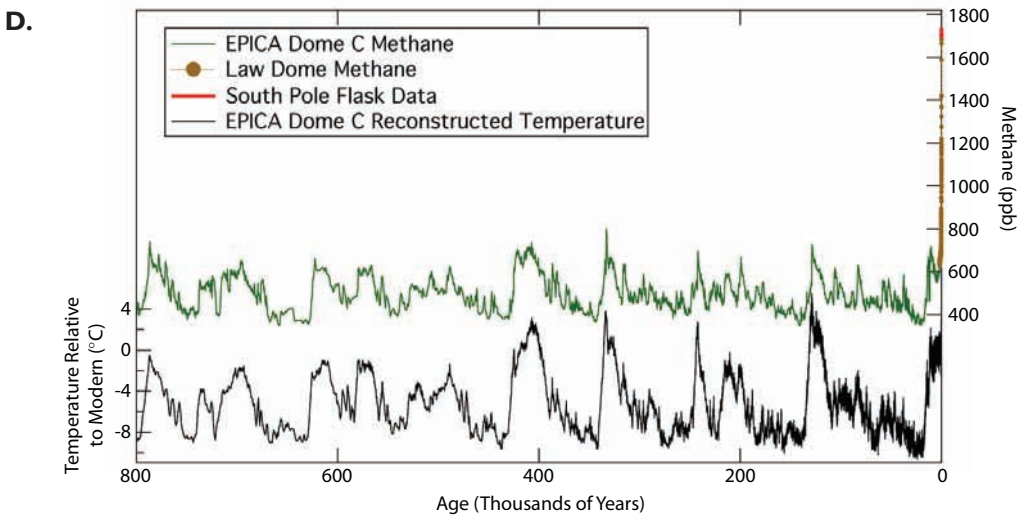



**Figure 5.6.** The history of atmospheric methane as derived from ice cores and direct measurements. A, Zonally averaged representation of seasonal and interannual trends in tropospheric methane and interhemispheric gradient over the last decade from NOAA Earth System Research Laboratory (ESRL) data. B, The last 2,000 years from ice cores and direct measurements (MacFarling Meure *et al.,* 2006) and NOAA ESRL data. NOAA ESRL data are updated from Dlugokencky *et al.* (1994). Unprocessed data and additional figures are available from NOAA ESRL Web pages: http://www.esrl.noaa.gov/gmd/Photo_Gallery/GMD_Figures/ccgg_figures/ and ftp://ftp.cmdl.noaa.gov/ccg/ch4/flask/. C, The last 100,000 years of methane history from the Greenland Ice Sheet Project 2 (GISP2) ice core in Greenland (Brook *et al.,* 1996, used with permission from *Science*; Grachev *et al.,* 2007; Brook and Mitchell, 2007). $\delta^{18}O$ is the stable isotope composition of the ice, a proxy for temperature, with more positive values indicating warmer temperatures. The amplitude of abrupt methane variations appears positively correlated with Northern Hemisphere summer insolation (Brook *et al.,* 1996). D, Ice core data from the EPICA Dome C ice cores for the last 800,000 years from Loulergue *et al.* (2008) with additional data for the late Holocene from MacFarling Meure *et al.* (2006) and NOAA ESRL. Temperature reconstruction is based on the D/H ratio of ice at Dome C. Abbreviations: nmol mol$^{-1}$, nanomoles per mole; ppb, parts per billion by mole (same as nanomoles per mole); ‰, per mil.

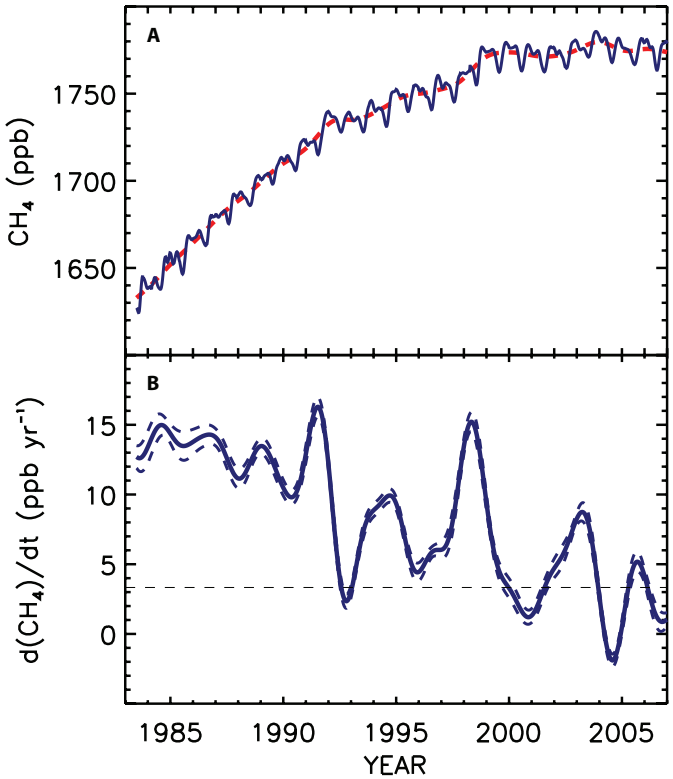



**Figure 5.7.** Recent trends in atmospheric methane from global monitoring data (NOAA Earth System Research Laboratory, ESRL). NOAA ESRL data are updated from Dlugokencky *et al.* (1994). Unprocessed data and additional figures are available from NOAA ESRL Web pages: http://www.esrl.noaa.gov/gmd/Photo_Gallery/GMD_Figures/ccgg_figures/ and ftp://ftp.cmdl.noaa.gov/ccg/ch4/flask/. A, Global average atmospheric methane mixing ratios (blue line) determined using measurements from the ESRL cooperative air sampling network. The red line represents the long-term trend. B, Solid line is the instantaneous global average growth rate for methane; dashed lines are uncertainties (1 standard deviation) calculated with a Monte Carlo method that assesses uncertainty in the distribution of sampling sites (Dlugokencky *et al.,* 2003).

servations (Frankenberg *et al.,* 2006). Coverage in the tropics greatly increases measurements there, but coverage in the Arctic remains poor because of the adverse impact of clouds on the retrievals. Use of these satellite data in inverse model studies will reduce uncertainties in emissions estimates, particularly in the tropics.

## 2.2 The Ice Core Record

The long-term record shows changes in methane on glacial-interglacial time scales of ~300–400 ppb (Fig. 5.6D), dominated by a strong ~100,000-year periodicity, with higher levels during warm interglacial periods and lower levels during ice ages. Periodicity of ~40,000 and 20,000 years is also apparent, associated with Earth's cycles of obliquity and precession (Delmotte *et al.,* 2004). Methane is believed to provide a positive feedback to warming ultimately caused by changes in the Earth's orbital parameters on these time scales. The cyclicity is widely attributed to processes affecting both northern high-latitude and tropical wetlands, including growth and decay of Northern Hemisphere ice sheets, and variations in the strength of the monsoon circulation and associated rainfall patterns in Asia, Africa, and South America (Delmotte *et al.,* 2004; Spahni *et al.,* 2005; Loulergue *et al.,* 2008).

The so-called "wetland hypothesis" postulates that abrupt warming in Greenland is associated with warmer and wetter climate in terrestrial wetland regions, which results in greater emissions of methane from wetlands.

The ice core record also clearly shows another scale of variability, abrupt shifts in methane on millennial time scales that are coincident with abrupt changes in temperature observed in Greenland ice cores (Fig. 5.6C). These abrupt shifts have been studied in detail in three deep ice cores from Greenland and in several Antarctic ice cores (Chappellaz *et al.,* 1993a; Brook *et al.,* 1996; Brook *et al.,* 2000; Severinghaus *et al.,* 1998; Severinghaus and Brook, 1999; Huber *et al.,* 2006; Grachev *et al.,* 2007). Detailed work using nitrogen and argon isotope ratios as gas phase indicators of warming in the ice core record shows clearly that the increase in methane associated with the onset of abrupt warming in Greenland is coincident with, or slightly lags (by a few decades at most), the warming (Severinghaus *et al.,* 1998; Severinghaus and Brook, 1999; Huber *et al.,* 2006; Grachev *et al.,* 2007). Methane closely follows the Greenland ice isotopic record (Fig. 5.6C), and the amplitude of methane variations associated with abrupt warming in Greenland appears to vary with time. Brook *et al.* (1996) suggested a long-term modulation of the atmospheric methane response to abrupt climate change related to global hydrologic changes on orbital time scales, an issue further quantified by Flückiger *et al.* (2004).

## 2.3 What Caused the Abrupt Changes in Methane in the Ice Core Record?

Because the modern natural methane budget is dominated by emissions from wetlands, it is logical to interpret the ice core record in this context. The so-called "wetland hypothesis" postulates that abrupt warming in Greenland is associated with warmer and wetter climate in terrestrial wetland regions, which results in greater emissions of methane from wetlands. Probable sources include tropical wetlands (including regions now below sea level) and high-latitude wetlands in regions that remained ice free or were south of the major ice sheets. Cave deposits in China, as well as marine and lake sediment records, indicate that enhanced monsoon rainfall in the Northern Hemisphere's tropics and subtropics was closely linked to abrupt warming in Greenland (*e.g.,* Peterson *et al.,* 2000; Wang *et al.,* 2004; Yuan *et al.,* 2004; Dykoski *et al.,* 2005; Kelly *et al.,* 2006). The cave records in particular are important because they are extremely well dated using uranium series isotopic techniques, and high-resolution oxygen isotope records from caves, interpreted as rainfall indicators, convincingly match large parts of the Greenland ice core methane record.

The wetland hypothesis is based on climate-driven changes in methane sources, but it is also possible that changes in methane sinks, primarily the OH radical, played a role in the

variations observed in ice cores. Both Kaplan *et al.* (2006) and Valdes *et al.* (2005) proposed that the glacial-interglacial methane change cannot be explained entirely by changes in emissions from wetlands, because in their global climate-biosphere models the difference between Last Glacial Maximum (LGM) and early Holocene methane emissions is not large enough to explain the observed changes in the ice core record. Both studies explain this apparent paradox by invoking increased production of volatile organic carbon (VOC) from the terrestrial biosphere in warmer climates. VOCs compete with methane for reaction with OH, increasing the methane lifetime and the steady-state methane concentration that can be maintained at a given emission rate. Neither of these studies is directly relevant to the abrupt changes in the ice core record, and there are considerable uncertainties in the modeling. Nonetheless, further work on the role of changes in the methane sink on time scales relevant to abrupt methane changes is warranted.

The wetland hypothesis has been challenged by authors calling attention to the large marine and terrestrial hydrate reservoirs. The challenge was most extensively developed by Kennett *et al.* (2003), who postulated that the abrupt shifts in methane in the ice core record were caused by abrupt release of methane from methane hydrates in sea-floor sediments on continental margins. This hypothesis originated from observations of negative carbon isotope excursions in marine sediment records in the Santa Barbara basin, which apparently coincided with the onset of abrupt warming in Greenland and increases in atmospheric methane in the ice core record. The "clathrate gun hypothesis" postulates that millennial-scale abrupt warming during the last ice age was actually driven by atmospheric methane from hydrate release, and further speculates on a central role for methane in causing late Quaternary climate change (Kennett *et al.,* 2003).

Some proponents of the clathrate gun hypothesis further maintain that wetlands were not extensive enough during the ice age to be the source of the abrupt variations in methane in the ice core record. For example, Kennett *et al.* (2003) maintain that large accumulations of carbon in wetland ecosystems are a prerequisite for significant methanogenesis and that these established wetlands are exclusively a Holocene phenomenon. Process-based studies of methane emissions from wetlands, on the other hand, emphasize the relationship between annual productivity and emissions (*e.g.,* Christensen *et al.,* 1996). In this view, methane production is closely tied to the production of labile carbon (Schlesinger, 1997) in the annual productivity cycle (Christensen *et al.,* 1996). From this perspective, it has been postulated that the ice core record reflects changes in rainfall patterns and temperature that could quickly influence the development of anoxic conditions, plant productivity, and methane emissions in regions where the landscape is appropriate for development of water-saturated soil (*e.g.,* Brook *et al.,* 2000; van Huissteten, 2004).

The hypothesis that there was very little methane emission from wetlands prior to the onset of the Holocene is at odds with models of both wetland distribution and emissions for pre-Holocene times, the latter indicating emissions consistent with, or exceeding, those inferred from the ice core record (*e.g.,* Chappellaz *et al.,* 1993b; Kaplan, 2002; van Huissteten, 2004; Valdes *et al.,* 2005; Kaplan *et al.,* 2006). Van Huissteten (2004) specifically considered methane emissions during the stadial and interstadial phases of Marine Isotope Stage 3 (~30,000–60,000 years ago), when ice core data indicate that several rapid changes in atmospheric methane occurred (Fig. 5.6C). Van Huissteten describes wetland sedimentary deposits in northern Europe dating from this period and used a process-based model to estimate methane emissions for the cold and warm intervals. The results suggest that emissions from Northern Hemisphere wetlands

The "clathrate gun hypothesis" postulates that millennial-scale abrupt warming during the last ice age was actually driven by atmospheric methane from hydrate release, and further speculates on a central role for methane in causing late Quaternary climate change.

could be sufficient to cause emissions variations inferred from ice core data. MacDonald *et al.* (2006) presented a compilation of basal peat ages for the circumarctic and showed that peat accumulation started early in the deglaciation (at about 16,000 years before present), and therefore emissions of methane from Northern Hemisphere peat ecosystems very likely played a role in the methane increase at the end of the last ice age. The coincidence of peatland development and the higher Northern Hemisphere summer insolation of late glacial and early Holocene time supports the hypothesis that such wetlands were methane sources at previous times of higher Northern Hemisphere summer insolation (MacDonald *et al.,* 2006), for example during insolation and methane peaks in the last ice age or at previous glacial-interglacial transitions (Brook *et al.,* 1996, 2000). In summary, although the sedimentary record of wetlands and the factors controlling methane production in wetlands are imperfectly known, it appears likely that wetlands were important in the pre-Holocene methane budget.

The clathrate gun hypothesis is important for understanding the future potential for abrupt changes in methane—concern for the near future is warranted if the clathrate reservoir was unstable on the time scale of abrupt late Quaternary climate change. However, as an explanation for late Quaternary methane cycles, the clathrate gun hypothesis faces several challenges, elaborated upon further in Section 4. First, the radiative forcing of the small variations in atmospheric methane burden during the ice age should have been quite small (Brook *et al.,* 2000), although it has been suggested that impacts on stratospheric water vapor may have increased the greenhouse power of these small methane variations (Kennett *et al.,* 2003). Second, the ice core record clearly shows that the abrupt changes in methane lagged the abrupt temperature changes in the Greenland ice core record, albeit by only decades (Severinghaus *et al.,* 1998; Severinghaus and Brook, 1999; Huber *et al.,* 2006; Grachev *et al.,* 2007). These observations imply that methane is a feedback to, rather than a cause of, warming, ruling out one aspect of the clathrate gun hypothesis (hydrates as trigger), but they do not constrain the cause of the abrupt shifts in methane. Third, isotopic studies of ice core methane do not support methane hydrates as a source for abrupt changes in methane (Sowers, 2006; Schaefer *et al.,* 2006). The strongest constraints come from hydrogen isotopes (Sowers, 2006) and are described further in Section 4.

## 3. POTENTIAL MECHANISMS FOR FUTURE ABRUPT CHANGES IN ATMOSPHERIC METHANE

Three general mechanisms are considered in this chapter as potential causes of abrupt changes in atmospheric methane in the near future large enough to cause abrupt climate change. These are outlined briefly in this section, and discussed in detail in Sections 4–6.

### 3.1 Destabilization of Marine Methane Hydrates

This issue is probably the most well known due to extensive research on the occurrence of methane hydrates in marine sediments, and the large quantities of methane apparently present in this solid phase in continental-margin marine sediments. Destabilization of this solid phase requires mechanisms for warming the deposits and/or reducing pressure on the appropriate time scale, transport of free methane gas to the sediment-water interface, and transport to the atmosphere (see Box 5.1). There are a number of physical impediments to abrupt release, in addition to the fact that bacterial methanotrophy consumes methane in oxic sediments and the ocean water column. Warming of bottom waters, slope failure, and their interaction are the most commonly discussed mechanisms for abrupt release.

## Box 5.2. The Ice Core Record and Its Fidelity in Capturing Abrupt Events

Around the time of discovery of the abrupt, but small, changes in methane in the late Quaternary ice core records (Fig. 5.6C) (Chappellaz *et al.,* 1993a), some authors suggested that very large releases of methane to the atmosphere might be consistent with the ice core record, given the limits of time resolution of ice core data at that time, and the smoothing of atmospheric records due to diffusion in the snowpack (*e.g.,* Thorpe *et al.,* 1996). Since that time, a large number of abrupt changes in methane in the Greenland ice core record (which extends to ~120,000 years before present) have been sampled in great detail, and no changes greatly exceeding those shown in Figure 5.6C have been discovered (Brook *et al.,* 1996, 2000, 2005; Chappellaz *et al.,* 1997; Severinghaus *et al.,* 1998; Severinghaus and Brook, 1999; Blunier and Brook, 2001; Huber *et al.* 2006; EPICA Community Members, 2006; Grachev *et al.,* 2007).

Could diffusion in the snowpack mask much larger changes? Air is trapped in polar ice at the base of the firn (snowpack), where the weight of the overlying snow transforms snow to ice, and air between the snow grains is trapped in bubbles (Fig. 5.8). The trapped air is therefore younger than the ice it is trapped in (this offset is referred to as the gas age-ice age difference). It is also mixed by diffusion, such that the air trapped at an individual depth interval is a mixture of air of different ages. In addition, bubbles do not all close off at the same depth, so there is additional mixing of air of different ages due to this variable bubble close-off effect. The overall smoothing depends on the parameters that control firn thickness, densification, and diffusion—primarily temperature and snow accumulation rate.

Spahni *et al.* (2003) used the firn model of Schwander *et al.* (1993) to study the impact of smoothing on methane data from the Greenland Ice Core Project (GRIP) ice core in Greenland for the late Holocene. They examined the impact of smoothing on abrupt changes in methane in the Greenland ice core record. Brook *et al.* (2000) investigated a variety of scenarios for abrupt changes in methane, including those proposed by Thorpe *et al.* (1996), and compared what the ice core record would record of those events with high-resolution data for several abrupt shifts in methane (Fig. 5.9).

Two aspects of the ice core data examined by Brook *et al.* (1996) argue against abrupt, catastrophic releases of methane to the atmosphere as an explanation of the ice core record. First, the abrupt shifts in methane concentration take place on time scales of centuries, whereas essentially instantaneous releases would be recorded in the Greenland ice core record as more abrupt events (Fig. 5.9). While this observation says nothing about the source of the methane, it does indicate that the ice core record is not recording an essentially instantaneous atmospheric change (Brook *et al.,* 2000). Second, the maximum levels of methane reached in the ice core record are not high enough to indicate extremely large changes in the atmospheric methane concentration (Fig. 5.9).

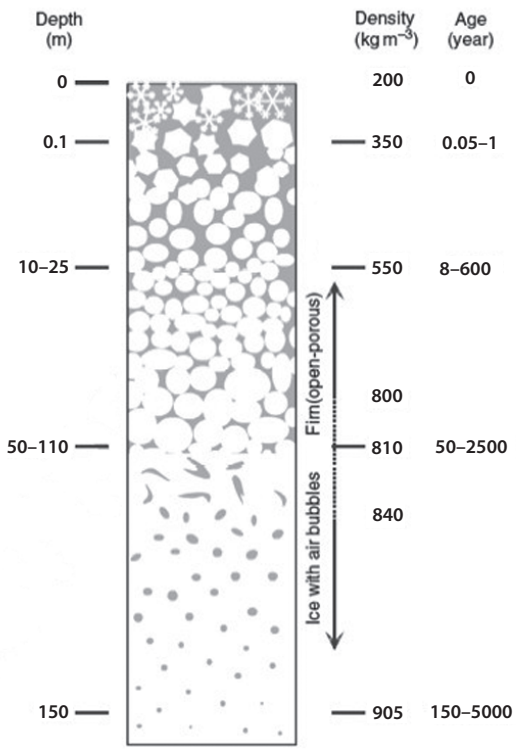



**Figure 5.8.** The firn column of a typical site on a polar ice sheet from Schwander, 2007; reprinted with permission from *Encyclopedia of Quaternary Science*. Abbreviations: m, meter; kg m$^{-3}$, kilograms per cubic meter.

A prominent concern about marine methane hydrates is that warming at the Earth's surface will ultimately propagate to hydrate deposits and melt them, releasing methane to the ocean-atmosphere system.

### 3.2 Destabilization of Permafrost Hydrates

Hydrate deposits at depth in permafrost are known to exist, and although their extent is uncertain, the total amount of methane in permafrost hydrates is very likely much smaller than in marine sediments. Surface warming eventually would increase melting rates of permafrost hydrates. Inundation of some deposits by warmer seawater and lateral invasion of the coastline are also concerns and may be mechanisms for more rapid change.

### 3.3 Changes in Wetland Extent and Methane Productivity

Although a destabilization of either the marine or terrestrial methane hydrate reservoirs is the most probable pathway for a truly abrupt change in atmospheric methane concentration, the potential exists for a more chronic, but substantial, increase in natural methane emissions in association with projected changes in climate. The most likely region to experience a dramatic change in natural methane emission is the northern high latitudes, where there is increasing evidence for accelerated warming, enhanced precipitation, and widespread permafrost thaw which could lead to an expansion of wetland areas into organic-rich soils that, given the right environmental conditions, would be fertile areas for methane production.

In addition, although northern high-latitude wetlands seem particularly sensitive to climate change, the largest natural source of methane to the atmosphere is from tropical wetlands, and methane emissions there may also be sensitive to future changes in temperature and precipitation. Modeling studies addressing this issue are therefore also included in our discussion.

## 4. POTENTIAL FOR ABRUPT METHANE CHANGE FROM MARINE HYDRATE SOURCES

### 4.1 Impact of Temperature Change on Marine Methane Hydrates

A prominent concern about marine methane hydrates is that warming at the Earth's surface will ultimately propagate to hydrate deposits and melt them, releasing methane to the ocean-atmosphere system. The likelihood of this type of methane release depends on the propagation of heat through the sea floor, the migration of methane released from hydrate deposits through sediments, and the fate of this methane in the water column.

#### 4.1.1 Propagation of Temperature Change to the Hydrate Stability Zone

The time dependence of changes in the inventory of methane in the hydrate reservoir depends on the time scale of warming and chemical diffusion. There is evidence from paleotracers (Martin *et al.,* 2005) and from modeling (Archer *et al.,* 2004) that the temperature of the deep sea is sensitive to the climate of the Earth's surface. In general, the time scale for changing the temperature of the ocean increases with water depth, reaching a maximum of about 1,000 years for the abyssal ocean. This means that abrupt changes in temperature at the surface ocean would not be transmitted immediately to the deep sea. There are significant regional variations in the ventilation time of the ocean, and in the amount of warming that might be expected in the future. The Arctic is expected to warm particularly strongly because

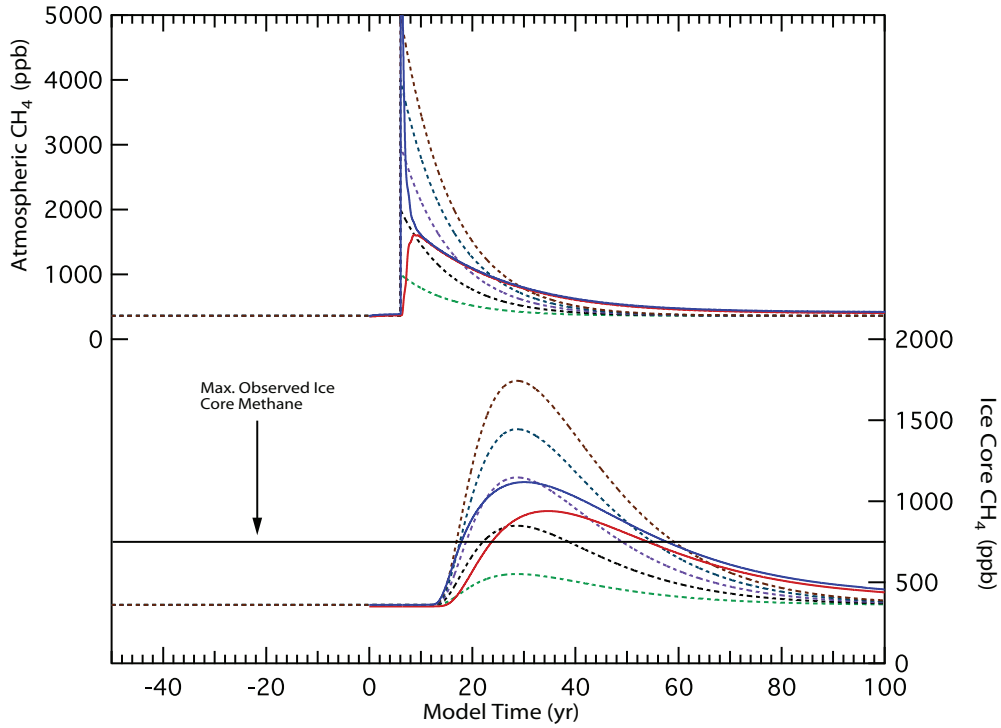



**Figure 5.9.** Model simulations of smoothing instantaneous release of methane from clathrates to the atmosphere, and the ice core response to those events. The ice core response was calculated by convolving the atmospheric histories in the top panel with a smoothing function appropriate for the GISP2 ice core. The solid lines are the atmospheric history and smoothed result for the model of a 4,000 teragram release of methane from Thorpe *et al.* (1996). The blue solid line represents how an Arctic ice core would record a release in the Northern Hemisphere, and the red solid line represents how an Antarctic ice core would record that event (from Brook *et al.,* 2000). The dashed lines represent instantaneous arbitrary increases of atmospheric methane to values of 1,000, 2,000, 3,000, 4,000, or 5,000 ppb (colored dashed lines in top panel) and the ice core response (bottom panel, same color scheme).

of the albedo feedback from the melting Arctic ice cap. Temperatures in the North Atlantic appear to be sensitive to changes in ocean circulation such as during rapid climate change during the last ice age (Dansgaard *et al.,* 1989).

The top of the hydrate stability zone is at 200 to 600 m water depth, depending mainly on the temperature of the water column. Within the sediment column, temperature increases with depth along the geothermal temperature gradient, 30–50 °C $km^{-1}$ (Harvey and Huang, 1995). The shallowest sediments that could contain hydrate only have a thin hydrate stability zone, and the stability zone thickness increases with water depth. A change in the temperature of the deep ocean will act as a change in the upper boundary condition of the sediment temperature profile. Warming of the overlying ocean may not put surface sediments into undersaturation, but the warmer overlying temperature propagates downward until a new profile with the same geothermal temperature gradient can be established. How long this takes is a strong (second order) function of the thickness of the stability zone, but the time scales are in general long. In 1,000 years, the temperature signal should have propagated about 180 m in the sediment. In steady state, an increase in ocean temperature will decrease the thickness of the stability zone. Dickens (2001b) calculated that the volume of the stability zone ought to decrease by about half with a temperature increase of 5 °C.

### 4.1.2 Impact on Stratigraphic-Type Deposits

Hydrate deposits formed within sedimentary layers are referred to as stratigraphic-type deposits. After an increase in temperature of the overlying water causes hydrate to melt at the base of the stability zone, the fate of the released methane is difficult to predict. The increase in pore volume and pressure could provoke gas

migration through the stability zone or a landslide, or the bubbles could remain enmeshed in the sediment matrix. Hydrate moves down to the base of the stability zone by the accumulation of overlying sediment at the sea floor, so melting of hydrate at the stability zone takes place continuously, not just in association with ocean warming.

When hydrate melts, most of the released methane goes into the gas phase to form bubbles, assuming that the porewaters were already saturated in dissolved methane. The fate of the new bubbles could be to remain in place, to migrate, or to diffuse away and react chemically (Hinrichs *et al.,* 1999; Wakeham *et al.,* 2003), and it is difficult to predict which will occur. The potential for gas migration through the stability zone is one of the more significant uncertainties in forecasting the ocean hydrate response to anthropogenic warming (Harvey and Huang, 1995).

In cohesive sediments, bubbles expand by fracturing the sediment matrix, resulting in elongated shapes (Boudreau *et al.,* 2005). Bubbles tend to rise because they are less dense than the water they are surrounded by, even at the 200+ atmosphere pressures in sediments of the deep sea. If the pressure in the gas phase exceeds the lithostatic pressure in the sediment, fracture and gas escape can occur (Flemings *et al.,* 2003). Modeled and measured (Dickens *et al.,* 1995) porewater pressures in the sediment column at Blake Ridge approach lithostatic pressures, indicating that new gas bubbles added to the sediment might be able to escape to the overlying water by this mechanism.

A differential-pressure mechanism begins to operate when the bubbles occupy more than about 10% of the volume of the pore spaces (Hornbach *et al.,* 2004). If a connected bubble spans a large enough depth range, the pressure of the porewater will be higher at the bottom of the bubble than it is at the top, because of the weight of the porewater over that depth span. The pressure inside the bubble will be more nearly constant over the depth span, because the compressed gas is not as dense as the porewater is. This will result in a pressure gradient at the top and the bottom of the bubble, tending to push the bubble upward. Hornbach *et al.* (2004) postulated that this mechanism might be responsible for allowing methane to escape from the sediment column, and they calculated the maximum thickness of an interconnected bubble zone required, before the bubbles would break through the overlying sediment column. In their calculations, and in stratigraphic deposits (they refer to them as "basin settings"), the thickness of the bubble column increases as the stability zone gets thicker. It takes more pressure to break through a thicker stability zone, so a taller column of gas is required. In compressional settings, where the dominant force is directed sideways by tectonics, rather than downward by gravity, the bubble layer is never as thick, reflecting an easier path to methane escape.

Multiple lines of evidence indicate that gas can be transported through the hydrate stability zone without freezing into hydrate. Seismic studies at Blake Ridge have observed the presence of bubbles along faults in the sediment matrix (Taylor *et al.,* 2000). Faults have been correlated with sites of methane gas emission from the sea floor (Aoki *et al.,* 2000; Zühlsdorff *et al.,* 2000; Zühlsdorff and Spiess, 2004). Seismic studies often show "wipeout zones" where the bubble zone beneath the hydrate stability zone is missing, and all of the layered structure of the sediment column within the stability zone is smoothed out. These are interpreted to be areas where gas has broken through the structure of the sediment to escape to the ocean (Riedel *et al.,* 2002; Wood *et al.,* 2002; Hill *et al.,* 2004). Bubbles associated with seismic wipeout zones are observed within the depth range that should be within the hydrate stability zone, assuming

that the temperature of the sediment column is the steady-state expression of the local average geothermal gradient (Gorman *et al.,* 2002). This observation has been explained by assuming that upward migration of the fluid carries with it heat, maintaining a warm channel where gas can be transported through what would otherwise be thermodynamically hostile territory (Taylor *et al.,* 2000; Wood *et al.,* 2002).

The sediment surface of the world's ocean has holes in it called pockmarks (Hovland and Judd, 1988; Hill *et al.,* 2004), interpreted to be the result of catastrophic or continuous escape of gas to the ocean. Pockmarks off Norway are accompanied by authigenic carbonate deposits associated with anaerobic oxidation of methane (Hovland *et al.,* 2005). Pockmarks range in size from meters to kilometers (Hovland *et al.,* 2005), with one 700-km$^2$ example on the Blake Ridge (Kvenvolden, 1999). If the Blake Ridge pockmark is the result of a catastrophic explosion, it might have released less than 1 GtC as methane (assuming a 500-m-thick layer of 4% methane yields 1 GtC). Since each individual pockmark releases a small amount of methane relative to the atmospheric inventory, pockmark methane release could impact climate as part of the ongoing "chronic" methane source to the atmosphere, if the frequency of pockmark eruptions increased. In this sense pockmarks do not represent "catastrophic" methane releases. However, Kennett *et al.* (2003) hypothesized that some apparently inactive pockmark fields may have formed during the last deglaciation and are evidence of active methane discharge at that time.

Another mechanism for releasing methane from the sediment column is by submarine landslides. These are a normal, integral part of the ocean sedimentary system (Hampton *et al.,* 1996; Nisbet and Piper, 1998). Submarine landslides are especially prevalent in river deltas because of the high rate of sediment delivery and because of the presence of submarine canyons. The tendency for slope failure can be amplified if the sediment accumulates more quickly than the excess porosity can be squeezed out. This accumulation can lead to instability of the sediment column, causing periodic Storegga-type landslides off the coast of Norway (see section below on Storegga Landslide), in the Mediterranean Sea (Rothwell *et al.,* 2000), or potentially off the East Coast of the United States (Dugan and Flemings, 2000). Maslin *et al.* (2004) find that 70% of the landslides in the North Atlantic over the last 45,000 years (45 kyr) occurred within the time windows of the two meltwater peaks, 15–13 and 11–8 kyr ago. These could have been driven by deglacial sediment loading or warming of the water column triggering hydrate melting.

Warming temperatures or sea-level changes may trigger the melting of hydrate deposits, provoking landslides (Kvenvolden, 1999; Driscoll *et al.,* 2000; Vogt and Jung, 2002). Paull *et al.* (1991) calculate that landslides can release up to about 1–2 GtC as methane; 1 Gt is enough to alter the radiative forcing by about 0.25 watts per square meter (W m$^{-2}$). The origin of these estimates is discussed in the section on the Storegga Landslide.

### 4.1.3 Impact on Structural-Type Hydrate Deposits

In stratigraphic-type hydrate deposits, hydrate concentration is highest near the base of the stability zone, often hundreds of meters below the sea floor. In shallower waters, where the stability zone is thinner, models predict smaller inventories of hydrate. Therefore, most of the hydrates in stratigraphic-type deposits tend to be deep. In contrast with this, in a few parts of the world, transport of presumably gaseous methane through faults or permeable channels results in hydrate deposits that are abundant at shallow depths in the sediment column, closer to the sea floor. These "structural-type" deposits could be vulnerable to temperature-change-driven melting on a faster time scale than the stratigraphic deposits are expected to be.

Another mechanism for releasing methane from the sediment column is by submarine landslides.

The Gulf of Mexico contains structural-type deposits and is basically a leaky oil field (MacDonald *et al.,* 1994, 2002, 2004; Sassen and MacDonald, 1994; Milkov and Sassen, 2000, 2001, 2003; Sassen *et al.,* 2001a; Sassen *et al.,* 2003). Natural oil seeps leave slicks on the sea surface that can be seen from space. Large chunks of methane hydrate have been found on the sea floor in contact with seawater (MacDonald *et al.,* 1994). One of the three

chunks MacDonald *et al.* saw had vanished when they returned a year later; presumably it had detached and floated away.

Collett and Kuuskraa (1998) estimate that 500 GtC might reside as hydrates in the gulf sediments, but Milkov (2004) estimates only 5 GtC. The equilibrium temperature change in the deep ocean to a large, 5,000-GtC fossil fuel release could be 3 °C (Archer *et al.,* 2004). Milkov and Sassen (2003) subjected a two-dimensional model of the hydrate deposits in the Gulf to a 4 °C temperature increase and predicted that 2 GtC from hydrate would melt. However, there are no observations to suggest that methane emission rates are currently accelerating, and temperature changes in Gulf of Mexico deep waters in the next 100 years are likely to be smaller than 3–4 °C. Sassen *et al.* (2001b) find no molecular fractionation of gases in near-surface hydrate deposits that would be indicative of partial dissolution, and suggest that the reservoir may in fact be growing.

Methane released from sediments in the ocean may reach the atmosphere directly, or it may dissolve in the ocean.

Other examples of structural deposits include the summit of Hydrate Ridge, off the coast of Oregon (Torres *et al.,* 2004; Tréhu *et al.,* 2004b), and the Niger Delta (Brooks *et al.,* 2000). The distribution of hydrate at Hydrate Ridge indicates up-dip flow along sand layers (Weinberger *et al.,* 2005). Gas is forced into sandy layers where it accumulates until the gas pressure forces it to vent to the surface (Tréhu *et al.,* 2004a). Tréhu *et al.* (2004b) estimate that 30–40% of pore space is occupied by hydrate, while gas fractions are 2–4%. Methane emerges to the sea floor with bubble vents and subsurface flows of 1 m $s^{-1}$, and in regions with bacterial mats and vesicomyid clams (Torres *et al.,* 2002). Further examples of structural deposits include the Peru Margin (Pecher *et al.,* 2001) and Nankai Trough, Japan (Nouzé *et al.,* 2004).

Mud volcanoes are produced by focused-upward fluid flow into the ocean and are sometimes associated with hydrate and petroleum deposits. Mud volcanoes often trap methane in hydrate deposits that encircle the channels of fluid flow (Milkov, 2000; Milkov *et al.,* 2004). The fluid flow channels associated with mud volcanoes are ringed with the seismic images of hydrate deposits, with authigenic carbonates, and with pockmarks (Dimitrov and Woodside, 2003) indicative of anoxic methane oxidation. Milkov (2000) estimates that mud volcanoes contain at most 0.5 GtC of methane in hydrate, about 100 times his estimate of the annual supply.

### 4.1.4 Fate of Methane Released as Bubbles

Methane released from sediments in the ocean may reach the atmosphere directly, or it may dissolve in the ocean. Bubbles are not generally a very efficient means of transporting methane through the ocean to the atmosphere. Rehder *et al.* (2002) compared the dissolution kinetics of methane and argon and found enhanced lifetime of methane bubbles below the saturation depth in the ocean, about 500 m, because a hydrate film on the surface of the methane bubbles inhibited gas exchange. Bubbles dissolve more slowly from petroleum seeps, where oily films on the surface of the bubble inhibit gas exchange, also changing the shapes of the bubbles (Leifer and MacDonald, 2003). On a larger scale, however, Leifer *et al.* (2000) diagnosed that the rate of bubble dissolution is limited by turbulent transport of methane-rich water out of the bubble stream into the open water column. The magnitude of the surface dissolution inhibition seems small; in the Rehder *et al.* (2002) study, a 2-cm bubble dissolves within 30 m above the stability zone, and only 110 m below the stability zone. Acoustic imaging of the bubble plume from Hydrate Ridge showed bubbles surviving from 600–700 m water depth, where they were released to just above the stability zone at 400 m (Heeschen *et al.,* 2003). One could imagine hydrate-film dissolution inhibition as a mechanism to concentrate the release of methane into the upper water column, but not really as a mechanism to get methane through the ocean directly to the atmosphere.

Methane can reach the atmosphere if the methane bubbles are released in waters that are only a few tens of meters deep, as in the case of melting the ice complex in Siberia (Xu *et al.,* 2001; Shakhova *et al.,* 2005; Washburn *et al.,* 2005), or during periods of lower sea level (Luyendyk *et al.,* 2005). If the rate of methane

release is large enough, the rising column of seawater in contact with the bubbles may saturate with methane, or the bubbles can be larger, potentially increasing the escape efficiency to the atmosphere.

### 4.1.5 Fate of Methane Hydrate in the Water Column

Pure methane hydrate is buoyant in seawater, so floating hydrate is another source of methane delivery from the sediment to the atmosphere (Brewer *et al.,* 2002). In sandy sediment, the hydrate tends to fill the existing pore structure of the sediment, potentially entraining sufficient sediment to prevent the hydrate/sediment mixture from floating, while in fine-grained sediments, bubbles and hydrate grow by fracturing the cohesion of the sediment, resulting in irregular blobs of bubbles (Gardiner *et al.,* 2003; Boudreau *et al.,* 2005) or pure hydrate. Brewer *et al.* (2002) and Paull *et al.* (2003) stirred surface sediments from Hydrate Ridge using the mechanical arm of a submersible remotely operated vehicle and found that hydrate did manage to shed its sediment load enough to float. Hydrate pieces of 0.1 m survived a 750-m ascent through the water column. Paull *et al.* (2003) described a scenario for a submarine landslide in which the hydrates would gradually make their way free of the turbidity current comprised of the sediment and seawater slurry.

### 4.1.6 Fate of Dissolved Methane in the Water Column

Methane is unstable to bacterial oxidation in oxic seawater. Rehder *et al.* (1999) inferred a methane oxidation lifetime in the high-latitude North Atlantic of 50 years. Methane oxidation is faster in the deep ocean near a particular methane source, where its concentration is higher (turnover time 1.5 years), than it is in the surface ocean (turnover time of decades) (Valentine *et al.,* 2001). Water-column concentration and isotopic measurements indicate complete water-column oxidation of the released methane at Hydrate Ridge (Grant and Whiticar, 2002; Heeschen *et al.,* 2005).

An oxidation lifetime of 50 years leaves plenty of time for transport of methane gas to the atmosphere. Typical gas-exchange time scales

for gas evasion from the surface ocean would be about 3–5 m per day. A surface mixed layer 100 m deep would approach equilibrium (degas) in about a month. Even a 1,000-m-thick winter mixed layer would degas about 30% during a 3-month winter window. The ventilation time of subsurface waters depends on the depth and the fluid trajectories in the water (Luyten *et al.,* 1983), but 50 years is enough time that a significant fraction of the dissolved methane from bubbles might reach the atmosphere before it is oxidized.

## 4.2 Geologic Data Relevant to Past Hydrate Release

### 4.2.1 The Storegga Landslide

One of the largest exposed submarine landslides in the ocean is the Storegga Landslide in the Norwegian continental margin (Mienert *et al.,* 2000, 2005; Bryn *et al.,* 2005). The slide excavated on average the top 250 m of sediment over a swath hundreds of kilometers wide, stretching halfway from Norway to Greenland (Fig. 5.10). There have been comparable slides on the Norwegian margin every approximately 100 kyr, roughly synchronous with the glacial cycles (Solheim *et al.,* 2005). The last one, Storegga proper, occurred about 8,150 years ago, after deglaciation. It generated a tsunami in what is now the United Kingdom (D'Hondt *et al.,* 2004; Smith *et al.,* 2004). The Storegga slide area contains methane hydrate deposits as indicated by a bottom simulating seismic reflector (BSR) (Bunz and Mienert, 2004; Mienert *et al.,* 2005; Zillmer *et al.,* 2005a,b) corresponding to the base of the hydrate stability zone (HSZ) at 200–300 m, and pockmarks

Pure methane hydrate is buoyant in seawater, so floating hydrate is another source of methane delivery from the sediment to the atmosphere.

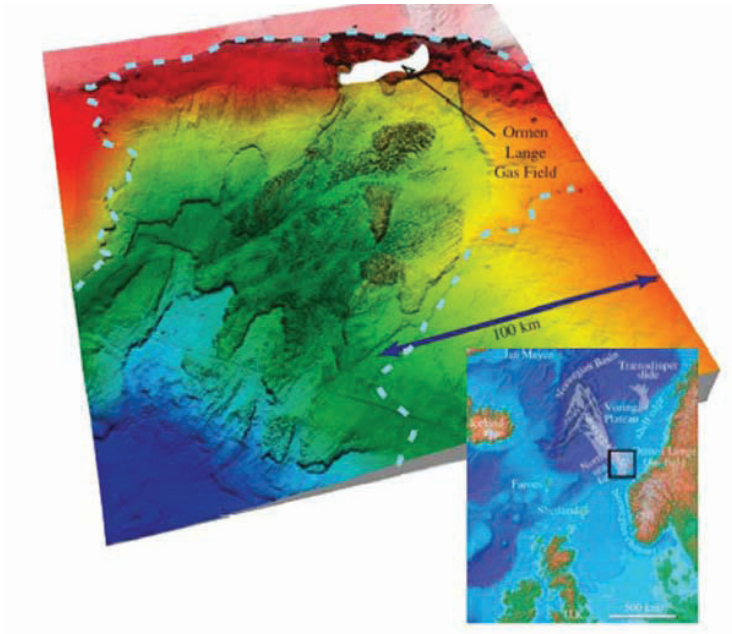



**Figure 5.10.** Image and map of the Storegga Landslide from Masson *et al.*, 2006; used with permission from *Philosophical Transactions of the Royal Society.* The slide excavated on average the top 250 m of sediment over a swath hundreds of kilometers wide. Colors indicate water depth, with yellow-orange indicating shallow water, and green-blue indicating deeper water.

(Hovland *et al.,* 2005) indicating gas expulsion from the sediment.

The proximal cause of the slide may have been an earthquake, but the sediment column must have been destabilized by either or both of two mechanisms. One is the rapid accumulation of glacial sediment shed by the Fennoscandian ice sheet (Bryn *et al.,* 2005). As explained above, rapid sediment loading traps porewater in the sediment column faster than it can be expelled by the increasing sediment load. At some point, the sediment column floats in its own porewater (Dugan and Flemings, 2000). This mechanism has the capacity to explain why the Norwegian continental margin, of all places in the world, might have landslides synchronous with climate change.

The other possibility is the dissociation of methane hydrate deposits by rising ocean temperatures. Rising sea level is also a player in this story, but a smaller one. Rising sea level tends to increase the thickness of the stability zone by increasing the pressure. A model of the stability zone shows this effect dominating deeper in the water column (Vogt and Jung, 2002); the stability zone is shown increasing by about 10 m for sediments in water depth below about 750 m. Shallower sediments are impacted more by long-term temperature changes, reconstructions of which show warming of 5–6 °C over a thousand years or so, 11–12 kyr ago. The landslide occurred 2–3 kyr after the warming (Mienert *et al.,* 2005). The slide started at a few hundred meters water depth, just off the continental slope, just where Mienert *et al.* (2005) calculate the maximum change in HSZ. Sultan *et al.* (2004) predict that warming in the near-surface sediment would provoke hydrate to dissolve by increasing the saturation methane concentration. This form of dissolution differs from heat-driven direct melting, however, in that it produces dissolved methane, rather than methane bubbles. Sultan *et al.* (2004) assert that melting to produce dissolved methane increases the volume, although laboratory analyses of volume changes upon this form of melting are equivocal. In any case, the volume changes are much smaller than for thermal melting that produces bubbles.

The amount of methane released by the slide can be estimated from the volume of the slide and the potential hydrate content. Hydrate just outside the slide area has been estimated by seismic methods to fill as much as 10% of the porewater volume, in a layer about 50 m thick near the bottom of the stability zone (Bunz and Mienert, 2004). If these results were typical of the entire $10^4$ $km^2$ area of the slide, the slide could have released 1–2 GtC of methane in hydrate (Paull *et al.,* 1991).

If 1 GtC $CH_4$ reached the atmosphere all at once, it would raise the atmospheric concentration from today's value of ~1,700 ppb to ~2,200 ppb, trapping about 0.25 additional $W/m^2$ of greenhouse heat, or more, considering indirect feedbacks. The methane radiative forcing would subside over a time scale of a decade or so, as the pulse of released methane was oxidized to $CO_2$, and the atmospheric methane concentration relaxed toward the long-term steady-state value. The radiative impact of the Storegga Landslide would then be somewhat

smaller in magnitude but opposite in sign to the eruption of a large volcano, such as the Mount Pinatubo eruption (–2 W/m$^2$), but it would last longer (10 years for methane and 2 years for a volcano).

It is tantalizing to wonder if there could be any connection between the Storegga Landslide and the 8.2-kyr climate event (Alley and Agustsdottir, 2005), which may have been triggered by freshwater release to the North Atlantic. However, ice cores record a 75-ppb drop in methane concentration during the 8.2-kyr event (Kobashi *et al.,* 2007), not a rise. A slowdown of convection in the North Atlantic would have cooled the overlying waters. Maslin *et al.* (2004) suggested that an apparent correlation between the ages of submarine landslides in the North Atlantic region and methane variations during the deglaciation supported the hypothesis that clathrate release by this mechanism influenced atmospheric methane. The lack of response for Storegga, by far the largest landslide known, and a relatively weak association of other large slides with increased methane levels (Fig. 5.11) suggest that it is unlikely that submarine landslides caused the atmospheric methane variations during this time period.

Much of our knowledge of the Storegga Landslide is due to research sponsored by the Norwegian oil industry, which is interested in tapping the Ormen Lange gas field within the headlands of the Storegga slide but is concerned about the geophysical hazard of gas extraction (Bryn *et al.,* 2005). Estimates of potential methane emission from the Storegga slide range from 1 to 5 GtC, which is significant but not apocalyptic. As far as can be determined, the Storegga Landslide had no impact on climate.

### 4.2.2 The Paleocene-Eocene Thermal Maximum

About 55 million years ago, the $\delta^{13}C$ signature of carbon in the ocean and on land decreased by 2.5–5 per mil (‰) on a time scale of less than 10 kyr, then recovered in parallel on a time scale of ~120–220 kyr (Kennett and Stott, 1991; Zachos *et al.,* 2001). Associated with this event, commonly called the Paleocene-Eocene Thermal Maximum (PETM), the $\delta^{18}O$ of $CaCO_3$ from intermediate depths in the ocean decreased by 2–3‰, indicative of a warming of about 5 °C (Fig. 5.12). The timing of the spikes is to a large extent synchronous. Planktonic foraminifera and terrestrial carbon records show a $\delta^{13}C$ perturbation a bit earlier than benthic foraminifera

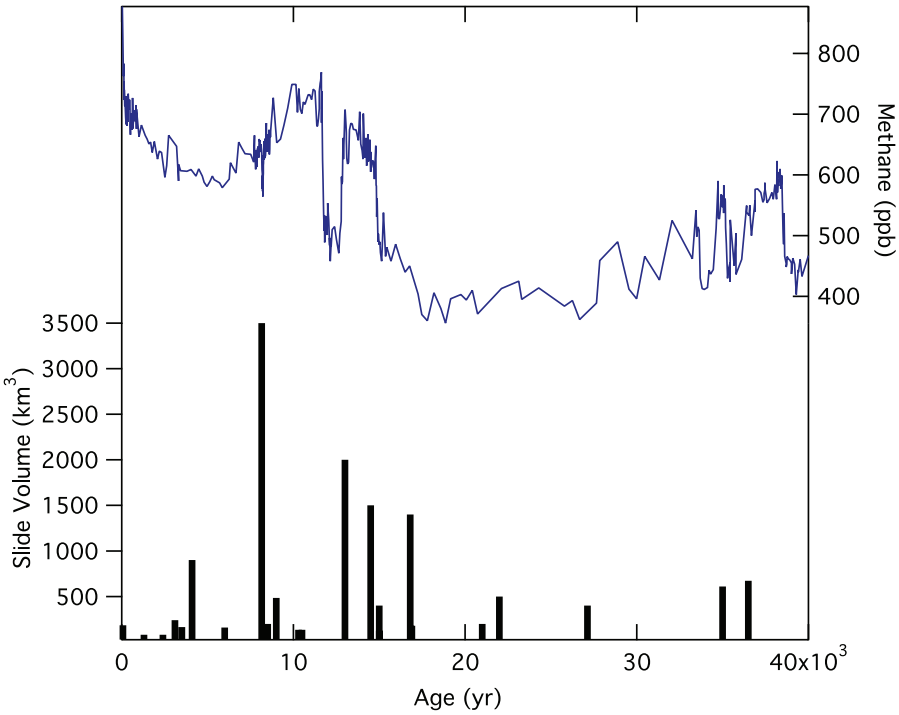



**Figure 5.11.** Timing of submarine landslides in the North Atlantic region and pre-industrial ice core methane variations. Landslide data from Maslin *et al.* (2004). Methane data from Brook *et al.* (2000) and Kobashi *et al.* (2007). Abbreviations: km$^3$, cubic kilometers; yr, year; ppb, parts per billion.

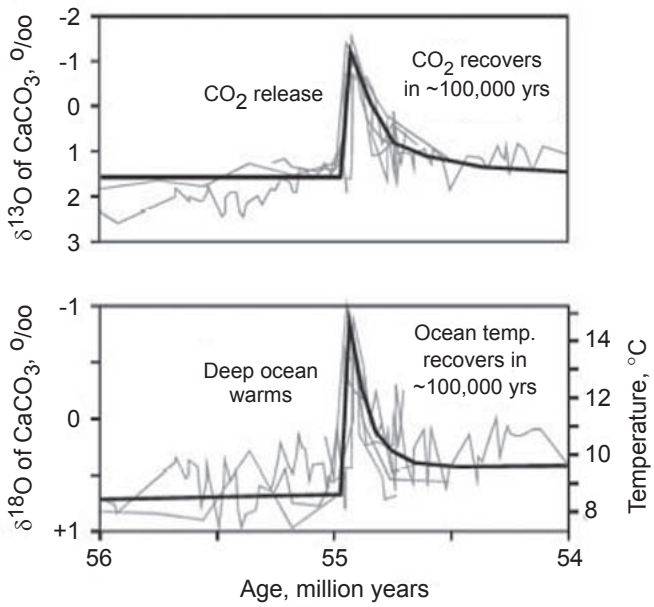



**Figure 5.12.** Carbon (top) and oxygen (bottom) isotope record for benthic foraminifera from sites in the south Atlantic and western Pacific Oceans for the Paleocene-Eocene Thermal Maximum (PETM), from Zachos *et al.* (2001), modified by Archer (2007); used with permission. ‰, per mil.

do, suggesting that the carbon spike invaded the deep ocean from the atmosphere (Thomas *et al.,* 2002). Similar events, also associated with transient warmings, have been described from other times in geologic history (Hesselbo *et al.,* 2000; Jenkyns, 2003). The PETM is significant to the present day because it is an analog to the potential fossil fuel carbon release if we burn all the coal reserves.

The PETM is significant to the present day because it is an analog to the potential fossil fuel carbon release if we burn all the coal reserves.

The change in isotopic composition of the carbon in the ocean is attributed to the release of some amount of isotopically light carbon to the atmosphere. However, it is not clear where the carbon came from, or how much of it there was. The magnitude of the carbon shift depends on where it was recorded. The surface change recorded in $CaCO_3$ in soils (Koch *et al.,* 1992) and in some planktonic foraminifera (Thomas *et al.,* 2002) is twice as large a change as is reported for the deep sea. Land records may be affected by changes in plant fractionation, driven by changing hydrological cycle (Bowen *et al.,* 2004). Ocean records may be affected by $CaCO_3$ dissolution (Zachos *et al.,* 2005) resulting in diagenetic imprints on the remaining $CaCO_3$, a necessity to use multiple species, or simple inability to find $CaCO_3$ at all.

We can estimate the change in the carbon inventory of the ocean by specifying an atmospheric partial pressure of $CO_2$ value ($pCO_2$), a mean ocean temperature, and insisting on equilibrium with $CaCO_3$ (Zeebe and Westbroek, 2003). The ocean was warmer, prior to the PETM event, than it is today. Atmospheric $pCO_2$ was probably at least 560 ppm at this time (Huber *et al.,* 2002). The present-day inventory of $CO_2$ in the ocean is about 40,000 GtC. According to simple thermodynamics, neglecting changes in the biological pump or circulation of the ocean, the geological steady-state inventory for late Paleocene, pre-PETM time could have been on the order of 50,000 GtC.

The lighter the isotopic value of the source, the smaller the amount of carbon that must be released to explain the isotopic shift (Fig. 5.12, top). Candidate sources include methane, which can range in its $\delta^{13}C$ isotopic composition from –30 to –110‰. If the ocean $\delta^{13}C$ value is taken at face value, and the source was methane at –60‰, then 2,000 GtC would be required to explain the isotopic anomaly. If the source were thermogenic methane or organic carbon at $\delta^{13}C$ of about –25‰, then 10,000 GtC would be required.

Buffett and Archer (2004) find that the steady-state hydrate reservoir size in the ocean is extremely sensitive to the temperature of the deep sea. At the temperature of Paleocene time but with everything else as in the present-day ocean, they predict less than a thousand GtC of methane in steady state. As the ocean temperature decreases, the stability zone gets thinner and covers less area. Their model was able to fit 6,000 GtC in the Arctic Ocean, however, using 6 °C temperatures from CCSM (Huber *et al.,* 2002) (which may be too cold) and assuming that the basin had been anoxic (Sluijs *et al.,* 2006).

Marine organic matter has an isotopic composition of –20‰ and would require 6,000 GtC to explain the isotopic anomaly. Svensen *et al.* (2004) proposed that lava intrusions into organic-rich sediments could have caused the isotopic shift. They cite evidence that the isotopic composition of methane produced from magma intrusion should be –35 to –50‰,

requiring therefore 2,500–3,500 GtC to explain the isotope anomaly in the deep ocean. If $CO_2$ were also released, from metamorphism of $CaCO_3$, the average isotopic composition of the carbon spike would be lower, and the mass of carbon greater. Storey *et al.* (2007) showed that the opening of the North Atlantic Ocean and associated igneous intrusions and volcanism correspond in time with the PETM. However, the time scale of carbon release (<10 kyr), indicated by the isotopic shift, is likely more abrupt than one would expect from this kind of volcanic activity. Furthermore, the volcanic activity continued for hundreds of thousands of years, leaving still unexplained the reason for the fast (<10,000 years) carbon isotope excursion.

A comet impact might have played a role in the PETM, and while the isotopic composition of comets is not well constrained, carbon in cometary dust tends to be about –45‰ (Kent *et al.,* 2003). Kent *et al.* (2003) calculate that an 11 km comet containing 20–25% organic matter, a rather large icy tarball, could deliver 200 GtC, enough to decrease the $\delta^{13}C$ of the atmosphere and upper ocean by 0.4‰. It is unlikely that a comet could deliver thousands of GtC, however. An impact strike to a carbonate platform or an organic-rich sediment of some sort could release carbon, but it would take a very large crater to release thousands of gigatons of carbon.

Volcanic carbon has an isotopic composition of –7‰, requiring a huge carbon release of ~20,000 GtC to explain the PETM. Excess carbon emissions have been attributed to superplume cycles in the mantle and flood-basalt volcanic activity (Larson, 1991). Schmitz *et al.* (2004) and Bralower *et al.* (1997) find evidence of increased volcanic activity during the PETM interval but view the activity as rearranging ocean circulation, triggering methane release, rather than being a major primary source of carbon itself, presumably because the potential volcanic carbon source is too slow.

Acidification of the ocean by invasion of $CO_2$ drove a shoaling of the depth of $CaCO_3$ preservation in the Atlantic (Zachos *et al.,* 2005) although, curiously, the signal is much smaller in the Pacific (Zachos *et al.,* 2003). The magnitude of the carbonate compensation depth (CCD) shift in the Atlantic would suggest a large carbon addition, on the order of 5,000 GtC or more (Archer *et al.,* 1997).

A large carbon release is also supported by the warming inferred from the $\delta^{18}O$ spike. The benthic $\delta^{18}O$ record is clearly interpretable as a temperature change, at a depth of several kilometers in the ocean, from about 8° to about 14 °C, in a few thousand years. Warming is also implied by Mg/Ca ratios in $CaCO_3$ (Zachos *et al.,* 2003) and other tracers (Sluijs *et al.,* 2006, 2007). The temperature can be altered by both $CH_4$ and $CO_2$. Schmidt and Shindell (2003) calculated that the steady-state atmospheric $CH_4$ concentration during the period of excess emission (ranging from 500–20,000 years) would be enough to explain the temperature change. However, the atmospheric-methane concentration anomaly would decay away a few decades after the excess emission ceased. At this point the temperature anomaly would die away also. Hence, as soon as the carbon isotopic composition stopped plunging negatively, the oxygen isotopic composition should recover as the ocean cools. The carbon isotopic composition meanwhile should remain light for hundreds of thousands of years (Kump and Arthur, 1999) until the carbon reservoir isotopic composition reapproached a steady-state value. The record shows instead that the oxygen and carbon isotopic anomalies recovered in parallel (Fig. 5.12). This suggests that $CO_2$ is the more likely greenhouse warmer rather than $CH_4$. It could be that the time scale for the $pCO_2$ to reach steady state might be different than the time scale for the isotopes to equilibrate, analogous to the equilibration of the surface ocean by gas exchange: isotopes take longer. However, in the Kump and Arthur (1999) model results, $pCO_2$ seems to take longer to equilibrate than $\delta^{13}C$. The first-order result is that the $CO_2$ and $\delta^{13}C$ time scales are much more similar than the $CH_4$ and $\delta^{13}C$ time scales would be.

A warming of 5 °C would require somewhere between one and two doublings of the atmospheric $CO_2$ concentration, if the climate sensitivity is in the range of IPCC predictions of 2.5–4.5 °C. Beginning from 600 ppm, we would increase the $pCO_2$ of the atmosphere to

somewhere in the range of 1,200–2,400 ppm. The amount of carbon required to achieve this value for hundreds of thousands of years (after equilibration with the ocean and with the $CaCO_3$ cycle) would be of order 20,000 GtC. This would imply a mean isotopic composition of the spike of mantle isotopic composition, not isotopically light methane. The amount of carbon required to explain the observed $\delta^{18}O$ would be higher if the initial atmospheric $pCO_2$ were higher than the assumed 600 ppm. The only way that a biogenic methane source could explain the warming is if the climate sensitivity were much higher in the Paleocene than it seems to be today, which seems unlikely because the ice albedo feedback amplifies the climate sensitivity today (Pagani *et al.,* 2006).

The bottom line conclusion about the source of the carbon isotopic excursion is that it is still not clear. There is no clear evidence in favor of a small, very isotopically depleted source of carbon. Mechanistically, it is easier to explain a small release than a large one, and this is why methane has been a popular culprit for explaining the $\delta^{13}C$ shift. Radiative considerations argue for a larger carbon emission, corresponding to a less fractionated source than pure biogenic methane. Thermogenic methane might do, such as the release of somewhat more thermogenic methane than in Gulf of Mexico sediments, if there were a thermogenic deposit that large. Perhaps it was some combination of sources, an initial less-fractionated source such as marine organic matter or a comet, followed by hydrate release.

The PETM is significant to the present day because it is a close analog to the potential fossil fuel carbon release if we burn all the coal reserves. There are about 5,000 GtC in coal, while oil and traditional natural gas deposits are hundreds of gigatons each (Rogner, 1997). The recovery time scale from the PETM (140 kyr) is comparable to the model predictions, based on the mechanism of the silicate weathering thermostat (400 kyr time scale, Berner *et al.,* 1983).

The magnitude of the PETM warming presents an important and currently unanswered problem. A 5,000-GtC fossil fuel release will warm the deep ocean by perhaps 2–4 °C, based on paleoclimate records and model results (Martin *et al.,* 2005). The warming during the PETM was 5 °C, and this was from an atmospheric $CO_2$ concentration higher than today (at least 600 ppm), so that a further spike of only 2,000 GtC (based on methane isotopic composition) would have only a tiny radiative impact, not enough to warm the Earth by 5 °C. One possible explanation is that our estimates for the climate sensitivity are too low by a factor of 2 or more. However, as mentioned above, one might expect a decreased climate sensitivity for an ice-free world rather than for the ice-age climate of today.

Another possible explanation is that the carbon release was larger than 2,000 GtC. Perhaps the global average $\delta^{13}C$ shift was as large as recorded in soils (Koch *et al.,* 1992) and some planktonic foraminifera (Thomas *et al.,* 2002). The source could have been thermogenic methane, or maybe it was not methane at all but $CO_2$, derived from some organic pool such as sedimentary organic carbon (Svensen *et al.,* 2004). At present, the PETM serves as a cautionary tale about the long duration of a release of new $CO_2$ to the atmosphere (Archer, 2005). However, our current understanding of the processes responsible for the $\delta^{13}C$ spike is not strong enough to provide any new constraint to the stability of the methane hydrate reservoir in the immediate future.

### 4.2.3 Santa Barbara Basin and the Clathrate Gun Hypothesis

Nisbet (2002) and Kennett *et al.* (2003) argue that methane from hydrates is responsible for the deglacial rise in the Greenland methane record between 20,000 and 10,000 years ago,

and for abrupt changes in methane at other times (Fig. 5.6C). Kennett *et al.* (2000) found episodic negative $\delta^{13}C$ excursions in benthic foraminifera in the Santa Barbara basin, which they interpret as reflecting release of hydrate methane during warm climate intervals. Biomarkers for methanotrophy are found in greater abundance and indicate greater rates of reaction during warm intervals in the Santa Barbara basin (Hinrichs *et al.,* 2003) and in the Japanese coastal margin (Uchida *et al.,* 2004). Cannariato and Stott (2004), however, argued that these results could have arisen from contamination or subsequent diagenetic overprints. Hill *et al.* (2006) measured the abundance of tar in Santa Barbara basin sediments, argued that tar abundance was proportional to methane emissions, and described increases in tar abundance and inferred destabilization of methane hydrates associated with warming during the last glacial-interglacial transition.

As discussed in Section 1, there are several arguments against the hypothesis of a clathrate role in controlling atmospheric methane during the last glacial period. Perhaps the most powerful so far is that the isotopic ratio of deuterium to hydrogen (D/H) in ice core methane for several abrupt transitions in methane concentration indicates a freshwater source, rather than a marine source, apparently ruling out much of a role for marine hydrate methane release (Sowers, 2006). However, the D/H ratio has not yet been measured for the entire ice core record. The timing of the deglacial methane rise was also more easily explained by wetland emissions than by catastrophic methane release (Brook *et al.,* 2000). The interhemispheric gradient of methane tells us that the deglacial increase in atmospheric methane arose in part from high northern latitudes (Dällenbach *et al.,* 2000), although more work is needed to verify this conclusion because constraining the gradient is analytically difficult. The deglacial methane rise could therefore be attributed at least in part to methanogenesis from decomposition of thawing organic matter from high-latitude wetlands. Regardless of the source of the methane, the climate forcing from the observed methane record (Fig. 5.6C and D) is too weak to argue for a dominant role for methane in the glacial cycles (Brook *et al.,* 2000).

## 4.3 Review of Model Results Addressing Past and Future Methane Hydrate Destabilization

### 4.3.1 Climate Impact of Potential Release

Our picture of methane release mechanisms has been refined since 1995, although it remains difficult to predict the fate of methane from melted hydrates.

Probably the most detailed analysis to date of the potential for methane release from hydrates on a century time scale is the study of Harvey and Huang (1995). Their study calculated the inventory of hydrate and the potential change in that inventory with an ocean warming. They treated as a parameter the fraction of methane in bubbles that could escape the sediment column to reach the ocean, and evaluated the sensitivity of the potential methane release to that escaped fraction. Our picture of methane release mechanisms has been refined since 1995, although it remains difficult to predict the fate of methane from melted hydrates. Harvey and Huang (1995) did not treat the invasion of heat into the ocean or into the sediment column. Their conclusion was that the radiative impact from hydrate methane will be much smaller than that of $CO_2$, or even between different scenarios for $CO_2$ release. The calculation should be redone, but it is unlikely that an updated calculation would change the bottom-line conclusion.

Schmidt and Shindell (2003) showed that the chronic release of methane from a large hydrate reservoir over thousands of years can have a significant impact on global climate. The accumulating $CO_2$ from the oxidation of the methane also has a significant climate impact. New $CO_2$ from methane oxidation accumulates in the atmosphere/ocean/terrestrial biosphere carbon pool and persists to affect climate for hundreds of thousands of years (Archer, 2005). If a pool of methane is released over a time scale of thousands of years, the climate impact from the accumulating $CO_2$ concentration may exceed that from the steady-state increase in the methane concentration (Harvey and Huang, 1995; Dickens, 2001a; Schmidt and Shindell, 2003; Archer and Buffett, 2005). After the emission stops, methane drops quickly to a lower steady state, while the $CO_2$ persists.

If hydrates melt in the ocean, much of the methane would probably be oxidized in the

While most methane hydrates are marine, the size of the contemporary terrestrial methane hydrate pool, although unknown, may be large.

ocean rather than reaching the atmosphere directly as methane. This reduces the century time scale climate impact of melting hydrate, but on time scales of millennia and longer the climate impact is the same regardless of where the methane is oxidized. Methane oxidized to $CO_2$ in the ocean will equilibrate with the atmosphere within a few hundred years, resulting in the same partitioning of the added $CO_2$ between the atmosphere and the ocean regardless of its origin. The rate and extent to which methane carbon can escape the sediment column in response to warming is very difficult to constrain at present. It depends on the stability of the sediment slope to sliding, and on the permeability of the sediment and the hydrate stability zone's cold trap to bubble methane fluxes.

### 4.4 Conclusions About Potential for Abrupt Release of Methane From Marine Hydrates

On the time scale of the coming century, it appears likely that most of the marine hydrate reservoir will be insulated from anthropogenic climate change. The exception is in shallow ocean sediments where methane gas is focused by subsurface migration. The most likely response of these deposits to anthropogenic climate change is an increased background rate of chronic methane release, rather than an abrupt release. Methane gas in the atmosphere is a transient species, its loss by oxidation continually replenished by ongoing release. An increase in the rate of methane emission to the atmosphere from melting hydrates would increase the steady-state methane concentration of the atmosphere. The potential rate of methane emission from hydrates is more speculative than the rate from other methane sources, such as the decomposition of peat in thawing permafrost deposits, or anthropogenic emission from agricultural, livestock, and fossil fuel industries, but the potential rates appear to be comparable to these sources.

## 5. TERRESTRIAL METHANE HYDRATES

There are two sources for methane in hydrates, biogenic production by microbes degrading organic matter in anaerobic environments and thermogenic production at temperatures above 110 °C, typically at depths greater than about 15 km. Terrestrial methane hydrates are primarily biogenic (Archer, 2007). They form and are stable under ice sheets (thicker than ~250 m) and within permafrost soils at depths of about 150 to 2,000 m below the surface (Kvenvolden, 1993; Harvey and Huang, 1995). Their presence is known or inferred from geophysical evidence (*e.g.,* well logs) on Alaska's North Slope, the Mackenzie River delta (Northwest Territories) and Arctic islands of Canada, the Messoyakha Gas Field and two other regions of western Siberia, and two regions of northeastern Siberia (Kvenvolden and Lorenson, 2001). Samples of terrestrial methane hydrates have been recovered from 900 to 1,110 m depth in the Mallik core in the Mackenzie River delta (Kvenvolden and Lorenson, 2001; Uchida *et al.,* 2002).

### 5.1 Terrestrial Methane Hydrate Pool Size and Distribution

While most methane hydrates are marine, the size of the contemporary terrestrial methane hydrate pool, although unknown, may be large. Estimates range from less than 10 Gt $CH_4$ (Meyer, 1981) to more than 18,000 Gt $CH_4$ (Dobrynin *et al.,* 1981) (both cited in Harvey and Huang, 1995). More recent estimates are 400 Gt $CH_4$ (MacDonald, 1990), 800 Gt $CH_4$ (Harvey and Huang, 1995), and 4.5–400 GtC; this is a small fraction of the ocean methane hydrate pool size (see Sec. 4).

Terrestrial methane hydrates are a potential fossil energy source. Recovery can come from destabilization of the hydrates by warming, reducing the pressure, or injecting a substance (*e.g.,* methanol) that shifts the stability line (see Box 5.1). The Messoyakha Gas Field in western Siberia, at least some of which lies in the terrestrial methane hydrate stability zone, began producing gas in 1969, and some production is thought to have come from methane hydrates, though methanol injection made this production very expensive (Kvenvolden, 1993; Krason, 2000). A more recent review of the geological evidence for methane production from hydrates at Messoyakha by Collett and Ginsburg (1998) could not confirm unequivocally that hydrates contributed to the produced gas. Due to low costs of other available energy resources, there had not been significant international industrial interest in hydrate methane extraction from

1970 to 2000 (Kvenvolden, 2000), and the fraction of terrestrial methane hydrate that is or will be technically and economically recoverable is not well established. In the United States, the Methane Hydrate Research and Development Act of 2000 and its subsequent 2005 Amendment have fostered the National Methane Hydrates R&D Program, supporting a wide range of laboratory, engineering, and field projects with one focus being on developing the knowledge and technology base to allow commercial production of methane from domestic hydrate deposits by the year 2015, beginning with Alaska's North Slope. Estimates of technically and economically recoverable methane in hydrates are being developed (Boswell *et al.,* 2005; Boswell, 2007).

### 5.2 Mechanisms To Destabilize Terrestrial Methane Hydrates

Terrestrial methane hydrates in permafrost are destabilized if the permafrost warms sufficiently or if the permafrost hydrate is exposed through erosion (see Box 5.3). Destabilization of hydrates in permafrost by global warming is not expected to be significant over the next few centuries (Nisbet, 2002; see Sec. 5.4). Nisbet (2002) notes that although a warming pulse will take centuries to reach permafrost hydrates at depths of several hundred meters, once a warming pulse enters the soil/sediment, it continues to propagate downward and will eventually destabilize hydrates, even if the climate has subsequently cooled.

Terrestrial methane hydrates under an ice sheet are destabilized if the ice sheet thins or retreats. The only globally significant ice sheets now existing are on Greenland and Antarctica; maps of the global distribution of methane hydrates do not show any hydrates under either ice sheet (Kvenvolden, 1993). It is likely, however, that hydrates formed under Pleistocene continental ice sheets (*e.g.,* Weitemeyer and Buffett, 2006; see Sec. 5.3.1).

Terrestrial methane hydrates can also be destabilized by thermokarst erosion (a melt-erosion process) of coastal-zone permafrost. Ice complexes in the soil melt where they are exposed to the ocean along the coast, the land collapses into the sea, and more ice is exposed (Archer, 2007). The Siberian coast is experiencing very high rates of coastal erosion (Shakhova *et al.,* 2005). Methane hydrates associated with this permafrost become destabilized through this process, and methane is released into the coastal waters (Shakhova *et al.,* 2005). Magnitudes of the emissions are discussed below.

De Batist *et al.* (2002) analyzed seismic reflection data from Lake Baikal sediments, the only freshwater nonpermafrost basin known to contain gas hydrates, and infer that hydrate destabilization is occurring in this tectonically active lacustrine basin *via* upward flow of hydrothermal fluids advecting heat to the base of the hydrate stability zone. If occurring, this means of destabilization is very unlikely to be

Terrestrial methane hydrates in permafrost are destabilized if the permafrost warms sufficiently or if the permafrost hydrate is exposed through erosion.

important globally, as the necessary geological setting is rare.

Mining terrestrial hydrates for gas production will necessarily destabilize them, but presumably most of this methane will be captured, used, and the carbon emitted to the atmosphere as $CO_2$.

## 5.3 Evidence of Past Release of Terrestrial Hydrate Methane

No direct evidence has been identified of past release of terrestrial hydrate methane in significant quantities. Analyses related to the PETM and clathrate gun hypothesis discussed in Section 4 have focused on methane emissions from the larger and more vulnerable marine hydrates. Emissions from terrestrial hydrates may have contributed to changes in methane observed in the ice core record, but there are so far no distinctive isotopic tracers of terrestrial hydrates, as is the case for marine hydrate (Sowers, 2006).

### 5.3.1. Quantity of Methane Released From Terrestrial Hydrates in the Past

Weitemeyer and Buffett (2006) modeled the accumulation and release of biogenic methane from terrestrial hydrates below the Laurentide and Cordilleran ice sheets of North America during the last glaciation. Methane was generated under the ice sheet from anaerobic decomposition of buried, near-surface soil organic matter, and hydrates formed if the ice sheet was greater than ~250 m thick. Hydrate destabilization arose from pressure decreases with ice sheet melting/thinning. They simulated total releases for North America of about 40–100 Tg $CH_4$, with most of the deglacial emissions occurring during periods of glacial retreat during a 500-year interval around 14 kyr before present (BP), and a 2,000-year interval centered on about 10 kyr BP. The highest simulated emission rates (~15–35 Tg $CH_4$ $yr^{-1}$) occurred during the dominant period of ice sheet melting around 11–9 kyr BP.

Shakova *et al.* (2005) measured supersaturated methane concentrations in northern Siberian coastal waters. This supersaturation is thought to arise from degradation of coastal shelf hydrate, hydrate that had formed in permafrost when the shelf was exposed during low sea level of the last glacial maximum. Methane concentrations in the Laptev and East Siberian Seas were supersaturated up to 800% in 2003 and 2,500% in 2004. From this and an empirical model of gas flux between the atmosphere and the ocean, they estimated summertime (*i.e.,* ice-free) fluxes of up to 0.4 Mg $CH_4$ $km^{-2}$ $y^{-1}$ (or 0.4 g $CH_4$ $m^{-2}$ $y^{-1}$). They assume that the methane flux from the sea floor is of the same order of magnitude and may reach 1–1.5 g $CH_4$ $m^{-2}$ $y^{-1}$. These fluxes are low compared to wetland fluxes (typically ~1–100 g $CH_4$ $m^{-2}$ $y^{-1}$; Bartlett and Harriss, 1993), but applied across the total area of shallow Arctic shelf, the total annual flux for this region may be as high as 1–5 Tg $CH_4$ $y^{-1}$, depending on degree of oxidation in the seawater. (See Table 5.1 above for global methane emissions by source.)

### 5.3.2 Climate Impact of Past Methane Release From Terrestrial Hydrates

Most studies of climate impacts from possible past methane hydrate releases have considered large releases from marine hydrates (see Sec. 4 above). It is generally not well known what fraction of the methane released from hydrate destabilization is either trapped in overlying sediments or oxidized to carbon dioxide before reaching the atmosphere (Reeburgh, 2004), and the same considerations are relevant to release from terrestrial sources.

Weitemeyer and Buffett (2006) estimated intervals of 500–2,000 years when methane hydrate destabilization from retreat of the North American ice sheet caused increases of atmospheric methane of 10–200 ppb, with the largest perturbation at 11–9 kyr before present. Any effect of methane oxidation before reaching the atmosphere was ignored; this oxidation would have reduced the impact on the atmospheric methane burden. This atmospheric perturbation is equivalent to about 2–25% of pre-industrial Holocene atmospheric methane burdens, and roughly equivalent to a radiative forcing of 0.002–0.1 W $m^{-2}$ (using contemporary values for methane radiative efficiency and indirect effects from Ramaswamy *et al.,* 2001).

Thermokarst erosion on the Arctic coast of Siberia is thought to cause hydrate destabilization and emissions of methane that are at most 1% of total global methane emissions (Shakhova *et al.* 2005), and so this process is very unlikely to be having a large climatic impact.

### 5.4 Estimates of Future Terrestrial Hydrate Release and Climatic Impact

Harvey and Huang (1995) modeled terrestrial methane hydrate release due to global warming (step function temperature increases of 5 °C, 10 °C, and 15 °C, and the propagation of this heat into hydrate-bearing permafrost). Over the first few centuries, the methane release is very small, and after 1,000 years, the cumulative methane release is <1%, 2%, and 5% of the total terrestrial methane hydrate pool size, respectively; by 5,000 years, this cumulative release has increased to 3%, 15%, and 30%, respectively. Even 5,000 years after a step function increase in temperature of 15 °C, the radiative forcing caused by terrestrial hydrate melting (direct effects of methane plus methane converted to carbon dioxide) was only ~0.3 W/m$^2$.

Methane release from hydrate destabilization due to decaying ice sheets is unlikely to be substantial unless there are significant hydrate pools under Greenland and/or Antarctica, which does not seem to be the case. Thermokarst erosion release is the only known present terrestrial hydrate methane source. This process can be expected to continue into the future, and it is very likely that emissions will remain a small fraction of the global methane budget and therefore have a small impact on radiative forcing. However, most recent modeling analyses have focused on marine hydrates (*e.g.,* Dickens, 2001c; Archer and Buffett, 2005), and more work on the terrestrial hydrate reservoir is clearly needed.

### 5.5 Conclusions

No mechanisms have been proposed for the abrupt release of significant quantities of methane from terrestrial hydrates (Archer, 2007). Slow and perhaps sustained release from permafrost regions may occur over decades to centuries from mining extraction of methane

from terrestrial hydrates in the Arctic (Boswell, 2007), over decades to centuries from continued thermokarst erosion of coastal permafrost in Eurasia (Shakhova *et al.,* 2005), and over centuries to millennia from the propagation of any warming 100–1,000 m down into permafrost hydrates (Harvey and Huang, 1995).

## 6. CHANGES IN METHANE EMISSIONS FROM NATURAL WETLANDS

### 6.1 Introduction

Natural wetlands are most extensive at high northern latitudes, where boreal and arctic wetlands contain substantial carbon in peat and are frequently associated with permafrost, and in the tropics, often associated with river and lake floodplains. Annual methane emissions from tropical wetlands are roughly twice that from boreal/arctic wetlands. Globally, wetlands are the largest single methane source to the atmosphere, with recent emission estimates ranging from 100 to 231 Tg $CH_4$ yr$^{-1}$ (Denman *et al.,* 2007), constituting more than 75% of the total estimated natural emissions. Variations in wetland distribution and saturation, in response to long-term variations in climate, are therefore thought to have been main determinants for variation in the atmospheric $CH_4$ concentration in the past (Chappellaz *et al.,* 1990; Chappellaz *et al.,* 1993a,b; Brook *et al.,* 1996, 2000; Delmotte *et al.,* 2004). Recent interannual variations in methane emissions have been dominated by fluctuations in wetland emissions (Bousquet *et al.,* 2006), although biomass burning also plays a significant role.

Thermokarst erosion release is the only known present terrestrial hydrate methane source.

Methane emissions from natural wetlands are sensitive to temperature and moisture (see below), and thus to climate variability and change. Emissions can also be influenced by anthropogenic activities that impact wetlands such as pollution loading (*e.g.,* Gauci *et al.,* 2004), land management (*e.g.,* Minkkinen *et al.,* 1997), and water management (*e.g.,* St. Louis *et al.,* 2000). While these anthropogenic impacts can be expected to change in the coming decades, they are unlikely to be a source of abrupt changes in methane emissions from natural wetlands, so this section will focus on climate change impacts.

Global climate-model projections suggest that the tropics, on average, and the northern high latitudes are likely to become warmer and wetter during the 21st century, with greater changes at high latitudes (Chapman and Walsh, 2007; Meehl *et al.,* 2007). Temperatures in the tropics by 2100 are projected to increase by 2–4 °C (Meehl *et al.,* 2007). Precipitation in the tropics is expected to increase in East Africa and Southeast Asia, show little change in West Africa and Amazonia, and decrease in Central America and northern South America (Meehl *et al.,* 2007).

Warming in the northern high latitudes in recent decades has been stronger than in the rest of the world (Serreze and Francis, 2006), and that trend is projected to continue, with multimodel projections indicating that arctic land areas could warm by between 3.5 and 8 °C by 2100 (Meehl *et al.,* 2007). The northern high latitudes are also expected to see an increase in precipitation by more than 20% in winter and by more than 10% in summer. Climate change of this magnitude is expected to have diverse impacts on the arctic climate system (Hassol, 2004), including the methane cycle. Principal among the projected impacts is that soil temperatures are expected to warm and permafrost, which is prevalent across much of the northern high latitudes, is expected to thaw and degrade. Permafrost thaw may alter the distribution of wetlands and lakes through soil subsidence and changes in local hydrological conditions. Since methane production responds positively to soil moisture and summer soil temperature, the projected strong warming and associated landscape changes expected in the northern high latitudes, coupled with the large carbon source (northern peatlands have ~250 GtC as peat within 1 to a few meters of the atmosphere; Turunen *et al.,* 2002), will likely lead to an increase in methane emissions over the coming century.

## 6.2 Factors Controlling Methane Emissions From Natural Wetlands

Methane is produced as a byproduct of microbial decomposition of organic matter under anaerobic conditions that are typical of saturated soils and wetlands. As this methane migrates from the saturated soil to the atmosphere (*via* molecular diffusion, ebullition (bubbling), or plant-mediated transport), it can be oxidized to carbon dioxide by microbial methanotrophs in oxygenated sediment or soil. In wetlands, a significant fraction of the methane produced is oxidized by methanotrophic bacteria before reaching the atmosphere (Reeburgh, 2004). If the rate of methanogenesis is greater than the rate of methanotrophy and pathways for methane to diffuse through the soil are available, then methane is emitted to the atmosphere. Dry systems, where methanotrophy exceeds methanogenesis, can act as weak sinks for atmospheric methane (see Table 5.1). Methane emissions are extremely variable in space and time, and therefore it is difficult to quantify regional-scale annual emissions (Bartlett and Harriss, 1993; Melack *et al.,* 2004). Recent reports of a large source (62–236 Tg $CH_4$ $yr^{-1}$) of methane from an aerobic process in plants (Keppler *et al.,* 2006) appear to be overstated (Dueck *et al.,* 2007; Wang *et al.,* 2008).

There are relatively few field studies of methane fluxes from tropical wetlands around the world, but work in the Amazon and Orinoco Basins of South America has shown that methane emissions appear to be most strongly controlled in aquatic habitats by inundation depth and vegetation cover (*e.g.,* flooded forest, floating macrophytes, open water) (Devol *et al.,* 1990; Bartlett and Harriss, 1993; Smith *et al.,* 2000; Melack *et al.,* 2004). Wet season (high water) fluxes are generally higher than dry season (low water) fluxes (Bartlett and Harriss, 1993).

At high latitudes, the most important factors influencing methane fluxes are water table depth, soil or peat temperature, substrate type and availability, and vegetation type (Fig. 5.13).

Water table depth determines both the fraction of the wetland soil or peat that is anaerobic and the distance from this zone of methane production to the atmosphere (*i.e.,* the length of the oxidation zone) and is often the single most important factor controlling emissions (Bubier *et al.,* 1995; Waddington *et al.,* 1996; MacDonald *et al.,* 1998). The strong sensitivity of $CH_4$ emissions to water table position suggests that changing hydrology of northern wetlands under climate change could drive large shifts in associated methane emissions.

Vegetation type controls plant litter tissue quality/decomposability, methanogen substrate input by root exudation (*e.g.,* King and Reeburgh, 2002), and the potential for plant-mediated transport of methane to the atmosphere (*e.g.,* King *et al.,* 1998; Joabsson and Christensen, 2001). Substrate type and quality, generally related to quantity of root exudation and to vegetation litter quality and degree of decomposition, can directly affect potential methane production. Vegetation productivity controls the amount of organic matter available for decomposition.

In wetland ecosystems, when the water table is near the surface and substantial methane emissions occur, the remaining controlling factors rise in relevance. Christensen *et al.* (2003) find that temperature and microbial substrate availability together explain almost 100% of the variations in mean annual $CH_4$ emissions across a range of sites across Greenland, Iceland, Scandinavia, and Siberia. Bubier *et al.* (1995) find a similarly strong dependence on soil temperature at a northern peatland complex in Canada. The observed strong relationship between $CH_4$ emissions and soil temperature reflects the exponential increase in microbial activity as soil temperatures warm. The strong warming expected across the northern high latitudes is likely to be a positive feedback on methane emissions.

The presence or absence of permafrost can also have a direct influence on $CH_4$ emissions. Across the northern high latitudes, permafrost features such as ice wedges, ice lenses, thermokarst, and ice heaving determine the surface microtopography. Small variations in surface topography have a strong bearing on plant community structure and evolution as well as soil hydrologic and nutritional conditions (Jorgenson *et al.,* 2001, 2006), all of which are controlling factors for methane emission. Projections of future methane emission are hampered by the difficulty of modeling landscape and watershed hydrology well enough at large scales to realistically represent small changes in wetland water table depth.

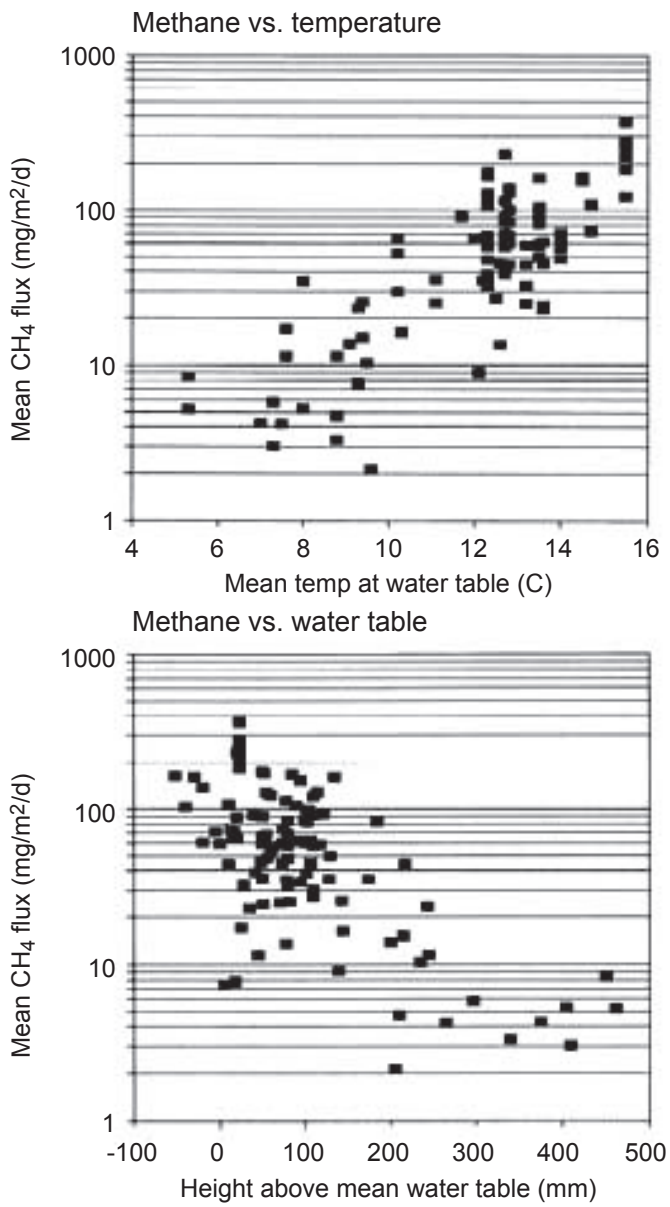



**Figure 5.13.** Relationships between water table height, temperature, and methane emissions for northern wetlands from Bubier *et al.* (1995). Abbreviations: mg/m²/d, milligrams per square meter per day; mm, millimeters; C, degrees Celsius.

## 6.3 Observed and Projected Changes in Natural Wetlands

### 6.3.1 Observed Changes in Arctic Wetlands and Lakes

Increased surface ponding and wetland formation have been observed in warming permafrost regions (Jorgenson *et al.,* 2001, 2006). These increases are driven primarily by permafrost-thaw-induced slumping and collapsing terrain features (thermokarst) that subsequently fill with water. For the Tanana Flats region in central Alaska, large-scale degradation of permafrost over the period 1949–95 is associated with substantial losses of birch forest and expansion of wetland fens (Jorgenson *et al.,* 2001).

In recent decades, lake area and the number of lakes in discontinuous permafrost regions have decreased in western Siberia (Smith *et al.,* 2005) and Alaska (Riordan *et al.,* 2006) but have increased in continuous permafrost regions in northwestern Siberia (Smith *et al.,* 2005). The differing trends in discontinuous and continuous permafrost zones can be understood if one considers that initial permafrost warming leads to development of thermokarst and lake and wetland expansion as the unfrozen water remains trapped near the surface by the icy soil beneath it. As the permafrost degrades more completely, lake or wetland drainage follows, as water more readily drains through the more ice-free soil to the ground-water system.

There is a considerable and growing body of evidence that soil temperatures are warming, active layer thickness (ALT) is increasing, and permafrost is degrading at unprecedented rates.

A strength of the Smith *et al.* (2005) study is that lake abundance is determined *via* satellite, permitting the study of thousands of lakes and evaluation of the net change across a broad area, which can in turn be attributed to regional driving mechanisms such as climate and permafrost degradation. A similar analysis for wetlands would be useful but is presently intractable because wetlands are not easy to pinpoint from satellite, as inundation, particularly in forested regions, cannot be easily mapped, and wetland-rich landscapes are often very spatially heterogeneous. (Frey and Smith, 2007).

Present-generation global climate or large-scale hydrologic models do not represent the thermokarst processes that appear likely to dictate large-scale changes in wetland extent over the coming century. However, wetland area can also respond to trends in precipitation minus evaporation (P–E). A positive P–E trend could lead, in the absence of large increases in runoff, to an expansion of wetland area and more saturated soil conditions, thereby increasing the area from which methane emission can occur. Most climate models predict that both arctic precipitation and evapotranspiration will rise during the 21st century if greenhouse gas concentrations in the atmosphere continue to rise. In at least one model, the NCAR CCSM3, the P–E trend is positive throughout the 21st century (Lawrence and Slater, 2005).

### 6.3.2 Observed and Projected Changes in Permafrost Conditions

There is a considerable and growing body of evidence that soil temperatures are warming, active layer thickness (ALT) is increasing, and permafrost is degrading at unprecedented rates (*e.g.,* Osterkamp and Romanovsky, 1999; Romanovsky *et al.,* 2002, Smith *et al.,* 2005; Osterkamp and Jorgenson, 2006). Continuous permafrost in Alaska, which has been stable over hundreds, or even thousands, of years, has suffered an abrupt increase in degradation since 1982 that "appears beyond normal rates of change in landscape evolution" (Jorgenson *et al.,* 2006). Similarly, discontinuous permafrost in Canada has shown a 200–300% increase in the rate of thawing over the 1995–2002 period relative to that of 1941–91 (Camill, 2005). Payette *et al.* (2004) present evidence of accelerated thawing of subarctic peatland permafrost over the last 50 years. An example of permafrost degradation and transition to wetlands in the Tanana Flats region of central Alaska is shown in Figure 5.14.

Model projections of soil temperature warming and permafrost degradation in response to the strong anticipated high-latitude warming vary considerably, although virtually all of them indicate that a significant amount of permafrost degradation will occur if the Arctic continues to warm (Anisimov and Nelson, 1997; Stendel and Christensen, 2002; Zhang *et al.,* 2003; Sazonova *et al.,* 2004). Buteau *et al.* (2004) find downward thawing rates of up to 13 cm $yr^{-1}$ in ice-rich permafrost for a 5 °C warming over 100 years. A collection of process-based

**Figure 5.14.** Transition from tundra (left, 1978) to wetlands (right, 1998) due to permafrost degradation over a period of 20 years (Jorgensen *et al.,* 2001). Photographs, taken from the same location in Tanana Flats in central Alaska, courtesy of NOAA (http://www.arctic.noaa.gov/detect/land-tundra.shtml).

models, both global and regional, all with varying degrees of completeness in terms of their representation of permafrost, indicates widespread large-scale degradation of permafrost (and by extension increased thermokarst development), sharply increasing ALTs, and a contraction of the area where permafrost can be found near the Earth's surface during the 21st century (Lawrence and Slater, 2005; Euskirchen *et al.,* 2006; Saito *et al.,* 2007; Zhang *et al.,* 2007; Lawrence *et al.,* 2008).

### 6.4 Observed and Modeled Sensitivity of Wetland Methane Emissions to Climate Change

Field studies indicate that methane emissions do indeed increase in response to soil warming and permafrost thaw. Christensen *et al.* (2003) note that a steady rise in soil temperature will enhance methane production from existing regions of methanogenesis that are characterized by water tables at or near the surface. While this aspect is important, changes in landscape-scale hydrology can cause significant change in methane emissions. For example, at a mire in subarctic Sweden, permafrost thaw and associated vegetation changes drove a 22–66% increase in $CH_4$ emissions over the period 1970 to 2000 (Christensen *et al.,* 2004). Bubier *et al.* (2005) estimated that in a Canadian boreal landscape with discontinuous permafrost and ~30% wetland coverage, methane fluxes increased by ~60% from a dry year to a wet year, due to changes in wetland water table depth, particularly at the beginning and end of the summer. Nykänen *et al.* (2003) also found higher methane fluxes during a wetter year at a subarctic mire in northern Finland. Walter *et al.* (2006) found that thawing permafrost along the margins of thaw lakes in eastern Siberia accounts for most of the methane released from the lakes. This emission, which occurs primarily through ebullition, is an order of magnitude larger where there has been recent permafrost thaw and thermokarst compared to where there has not. These hotspots have extremely high emission rates but account for only a small fraction of the total lake area. Methane released from these hotspots appears to be Pleistocene age, indicating that climate warming may be releasing old carbon stocks previously stored in permafrost (Walter *et al.,* 2006). At smaller scales, there is strong evidence that thermokarst development substantially increases $CH_4$ emissions from high-latitude ecosystems. Mean $CH_4$ emission rate increases between permafrost peatlands and collapse wetlands of 13-fold (Wickland *et al.,* 2006), 30-fold (Turetsky *et al.,* 2002), and up to 19-fold (Bubier *et al.,* 1995) have been reported.

A number of groups have attempted to predict changes in natural wetland methane emissions on a global scale. These studies broadly suggest that natural methane emissions from wetlands will rise as the world warms. Shindell *et al.* (2004) incorporate a linear parameterization for methane emissions, based on a detailed process model, into a global climate model and find that overall wetland methane emissions increased by 121 Tg $CH_4$ $y^{-1}$, 78% higher than their baseline estimate. They project a tripling of northern high-latitude methane emissions, and a 60% increase in tropical wetland methane emissions in a doubled $CO_2$ simulation. The increase is attributed to a rise in soil temperature in

## Box 5.3. High-Latitude Terrestrial Feedbacks

In recent decades, the Arctic has witnessed startling environmental change. The changes span many facets of the arctic system including rapidly decreasing sea-ice extent, melting glaciers, warming and degrading permafrost, increasing runoff to the Arctic Ocean, expanding shrub cover, and important changes to the carbon balance (Serreze *et al.,* 2000; Hassol, 2004; Hinzman *et al.,* 2005). The observed environmental trends are driven largely by temperatures that are increasing across the Arctic at roughly twice the rate of the rest of the world (Serreze and Francis, 2006). If the arctic warming continues and accelerates, as is predicted by all global climate models (Chapman and Walsh, 2007), it may invoke a number of feedbacks that have the potential to alter and possibly accelerate arctic *and* global climate change. If the feedbacks operate constructively, even relatively small changes in the Arctic could conspire to amplify global climate change. Continued environmental change, especially if it occurs rapidly, is likely to have adverse consequences for highly vulnerable arctic and global ecosystems and negative impacts on human activities, including costly damage to infrastructure, particularly in the Arctic.

The Arctic can influence global climate through both positive and negative feedbacks (Fig. 5.15). For example, sea-ice retreat reduces surface albedo, enhances absorption of solar radiation, and ultimately leads to greater pan-Arctic warming. Large-scale thawing of permafrost alters soil structural (thermokarst) and hydrologic properties (Jorgenson *et al.,* 2001) with additional effects on the spatial extent of lakes and wetlands (Smith *et al.,* 2005; Riordan *et al.,* 2006), runoff to the Arctic Ocean, ecosystem functioning (Jorgenson *et al.,* 2001; Payette *et al.,* 2004), and the surface energy balance. Warming is also expected to enhance decomposition of soil organic matter, releasing carbon to the atmosphere (a positive feedback) (Zimov *et al.,* 2006) and also releasing nitrogen which, in nutrient-limited arctic ecosystems, may prompt shrub growth (a negative feedback due to carbon sequestration) (Sturm *et al.,* 2001). This greening-of-the-Arctic negative feedback may itself be offset by a positive radiative feedback related to lower summer and especially winter albedos of shrubs and trees relative to tundra (Chapin *et al.,* 2005), which promotes an earlier spring snowmelt that among other things affects soil temperature and permafrost (Sturm *et al.,* 2001).

The future of the Arctic as a net sink or source of carbon to the atmosphere depends on the delicate balance between carbon losses through enhanced soil decomposition and carbon gains to the ecosystem related to the greening of the Arctic (McGuire *et al.,* 2006). Irrespective of the carbon balance, anticipated increases in methane emissions mean that the Arctic is likely to be an effective greenhouse gas source (Friborg *et al.,* 2003; McGuire *et al.,* 2006).

The Arctic is a complex and interwoven system. On the basis of recent evidence of change, it appears that many of these processes are already operating. Whether or not the positive or negative feedbacks will dominate is a critical question facing climate science. In a recent paper reviewing the integrated regional changes in arctic climate feedbacks, McGuire *et al.* (2006) conclude that the balance of evidence indicates that the positive feedbacks to global warming will likely dominate over the next century, but their relationship to global climate change remains difficult to predict, especially since much of the research to date has considered these feedbacks in isolation.

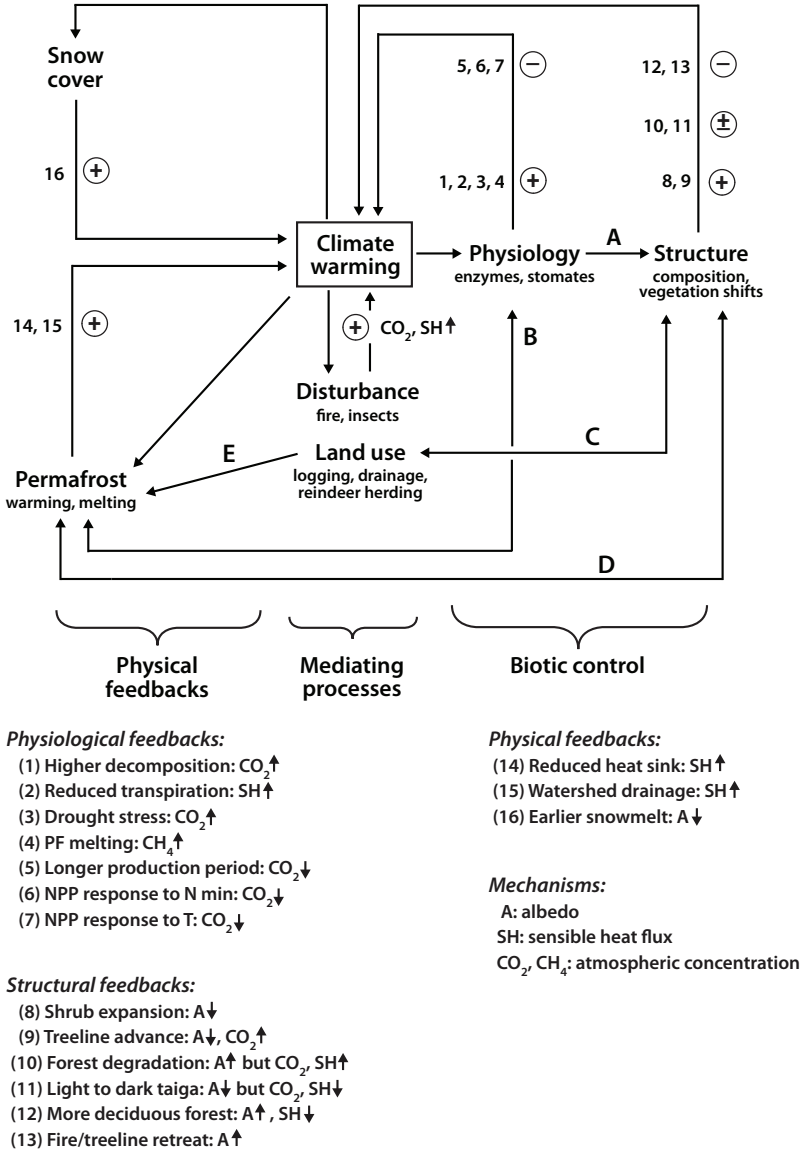



**Figure 5.15.** Terrestrial responses to warming in the Arctic that influence the climate system. Responses of permafrost on the left are coupled with functional (physiological) and structural biotic responses on the right either directly (arrows B and D) or through mediating processes of disturbance and land use (arrows C and E). Functional and structural biotic responses are also coupled (arrow A). Physical responses will generally result in positive feedbacks. In general, functional responses of terrestrial ecosystems act as either positive or negative feedbacks to the climate system. In contrast, most of the structural responses to warming are ambiguous because they result in both positive and negative feedbacks to the climate system. Abbreviation: NPP, net primary production. Figure adapted from McGuire *et al.* (2006).

combination with wetland expansion driven by a positive P–E trend predicted by the model. About 80% of the increase was due to enhanced flux rates, and 20% due to expanded wetland area or duration of inundation. The predicted increase in the atmospheric methane burden was 1,000 Tg, ~20% of the current total, equivalent to an increase of ~430 ppb, assuming a methane lifetime of 8.9 years. Utilizing a similar approach but with different climate and emission models, Gedney *et al.* (2004) project that global wetland emissions (including rice paddies) will roughly double, despite a slight reduction in wetland area. The northern wetland methane emissions, in particular, increase by 100% (44 to 84 Tg $CH_4$ $yr^{-1}$) in response to increasing soil temperatures and in spite of a simulated 10% reduction in northern wetland areal extent. Using a more process-based ecosystem model, which includes parameterizations for methane production and emission, Zhuang *et al.* (2007) model a doubling of methane emissions over the 21st century in Alaska, once again primarily in response to the soil temperature influence on methanogenesis, and secondarily to an increase in net primary productivity of Alaskan ecosystems. These factors outweigh a negative contribution to methane emissions related to a simulated drop in the water table. It is important to note that these models simulate only

the direct impacts of climate change (altered temperature and moisture regimes, and in one case enhanced vegetation productivity) but not indirect impacts, such as changing landscape hydrology with permafrost degradation and changing vegetation distribution. At this time, it is not known whether direct or indirect effects will have a stronger impact on net methane emissions. These models all predict fairly smooth increases in annual wetland emissions, with no abrupt shifts in flux.

### 6.5 Conclusion About Potential for Abrupt Release of Methane From Wetlands

Tropical wetlands are a stronger methane source than boreal and arctic wetlands and will likely continue to be over the next century, during which fluxes from both regions are expected to increase. However, four factors differentiate northern wetlands from tropical wetlands and make them more likely to experience a larger increase in fluxes: (1) high-latitude amplification of climatic warming will lead to a stronger temperature impact, (2) for regions with permafrost, warming-induced permafrost degradation could make more organic matter available for decomposition and substantially change the system hydrology, (3) the sensitivity of microbial respiration to temperature generally decreases with increasing temperatures (*e.g.,* Davidson and Janssens, 2006), and (4) most northern wetlands have substantial carbon as peat. On the other hand, two characteristics of northern peatlands counter this: (1) northern peatlands are complex, adaptive ecosystems, with internal feedbacks and self-organizing structure (Belyea and Baird, 2007) that allow them to persist in a relatively stable state for millennia and that may reduce their sensitivity to hydrological change, and (2) much of the organic matter in peat is well-decomposed (*e.g.,* Frolking *et al.,* 2001) and may not be good substrate for methanogens.

The balance of evidence suggests that anticipated changes to northern wetlands in response to large-scale permafrost degradation, thermokarst development, a positive P–E trend in combination with substantial soil warming, enhanced vegetation productivity, and an abundant source of organic matter will likely conspire to drive a chronic increase in $CH_4$ emissions from the northern latitudes during the 21st century. Due to the strong interrelationships between temperature, moisture, permafrost, and nutrient and vegetation change, and the fact that negative feedbacks such as the draining and drying of wetlands are also possible, it is difficult to establish how large the increase will be over the coming century. Current models suggest that a doubling of $CH_4$ emissions from northern wetlands could be realized fairly easily. However, since these models do not realistically represent all the processes thought to be relevant to future northern high-latitude $CH_4$ emissions, much larger (or smaller) increases cannot be discounted.

It is worth noting that our understanding of the northern high-latitude methane cycle continues to evolve. For example, a recent field study suggests that prior estimates of methane emissions from northern landscapes may be biased low due to an underestimation of the contribution of ebullition from thermokarst hot spots in Siberian thaw lakes (Walter *et al.,* 2006). Another recently discovered phenomenon is the cold adaptation of some methanogenic microorganisms that have been found in permafrost deposits in the Lena River basin (Wagner *et al.,* 2007). These microbes can produce methane even in the very cold conditions of permafrost, often drawing on old soil organic matter. The activity levels of these cold-adapted methanogens are sensitive to temperature, and even a modest soil warming can lead to an accumulation of methane deposits which, under scenarios where permafrost degradation leads to thermokarst or coastal erosion, could be quickly released to the atmosphere.

These recent studies highlight the fact that key uncertainties remain in our understanding of natural methane emissions from wetlands and their susceptibility to climate change as well as in our ability to predict future emissions. Among the most important uncertainties in our understanding and required improvements to process-based models are (1) the contribution of ebullition and changes in ebullition to total methane emissions; (2) the rate of change in permafrost distribution and active layer thickness and associated changes in distribution of wetlands and lakes as well as, more generally, terrestrial ecosystems; (3) model representation of soil thermal and hydrologic processes and their response to climate change; (4) the contribution that shifts in vegetation and changes in peatland functioning will have on the methane cycle; and (5) representation of the highly variable and regionally specific methane production and emission characteristics. Even with resolution of these issues, all predictions of future methane emissions are based on the accurate simulation and prediction of high-latitude climate. Improvements of many aspects of modeling the high-latitude climate system are required, including improvements to the treatment of snow, polar clouds, subsoil processes, subpolar oceans, and sea ice in global climate models.

## 7. FINAL PERSPECTIVES

Although the prospect of a catastrophic release of methane to the atmosphere as a result of anthropogenic climate change over the next century appears very unlikely based on current knowledge, many of the processes involved are still poorly understood, and developing a better predictive capability requires further work. On a longer time scale, methane release from hydrate reservoirs is likely to be a major influence in global warming over the next 1,000 to 100,000 years. Changes in climate, including warmer temperatures and more precipitation in some regions, will likely increase the chronic emissions of methane from both melting hydrates and natural wetlands over the next century. The magnitude of this effect cannot be predicted with great accuracy yet, but is likely to be equivalent to the current magnitude of many anthropogenic methane sources, which have already more than doubled the levels of methane in the atmosphere since the start of the Industrial Revolution.