Chapter 5. Potential for Abrupt Changes in Atmospheric Methane

Lead Author: Edward Brook,* Oregon State University, Corvallis
Contributing Authors: David Archer, University of Chicago
Ed Dlugokencky, NOAA Earth System Research Laboratory, Boulder, CO
Steve Frolking, University of New Hampshire, Durham
David Lawrence, NCAR, Boulder

---

*SAP 3.4 FACA Committee Member

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 emissions from northern high-latitude and tropical wetlands.

- The size of the 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 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 source sector.

- Observations show that there have not yet been significant increases in methane emissions from northern high-latitude hydrates and wetlands resulting from increasing Arctic temperatures.

- While catastrophic release of methane to the atmosphere appears very unlikely, 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.

Recommendations

- Monitoring the abundance of atmospheric methane and its isotopic composition should be maintained and expanded to allow detection of change in net emissions from northern and tropical wetland regions. Specifically, systematic measurements of CH_4 from tall towers and aircraft in the Arctic and sub-Arctic regions would allow detection of changes in emissions from these sparsely monitored but important regions. For the tropics, expanded surface measurements and continued observations of CH_4 abundances are required.

- 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 sub-surface 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. This 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 development of high-resolution proxies of low-latitude climate and better records of pre-Last Glacial Maximum wetlands are also needed.

1. Background: Why Are Abrupt Changes in Methane a Potential Concern?

1.1 Introduction

Methane (CH_4) is the most important greenhouse gas that humans directly influence, after CO_2. 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 be 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 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) (*MacFarlane-Meure et al., 2006; Etheridge et al., 1998*) 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 = 0.001Gt, 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*).

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 1775 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 because of changing climate (*Fiore et al., 2006*). Despite attempts to explain this surprising observation, 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.

1.3 The Modern Methane Budget

The largest individual term in the global methane budget is removal (removal terms are referred to as "sinks") 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 IPCC Fourth Assessment Report *(Forster et al., 2007)*, the globally averaged OH concentration is $\sim 10^6$ 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 NOAA (National Oceanic and Atmospheric Administration) Earth System Research Laboratory (ESRL) global observations of CH_4 and its trend gives average emissions of 556±10 teragrams (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.

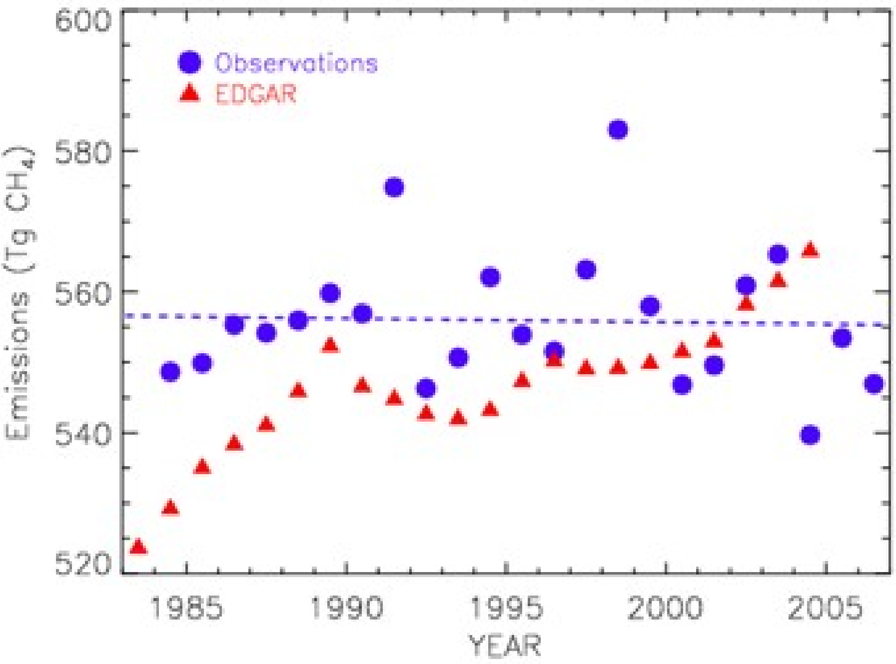


Figure 5.1. Methane emissions as function of time calculated with constant lifetime; emissions from EDGAR inventory with constant natural emissions shown as red triangles. EDGAR is Emission Database for Global Atmospheric Research (described in *Olivier and Berdowski, 2001*); 2001 to 2004 emissions are preliminary (source: http://www.milieuennatuurcompendium.nl/indicatoren/nl0167-Broeikasgasemissies%2C-mondiaal.html?i=9-20).

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 1-box model is shown in Fig. 5.1 and 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 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 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.

Figure 5.2. Global network of monitoring sites (blue dots) for long-term observation of atmospheric methane as of this date (http://gaw.kishou.go.jp/wdcgg/).

1.5 Abrupt Changes in Atmospheric Methane?

Concern about abrupt changes in atmospheric methane stems largely from the massive 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 below). The total amount of carbon in the modern atmosphere 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.

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 Fig. 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 stability zone thickness 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. Source: http://geology.usgs.gov/connections/mms/joint_projects/methane.htm.

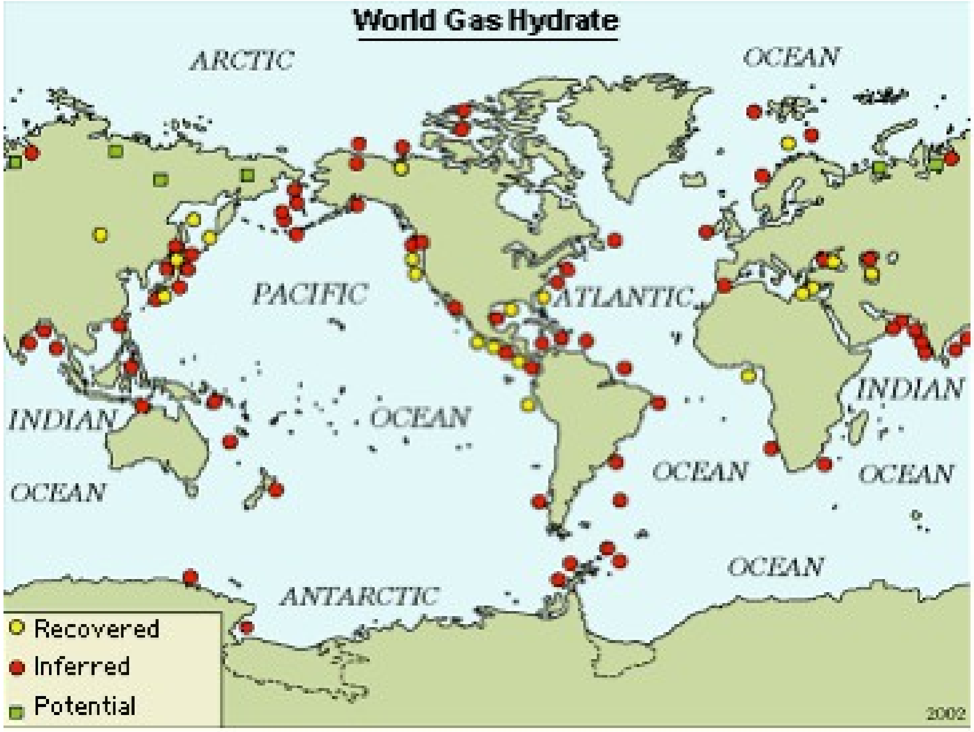


Figure 5.4. Map of methane hydrate deposit locations. Source: http://geology.usgs.gov/connections/mms/joint_projects/methane.htm.

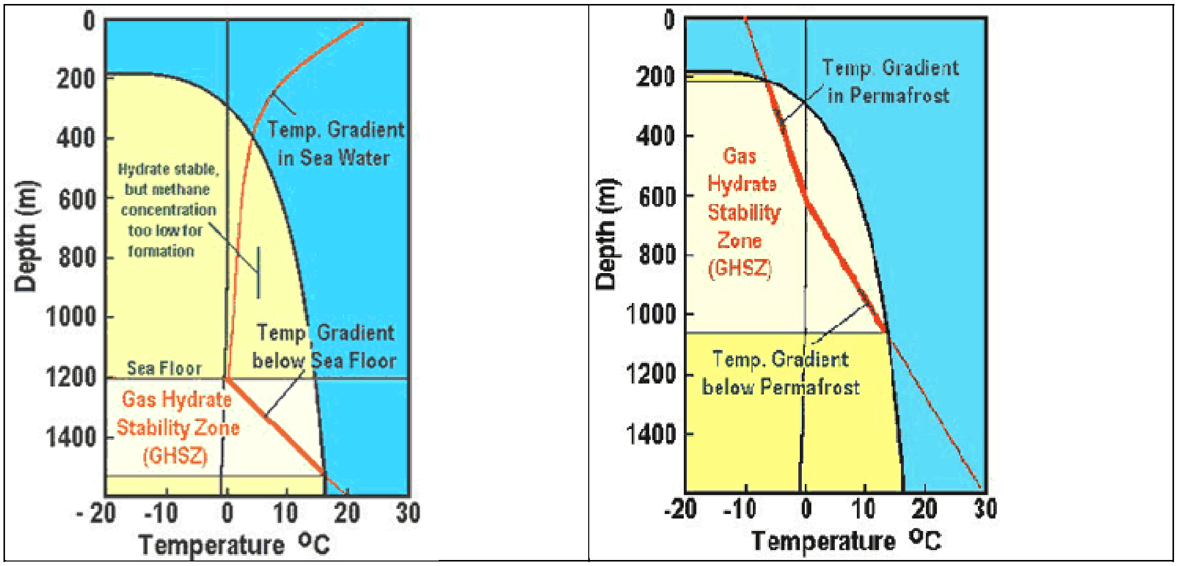


Figure 5.5. Schematic diagram of hydrate stability zone for typical continental margin (left) and permafrost (right) settings. The red line shows the temperature gradient with depth. The hydrate stability zone is technically the depth interval where the in situ temperature is lower than the temperature 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).

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 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

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 650,000 years (*Spahni et al., 2005*). There are no direct constraints on methane levels beyond 800,000 years, the age at the bottom of the oldest ice core now available (European Project for Ice Coring in Antarctica (EPICA) Dome C ice core). New international plans to drill at a very low accumulation rate site in Antarctica may in the future extend the record to 1.5 million years (*Brook and Wolff, 2005*).

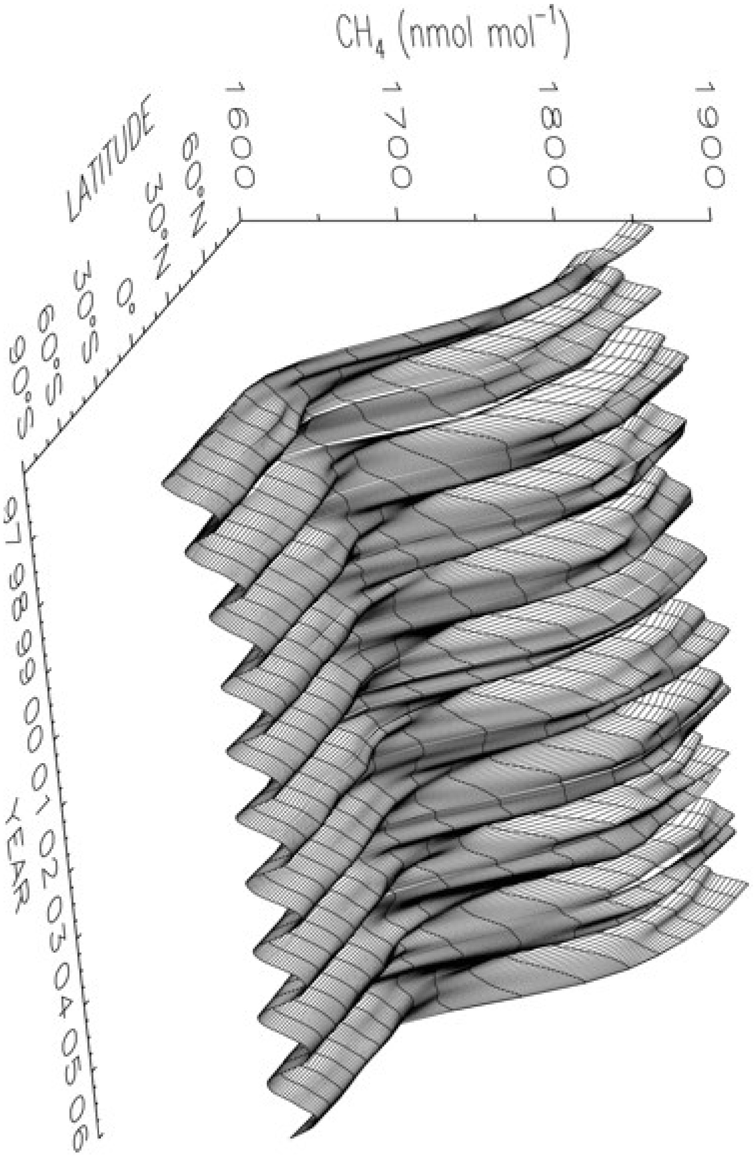

CH_4 (nmol mol^{-1})
1600
1700
1800
1900
LATITUDE
60°N
30°N
0°
30°S
60°S
90°S
97
98
99
00
01
02
03
04
05
06
YEAR

Fig. 5.6A

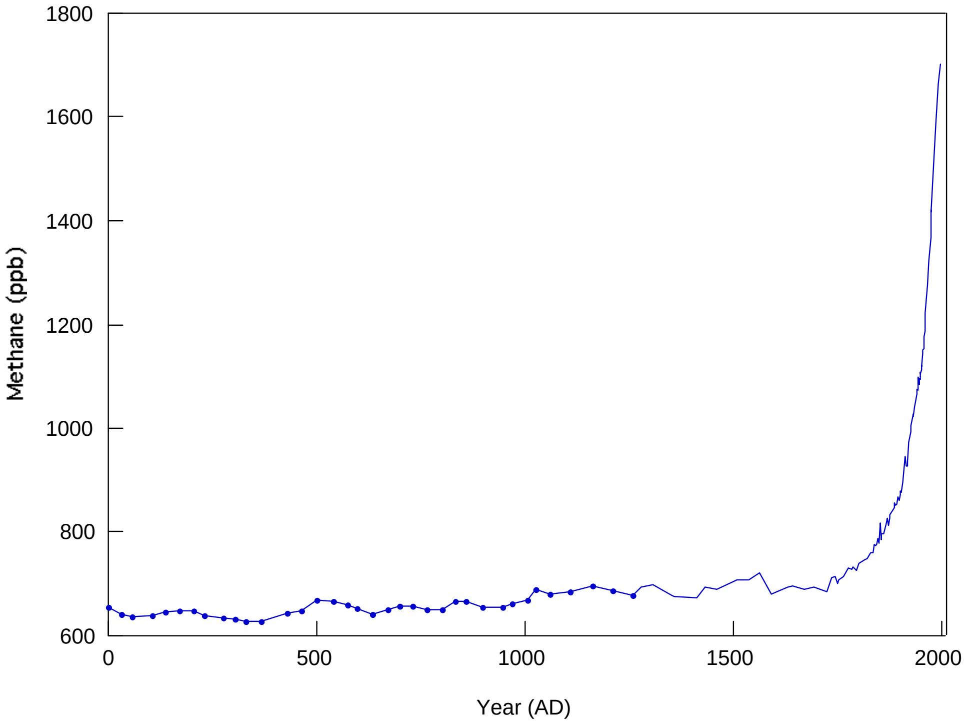


Fig. 5.6B

1

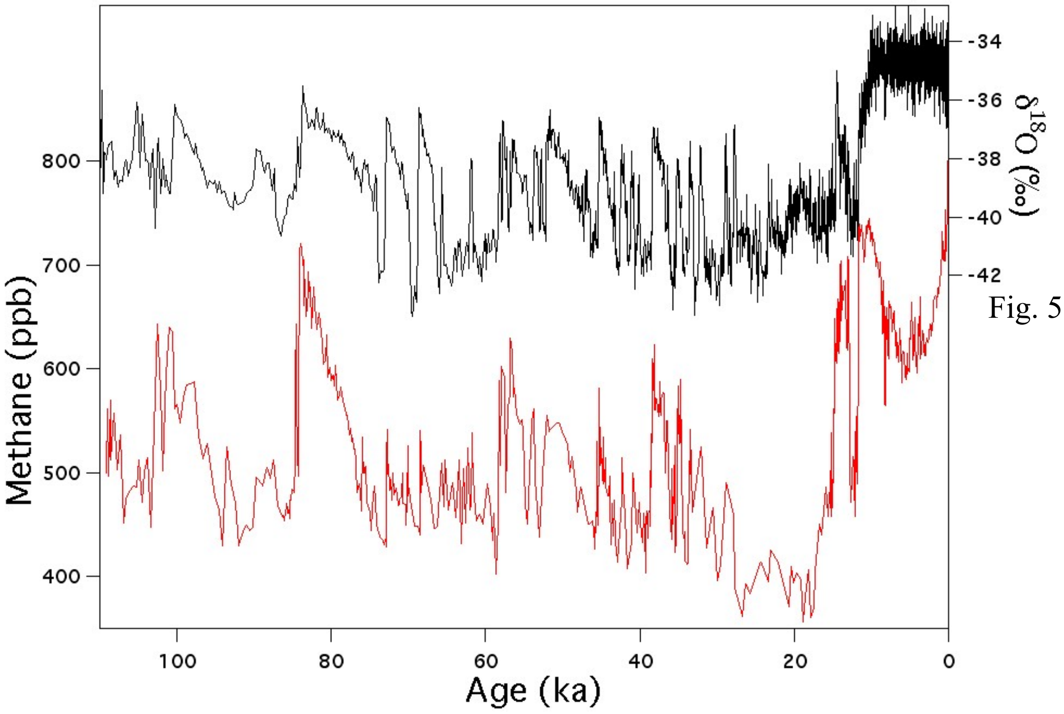


Fig. 5.6C

2

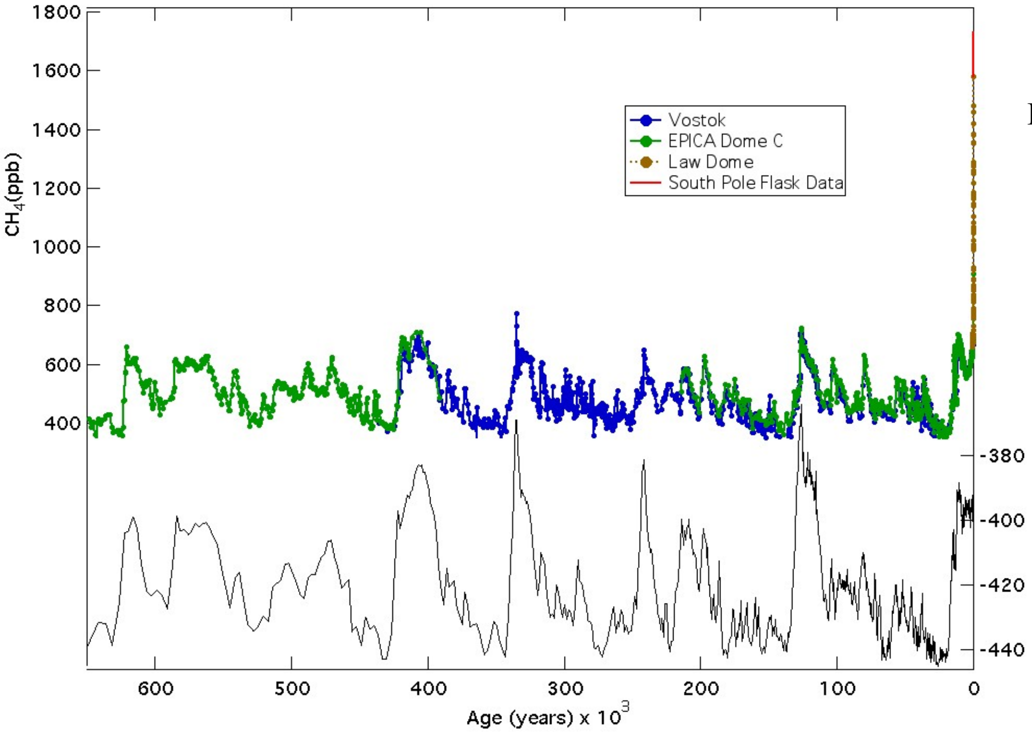


Fig 5.6D

Figure 5.6. The history of atmospheric methane 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 1,000 years from ice cores and direct measurements (*MacFarling-Meure et al., 2006*) and NOAA ESRL data. C. The last 100,000 years of methane history from the Greenland Ice Sheet Project 2 (GISP2) ice core in Greenland. $\delta^{18}O$ 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. A composite of ice core data from the Vostok and EPICA Dome C ice cores for the last 650,000 years from *Spahni et al. (2005)* with additional data from *MacFarling-Meure et al. (2006)* and NOAA ESRL. δD is a temperature proxy. Abbreviations: nmol mol^{-1}, nanomoles per mole; ppb, parts per billion by mole (same as nanomoles per mole); ‰, per mil.

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 Mt. 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 observations (*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.

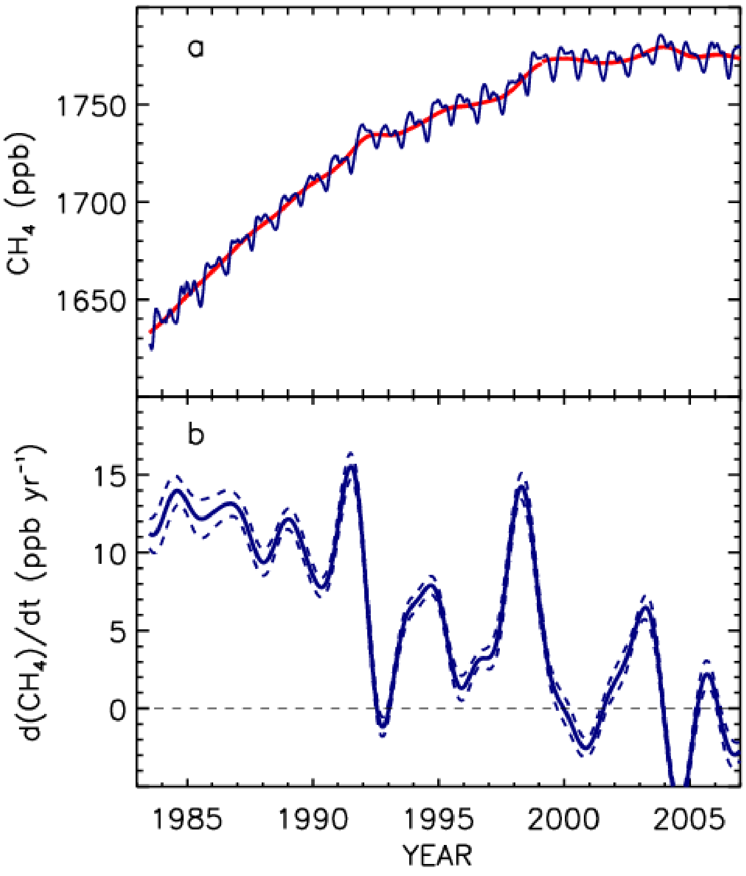


Figure 5.7. Recent trends in atmospheric methane from global monitoring data (NOAA ESRL). A, Global average atmospheric methane mixing ratios (blue line) determined using measurements from the ESRL cooperative air sampling network. The red line represents the long-term trend. B, Solid line is the instantaneous 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*).

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 be 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).*

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*). 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*). 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 tropics and subtropics was closely linked to abrupt warming in Greenland (e.g., *Kelly et al., 2006; Wang et al., 2004; Yuan et al., 2004; Dykoski et al., 2005; Peterson et al.,* *2000*). 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 isotopic 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 appear to have 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 *(Kaplan et al., 2002; 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; von 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., *Valdes et al., 2005; Kaplan et al., 2002; 2006; Chappellaz et al., 1993b; von Huissteten, 2004*). *von 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). *Von 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 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 circum-Arctic 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 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 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 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.

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 extents 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; Blunier and Brook, 2001; Chappellaz et al., 1997; Severinghaus et al. 1998; Severinghaus and Brook, 1999; Huber et al. 2006; EPICA Members, 2006).*

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 close off all at the same depth, so there is additional mixing of air with 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 obtain a smoothing function for the Greenland Ice Core Project (GRIP) ice core in Greenland for the late Holocene, which has a Gaussian shape with width at half-height of about 20 years. This result is consistent with previous work by *Brook et al. (2000)* for the Greenland Ice Sheet Project (GISP2) ice core. They examined the impact of smoothing on abrupt changes in methane in the Greenland ice core record. (GISP2 and GRIP are in similar glaciological environments and their firn characteristics are very similar.) *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 record 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).

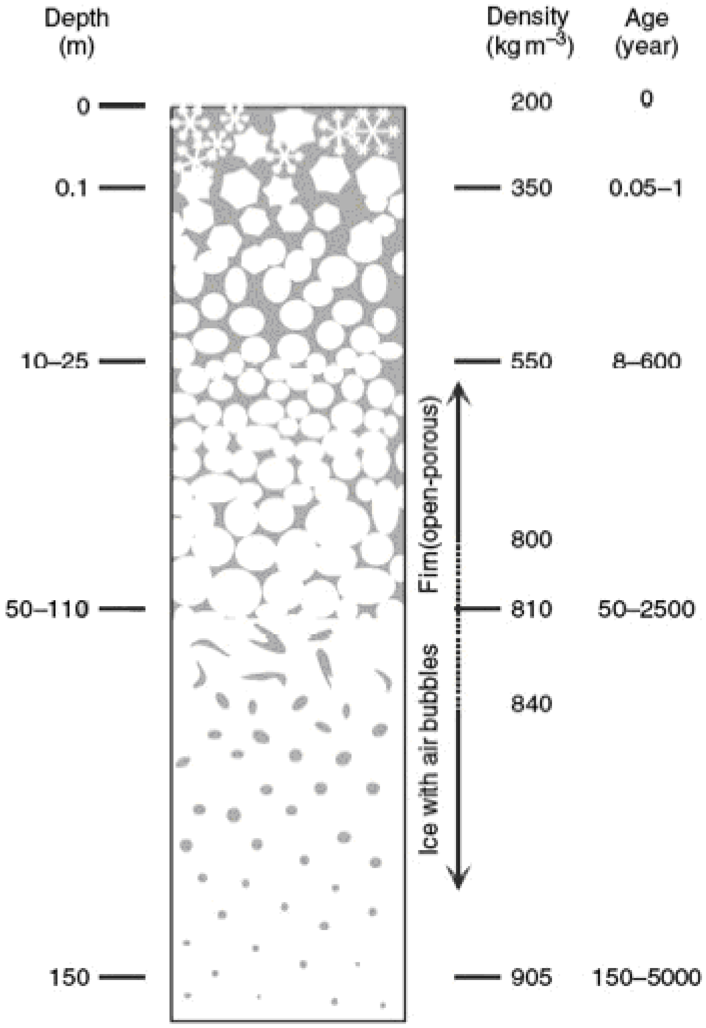


Figure 5.8. The firn column of a typical site on a polar ice sheet, from *Schwander (2006)*. Abbreviations: m, meter; kg m^{-3}, kilograms per cubic meter.

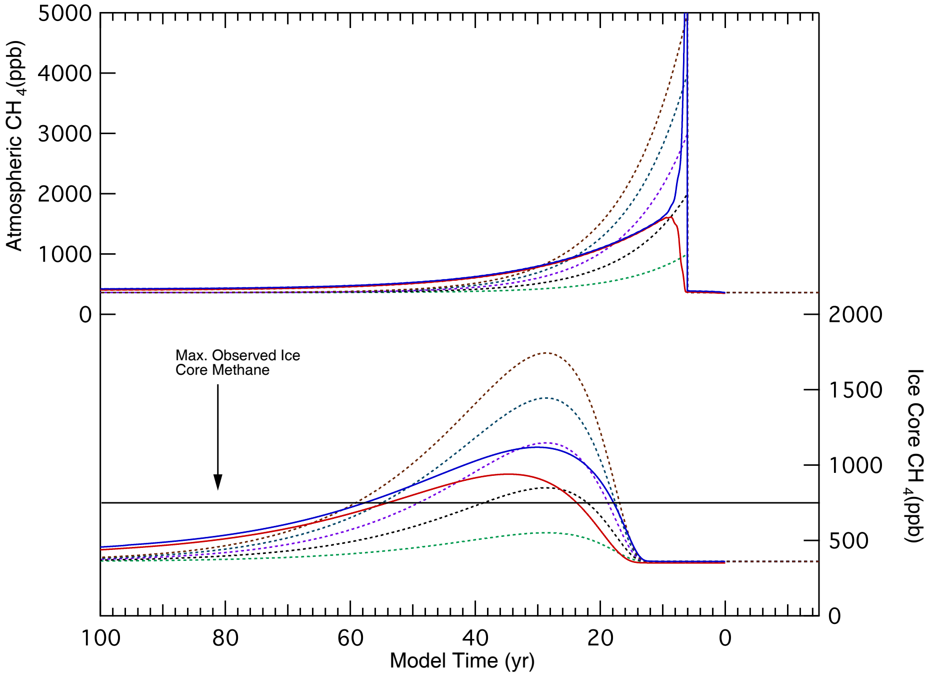


Figure 5.9. Model simulations of smoothing instantaneous release of methane from clathrates to the atmosphere, and the ice core response to those events. The ice core response was calculated by convolving the atmospheric histories in the top panel with a smoothing function appropriate for the GISP2 ice 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. (2006)*. 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).

3. Potential Mechanisms for Future Abrupt Changes in Atmospheric Methane

Three categories of mechanism 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 Sections 4-6 discuss these mechanisms in more detail.

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.

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 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 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 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

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.

There is a differential-pressure mechanism which 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 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; Zuhlsdorff et al., 2000; Zuhlsdorff 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 which 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 1GtC 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.

The Gulf of Mexico 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 they 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. In the Community Climate System Model (CCSM) under doubled CO_2 (after 80 years of 1%/year CO_2 increase, from C. Bitz, personal commun., 2007), waters at 500 m depth in the Gulf warm about 0.75°C, and 0.2° at 1,000 m. In situ temperatures at 500 m are much closer to the hydrate melting temperature, so the relative change in the saturation state is much more significant at 500 m than deeper. 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. *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.

Other examples of structural deposits include the summit of Hydrate Ridge, off the coast of Oregon, USA (*Torres et al., 2004; Trehu 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 (*Trehu et al., 2004a*). *Trehu 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 (*Nouze 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 in 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 (*Shakhova et al., 2005; Washburn et al., 2005; Xu et al., 2001*) or during time 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 potential way to deliver methane 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, bubble 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 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 Slide 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 seismic bottom simulating reflector (BSR) (*Bunz and Mienert, 2004; Mienert et al., 2005; Zillmer et al., 2005a, b*) corresponding to the base of the hydrate stability zone 200-300 m, and pockmarks (*Hovland et al., 2005*) indicating gas expulsion from the sediment.

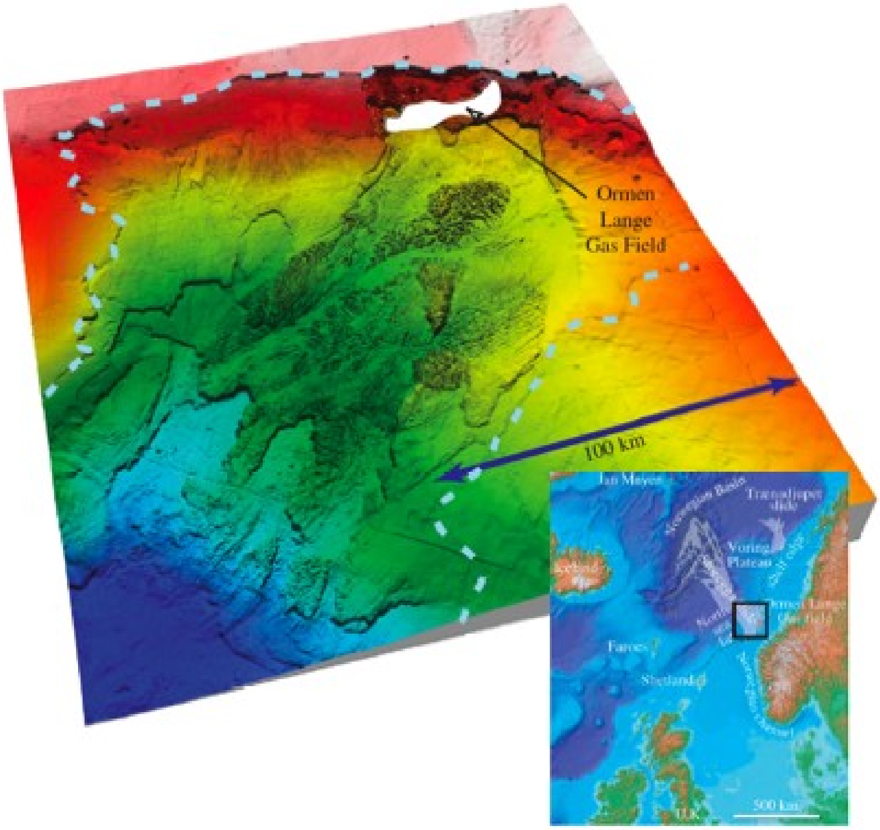


Figure 5.10. Image and map of the Storegga Landslide from *Masson et al. (2006)*. The slide excavated on average the top 250 m of sediment over a swath hundreds of kilometers wide. Colors indicate water depth, with yellow-orange indicating shallow water, and green-blue indicating deeper water.

The slide was presumably triggered by 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, should 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 ~2200 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 Mt. Pinatubo eruption (-2 W/m^2), but it would last for 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 been triggered by freshwater release to the North Atlantic. However, ice cores record a 75 pbb 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.

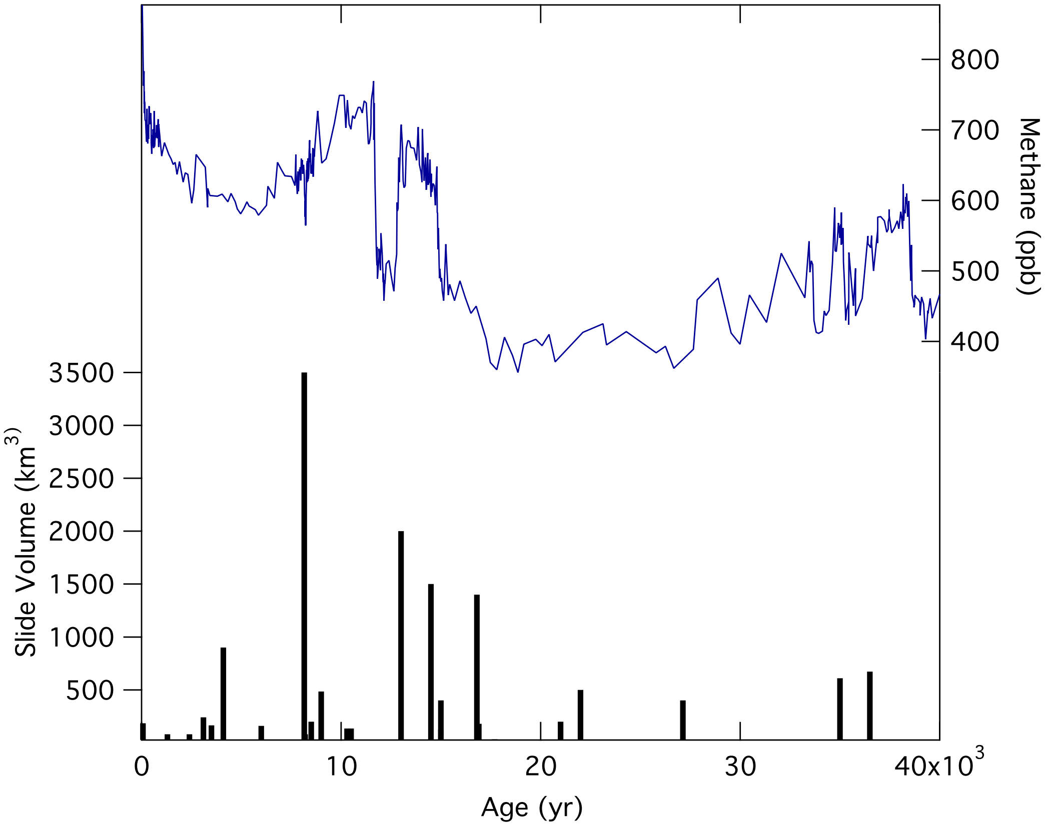


Figure 5.11. Timing of submarine landslides in the North Atlantic region and pre-industrial ice core methane variations. Landslide data from *Maslin et al. (2004)*. Methane data from *Brook et al. (2000)* and *Kobashi et al. (2007)*. Abbreviations: km^3, cubic kilometers; yr, year; ppb, parts per billion.

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 1to 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 δ^{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 do, suggesting that the carbon spike invaded the deep ocean from the atmosphere (*Thomas et al., 2002*). Similar events, also associated with transient warmings, although less well documented, 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.

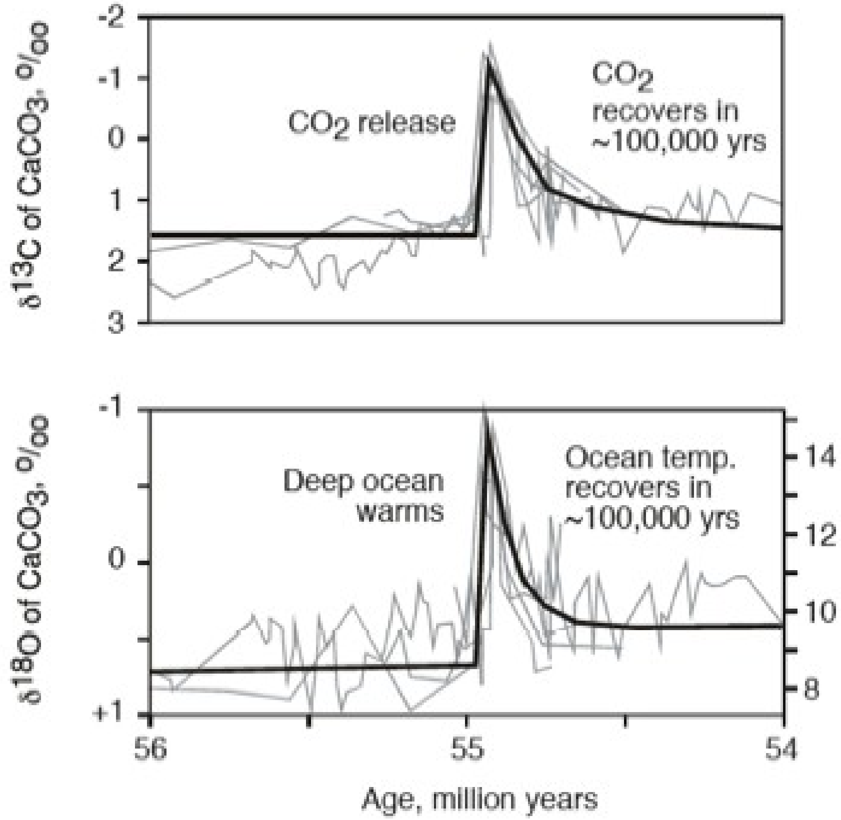


Figure 5.12. Carbon (top) and oxygen (bottom) isotope record for benthic foraminifera from sites in the south Atlantic and western Pacific Oceans for the Paleocene-Eocene Thermal Maximum (PETM), from *Zachos et al. (2001)*, modified by *Archer (2007)*. ‰, per mil.

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 corresponds in time with the PETM. However, 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*). However, these events tend to take millions of years to play out (*Dickens et al., 1995*). *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*). 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 Gt 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 possibility 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 possibility 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 (*Dallenbach 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 or 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 Quantity of Methane Potentially Released

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.

4.3.2 Climate Impact of Potential Release

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 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 during 1970-2000 *(Kvenvolden, 2000),* and the fraction of terrestrial methane hydrate that is or will be technically and economically recoverable is not well established. In the U.S., 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, 2005, 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 (*Shakova et al., 2005*). Methane hydrates associated with this permafrost become destabilized through this process, and methane is released into the coastal waters (*Shakova 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 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 Terrestrial Hydrate Methane Release

No direct evidence has been identified of past terrestrial hydrate methane release in significant quantities. Analyses related to the PETM and clathrate gun hypothesis discussed in Sec. 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 2500% 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 *(Shakova 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. Thermoskarst 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, 2004*), 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 (*Shakova 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 have 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.

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*).

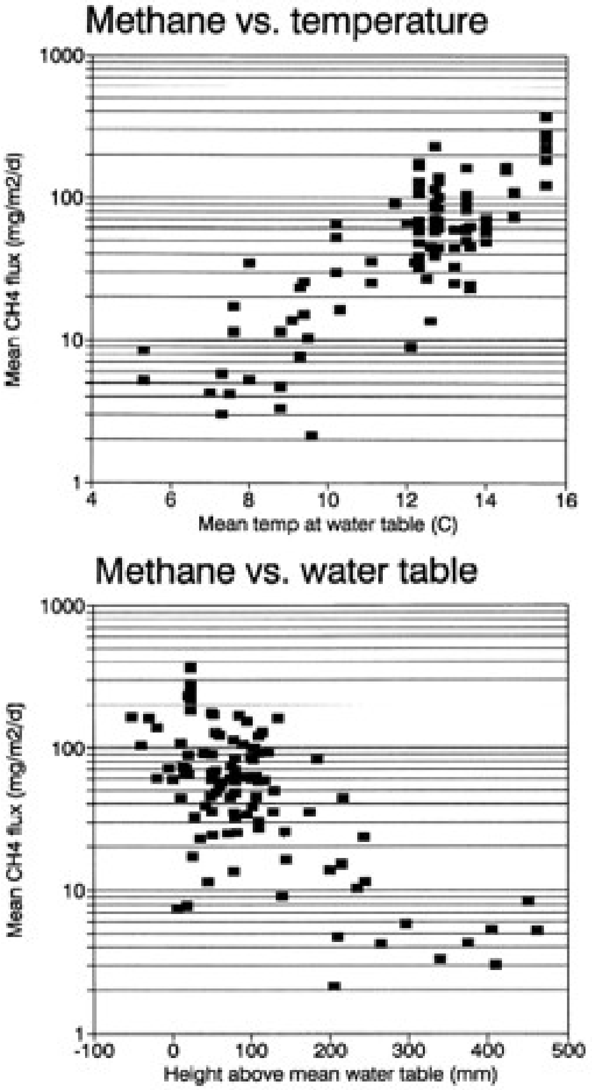
Warming in the northern high latitudes in recent decades has been stronger than in the rest of the world (*Serreze and Francis, 2006*), and that trend is projected to continue, with multimodel projections indicating that Arctic land areas could warm by between 3.5° and 8°C by 2100 (*Meehl et al., 2007*). 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 (*ACIA, 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 in overstated (*Dueck et al., 2007; Wang et al., 2008*).

There have not been many field studies measuring 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/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.


Methane vs. temperature

Methane vs. water table

Figure 5.13. Relationships between water table height, temperature, and methane emissions for northern wetlands from *Bubier et al. (1995)*. Abbreviations: mg/m^2/d, milligrams per square meter per day; mm, millimeters; C, degrees Celsius.

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/watershed hydrology well enough at large scales to realistically represent small changes in wetland water table depth.

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 count 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.

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.

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*). Photos, taken from the same location in Tanana Flats in central Alaska, obtained from http://www.arctic.noaa.gov/detect/land-tundra.shtml.

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^{o}C warming over 100 years. A collection of process-based 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; Lawrence et al., 2007; Saito et al., 2007; Zhang et al., 2007*).

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; ACIA, 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, particularly in the Arctic, including costly damage to infrastructure and marginalization of many Arctic communities.

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 feedbacks 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 whether or not the myriad feedbacks will interact to significantly amplify (or mitigate) global climate change remains difficult to predict, especially since much of the research to date has considered these feedbacks in isolation.

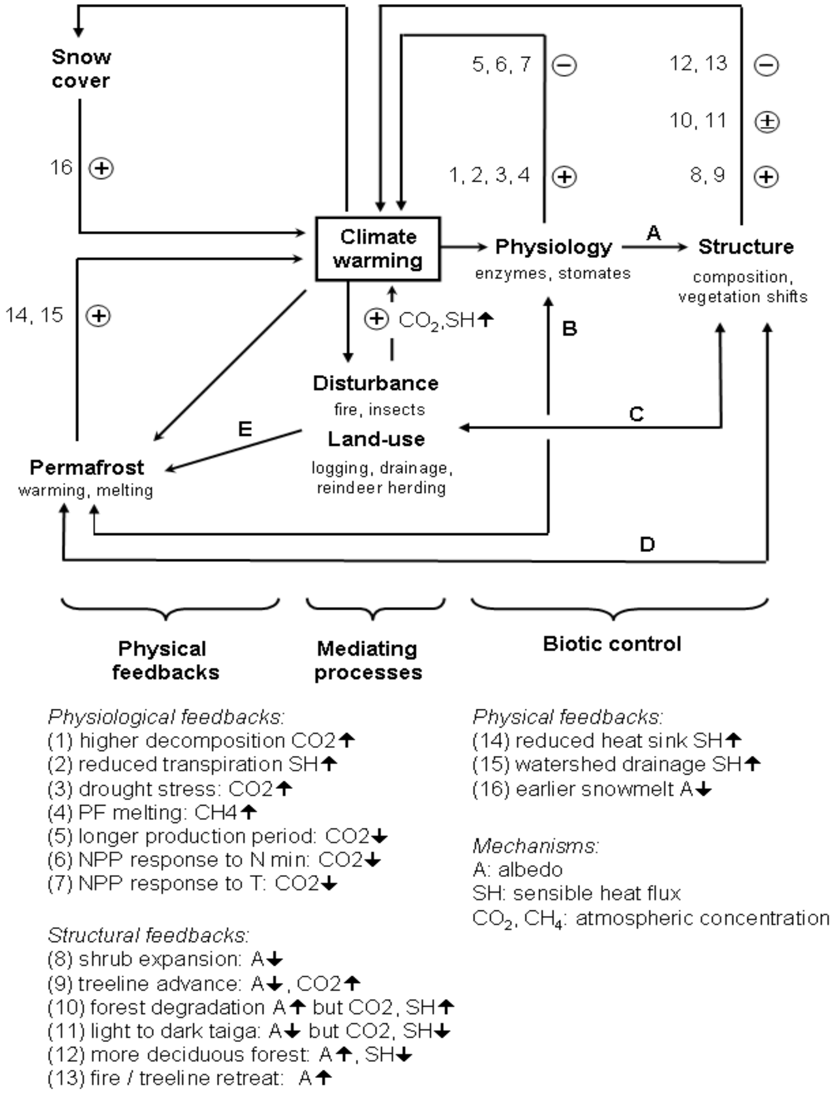


Figure 5.15. Terrestrial responses to warming in the Arctic that influence the climate system. Responses of permafrost on the left are coupled with functional (physiological) and structural biotic responses on the right either directly (arrows B and D) or through mediating processes of disturbance and land use (arrows C and E). Functional and structural biotic responses are also coupled (arrow A). Response pathways are identified at three timescales (seconds to months, months to years, and years to decades). 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)*.

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 have the ability to drive a more significant change in methane emissions. For example, at a mire in sub-Arctic Sweden, permafrost degradation and associated vegetation changes have driven a 22-66% increase in landscape-scale 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, landscape-scale 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 sub-Arctic mire in northern Finland. *Walter et al. (2006)* find 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 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/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/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 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 interesting recently discovered phenomena 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 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 facets critical to the high-latitude climate system are required, including improvements to the treatment of snow, polar clouds, subsoil processes, sub-polar 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 reservoir is likely to be a major player in global warming over the next 1,000-100,000 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 sources, which have already more than doubled the levels of methane in the atmosphere since the start of the Industrial Revolution.

References

ACIA, 2004: Impacts of a warming Arctic: Arctic climate impact assessment. Cambridge University Press, 144 pp.

Alley, R.B., and A.M. Agustsdottir, 2005: The 8k event: cause and consequences of a major Holocene abrupt climate change. *Quaternary Science Reviews*, **24(10-11)**, 1123-1149.

Anisimov, O.A., and F.E. Nelson, 1997: Permafrost zonation and climate change in the northern hemisphere: Results from transient general circulation models. *Clim. Change*, **35**, 241-258.

Aoki, Y., S. Shimizu, T. Yamane, T. Tanaka, K. Nakayama, T. Hayashi, and Y. Okuda, 2000: Methane hydrate accumulation along the western Nankai Trough. *Gas Hydrates: Challenges for the Future*, 136-145.

Archer, D., 2005: Fate of fossil-fuel CO_2 in geologic time. *J. Geophysical Res. Oceans*, doi:10.1029/2004JC002625.

Archer, D., 2007: Methane hydrate stability and anthropogenic climate change. *Biogeosciences*, **4**, 521–544,.

Archer, D.E., and B. Buffett, 2005:Time-dependent response of the global ocean clathrate reservoir to climatic and anthropogenic forcing. *Geochem., Geophys., Geosys.*, **6(3)**, doi: 10.1029/2004GC000854.

Archer, D., H. Kheshgi, and E. Maier-Riemer, 1997: Multiple timescales for neutralization of fossil fuel CO_2. *Geophys. Res. Letters*, **24**, 405-408.

Archer, D., P. Martin, B. Buffett, V. Brovkin, S. Rahmstorf, and A. Ganopolski, 2004: The importance of ocean temperature to global biogeochemistry. *Earth and Planetary Science Letters*, **222**, 333-348.

Bartlett K.B., and R.C. Harriss, 1993: Review and assessment of methane emissions from wetlands. *Chemosphere*, **26**, 261-320.

Belyea L.R., and A.J. Baird, 2007: Beyond “the limits to peat bog growth”: Cross-scale feedback in peatland development. *Ecol. Mongr.*, **76**, 299–322.

Bergamaschi, P., et al., 2007: Satellite chartography of atmospheric methane from SCIAMACHY on board ENVISAT: 2. Evaluation based on inverse model simulations. *J. Geophys. Res.*, **112**, D02304, doi:10.1029/2006JD007268.

Berner, R.A., A.C. Lasaga, and R.M. Garrels, 1983: The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.*, **283**, 641-683.

Blake, D.R., and F.S. Rowland, 1988: Continuing worldwide increase in tropospheric methane, 1978-1987. *Science*, **239**, 1129-1131.

Blunier, T., and E.J. Brook, 2001: Timing of millennial-scale climate change in Antarctica and Greenland during the last glacial period. *Science*, **291**, 109-112.

Boswell, R., 2005: Changing perspectives on the resource potential of methane hydrates. In: Fire in the Ice, newsletter of the U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, summer http://www.netl.doe.gov/technologies/oil-gas/publications/Hydrates/Newsletter/.

Boswell, R., 2007: Resource potential of methane hydrate coming into focus. *J. Petrol. Sci. Engin.*, **56**, 9-13.

Boudreau, B.P., C. Algar, B.D. Johnson, I. Croudace, A. Reed, Y. Furukawa, K.M. Dorgan, P.A. Jumars, A.S. Grader, and B.S. Gardiner, 2005: Bubble growth and rise in soft sediments. *Geology*, **33(6)**, 517-520.

Bousquet, P., P. Ciais, J.B. Miller, E.J. Dlugokencky, D.A. Hauglustaine, C. Prigent, G.R. Van der Werf, P. Peylin, E.G. Brunke, C. Carouge, R.L. Langenfelds, J. Lathiere, F. Papa, M. Ramonet, M. Schmidt, L.P. Steele, S.C. Tyler, and J. White, 2006: Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature*, **443,** 439-443.

Bowen, G.J., D.J. Beerling, P.L. Koch, J.C. Zachos, and T. Quattlebaum, 2004: A humid climate state during the Palaeocene/Eocene thermal maximum. *Nature*, **432(7016)**, 495-499.

Bralower, T.J., D.J. Thomas, J.C. Zachos, M.M. Hirschmann, U. Rohl, H. Sigurdsson, E. Thomas, and D.L. Whitney, 1997: High-resolution records of the late Paleocene thermal maximum and circum-Caribbean volcanism: Is there a causal link? *Geology*, **25(11)**, 963-966.

Brewer, P.G., C. Paull, E.T. Peltzer, W. Ussler, G. Rehder, and G. Friederich, 2002: Measurements of the fate of gas hydrates during transit through the ocean water column. *Geophysical Research Letters*, **29(22)**.

Brook, E., and E. Wolff, 2005: The future of ice core science. *Eos*, **87**, 39.

Brook, E.J., S. Harder, J.P. Severinghaus, E. Steig, and C. Sucher, 2000: On the origin and timing of rapid changes in atmospheric methane during the last glacial period. *Global Biogeochemical Cycles*, **14**, 559-572.

Brook, E.J., T. Sowers, and J. Orchardo, 1996: Rapid variations in atmospheric methane concentration during the past 110 ka. *Science*, **273**, 1087-1091.

Brook, E., J.W.C. White, A. Schilla, M. Bender, B.A. Barnett, J. Serveringhaus, K.C. Taylor, R.B. Alley, and E.J. Steig, 2005: Timing of millennial-scale climate change at Siple Dome, West Antarctica, during the last glacial period. *Quaternary Science Reviews*, **24**, 1333-1343.

Brooks, J.M., W.R. Bryant, B.B. Bernard, and N.R. Cameron, 2000: The nature of gas hydrates on the Nigerian continental slope. *Gas Hydrates: Challenges for the Future*, 76-93.

Bryn, P., K. Berg, C.F. Forsberg, A. Solheim, and T.J. Kvalstad, 2005: Explaining the Storegga slide. *Marine and Petroleum Geology*, **22(1-2)**, 11-19.

Bubier, J.L., T.R. Moore, L. Bellisario, N.T. Comer, and P.M. Crill, 1995: Ecological Controls on Methane Emissions from a Northern Peatland Complex in the Zone of Discontinuous Permafrost, Manitoba, Canada. *Glob. Biogeochem. Cyc.*, **9,** 455-470.

Bubier JL, T.R. Moore, K. Savage, and P. Crill, 2005: A comparison of methane flux in a boreal landscape between a dry and a wet year. *Global Biogeochemical Cycles*, **19**, GB1023, doi:10.1029/2004GB002351.

Buffett, B., and D.E. Archer, 2004: Global inventory of methane clathrate: Sensitivity to changes in environmental conditions. *Earth and Planetary Science Letters*, **227**, 185-199.

Bunz, S., and J. Mienert, 2004: Acoustic imaging of gas hydrate and free gas at the Storegga slide. *Journal of Geophysical Research-Solid Earth*, **109(B4)**.

Buteau, S., R. Fortier, G. Delisle, and M. Allard. 2004: Numerical simulation of the impacts of climate warming on a permafrost mound. *Permafr. Periglac. Proc.*, **15,** 41-57.

Camill, P, 2005: Permafrost thaw accelerates in boreal peatlands during late-20th century climate warming. *Clim. Change*, **68,** 135-152.

Cannariato, K.G., and L.D. Stott, 2004: Evidence against clathrate-derived methane release to Santa Barbara Basin surface waters? *Geochemistry Geophysics Geosystems*, **5**.

Chapin, F.S., M. Sturm, M.C. Serreze, J.P. McFadden, J.R. Key, A.H. Lloyd, A.D. McGuire, T.S. Rupp, A.H. Lynch, J.P. Schimel, J. Beringer, W.L. Chapman, H.E. Epstein, L.D. Euskirchen, L.D. Hinzman, G. Jia, C.L. Ping, K.D. Tape, C.D.C. Thompson, D.A. Walker, and J.M. Welker, 2005: Role of land-surface changes in arctic summer warming. *Science*, doi:10.1126/science.1117368.

Chapman, W.L., and J.E. Walsh, 2007: Simulations of Arctic temperature and pressure by global coupled models. *J. Clim.*, **20,** 609-632.

Chappellaz, J., J.M. Barnola, D. Raynaud, Y.S. Korotkevich, and C. Lorius, 1990: Ice-core record of atmospheric methane over the past 160,000 years. *Nature*, **345**, 127-131.

Chappellaz, J., T. Blunier, S. Kints, A. Dällenbach, J-M. Barnola, J. Schwander, D. Raynaud, and B. Stauffer, 1997: Changes in the atmospheric CH_4 gradient between Greenland and Antarctica during the Holocene. *Journal of Geophysical Research*, **102**, 15987-15997.

Chappellaz, J., T. Blunier, D. Raynaud, J.M. Barnola, J. Schwander, and B. Stauffer, 1993a: Synchronous changes in atmospheric CH_4 and Greenland climate between 40 and 8 kyr BP. *Nature*, **366**, 443- 445.

Chappellaz, J.A., I.Y. Fung, and A.M. Thompson, 1993b: The atmospheric CH_4 increase since the Last Glacial Maximum (1). Source estimates. *Tellus*, **45B(3)**, 228-241.

Christensen, T.R., A. Ekberg, L. Strom, M. Mastepanov, N. Panikov, O. Mats, B.H. Svensson, H. Nykanen, P.J. Martikainen, and H. Oskarsson, 2003: Factors controlling large scale variations in methane emissions from wetlands. *Geophys. Res. Lett.*, **30(7)**, 1414, doi:10.1029/2002GL016848

Christensen, T.R., T.R. Johansson, H.J. Akerman, M. Mastepanov, N. Malmer, T. Friborg, P. Crill, and B.H. Svensson, 2004: Thawing sub-arctic permafrost: Effects on vegetation and methane emissions. *Geophys. Res. Lett.*, **31**, L04501, doi:10.1029/2003GL018680.

Christensen, T.R., I.C. Prentice, J. Kaplan, A. Haxeltine, and S. Sitch, 1996: Methane flux from northern wetlands and tundra: an ecosystem modeling approach. *Tellus*, **48B**, 652-661.

Collett T.S., and G.D. Ginsburg, 1998: Gas hydrates in the Messoyakha Gas Field of the West Siberian Basin—A re-examination of the geologic evidence. *Int. J. Offshore and Polar Engineering*, **8**, 22-29.

Collett, T.S., and V.A. Kuuskraa, 1998: Hydrates contain vast store of world gas resources. *Oil and Gas Journal*, **96**, 90-95.

Dallenbach, A., T. Blunier, J. Fluckiger, B. Stauffer, J. Chappellaz, and D. Raynoud, 2000: Changes in the atmospheric CH_4 gradient between Greenland and Antarctica during the Last Glacial and the transition to the Holocene. *Geophys. Res. Lett.*, **27**, 1005-1008.

Dansgaard, W., J.W.C. White, and S.J. Johnson. 1989. The abrupt termination of the Younger Dryas climate event. *Nature*, **339**, 532-534.

Davidson, EA, and I.A. Jannssens, 2006: Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, **440**, 165-173.

De Batist M, J. Klerkx, P. Van Rensbergen, M. Vanneste, J. Poort, A.Y. Golmshtok, A.A. Kremlev, O.M. Khlystov, and P. Krinitsky, 2002: Active hydrate destabilization in Lake Baikal, Siberia? *Terra Nova*, **14**, 436-442.

Delmotte, M., J. Chappellaz, E. Brook, P. Yiou, J.M. Barnola, C. Goujon, D. Raynaud, and V. I. Lipenkov, 2004: Atmospheric methane during the last four glacial-interglacial cycles: Rapid changes and their link with Antarctic temperature. *Journal of Geophysical Research*, **109**, D12104, doi:10.1029/2003JD004417.

Denman, K.L., G. Brasseur, A. Chidthaisong, P. Ciais, P.M. Cox, R.E. Dickinson, D. Hauglustaine, C. Heinze, E. Holland, D. Jacob, U. Lohmann, S Ramachandran, P.L. da Silva Dias, S.C. Wofsy and X. Zhang, 2007: Couplings between changes in the climate system and biogeochemistry. *In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom, and New York.

Devol, A.H., J.E. Richey, B.R. Forsberg, and L.A. Martinelli, 1990: Seasonal dynamics in methane emissions from the Amazon River floodplain to the troposphere. *J. Geophys. Res.*, **95**, 16417-16426.

D'Hondt, S., B.B. Jorgensen, D.J. Miller, A. Batzke, R. Blake, B.A. Cragg, H. Cypionka, G.R. Dickens, T. Ferdelman, K.U. Hinrichs, N.G. Holm, R. Mitterer, A. Spivack, G.Z. Wang, B. Bekins, B. Engelen, K. Ford, G. Gettemy, S.D. Rutherford, H. Sass, C.G. Skilbeck, I.W. Aiello, G. Guerin, C.H. House, F. Inagaki, P. Meister, T. Naehr, S. Niitsuma, R.J. Parkes, A. Schippers, D.C. Smith, A. Teske, J. Wiegel, C.N. Padilla, and J.L.S. Acosta, 2004: Distributions of microbial activities in deep subseafloor sediments. *Science*, **306(5705)**, 2216-2221.

Dickens, G.R., 2001a: Modeling the global carbon cycle with a gas hydrate capacitor: significance for the latest Paleocene thermal maximum. In: *Natural Gas Hydrates*. [Paull, C.K., and W.P. Dillon (eds.)]. American Geophysical Union *Occurrence, Distribution, and Detection, Geophysical Monographs*, **124**, 19-38.

Dickens, G.R., 2001b: On the fate of past gas: what happens to methane released from a bacterially mediated gas hydrate capacitor? *Geochem. Geophys. Geosyst.*, **2**, 2000GC000131.

Dickens, G.R., 2001c: The potential volume of oceanic methane hydrates with variable external conditions. *Org. Geochem.*, **32**, 1179-1193.

Dickens, G.R., J.R. O'Heill, D.K. Rea, and R.M, 1995: Owens, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, **19**, 965-971.

Dimitrov, L., and J. Woodside, 2003: Deep sea pockmark environments in the eastern Mediterranean. *Marine Geology*, **195(1-4)**, 263-276.

Dlugokencky, E.J., E.G. Dutton, P.C. Novelli, P.P. Tans, K.A. Masarie, K.O. Lantz, and S. Madronich, 1996: Changes in CH_4 and CO growth rates after the eruption of Mt Pinatubo and their link with changes in tropical tropospheric UV flux. *Geophys. Res. Lett.*, **23(20)**, 2761-2764.

Dlugokencky, E.J., K.A. Masarie, P.M. Lang, and P.P. Tans, 1998: Continuing decline in the growth rate of the atmospheric methane burden. *Nature*, **393**, 447-450.

Dlugokencky, E.J., S. Houweling, L. Bruhwiler, K.A. Masarie, P.M. Lang, J.B. Miller, and P.P. Tans, 2003: Atmospheric methane levels off: Temporary pause or a new steady state? *Geophys. Res. Lett.*, **30(19)**, doi:10.1029/2003GL018126..

Dobrynin, V.M., Y.P. Korotajev, and D.V. Plyuschev, 1981: Gas hydrates: A possible energy resource. [Meyer, R.F., and J.C. Olson (eds.)]. *Long Term Energy Resources*, v. I, Pitman, Boston, 727-729.

Driscoll, N.W., J.K. Weissel, and J.A. Goff, 2000: Potential for large-scale submarine slope failure and tsunami generation along the US mid-Atlantic coast. *Geology*, **28(5)**, 407-410.

Dueck, T., et al., 2007: No evidence for substantial aerobic methane emission by terrestrial plants: A ^{13}C-labelling approach. *New Phytologist*, doi: 10.1111/j.1469-8137.2007.02103.x.

Dugan, B., and P.B. Flemings, 2000: Overpressure and fluid flow in the New Jersey continental slope: Implications for slope failure and cold seeps. *Science*, **289**, 288-291.

Dykoski, C.A., R.L. Edwards, H. Cheng, D.X. Yuan, Y.J. Cai, M.L. Zhang, Y.S. Lin, Z.S. An, and J. Revenaugh, 2005: A high resolution, absolute-dated Holocene and deglacial Asian monsoon record from Dongge Cave, China. *Earth Planet. Sci. Lett.*, **233**, 71-86.

EPICA Community Members, 2006: One-to-one coupling of glacial climate variability in Greenland and Antarctica. *Nature*, **444**, doi:10.1038/nature05301.

Etheridge, D.M., L.P. Steele, R.J. Francey, and R.L. Langenfelds, 1998: Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions and climatic variability. *J. Geophys. Res.*, **103**, 15979-15993.

Euskirchen, E.S., A.D. McGuire, D.W. Kicklighter, Q. Zhuang, J.S. Clein, R.J. Dargaville, D.G. Dye, J.S. Kimball, K.C. McDonald, J.M. Melillo, V.E. Romanovsky, and N.V. Smith, 2006: Importance of recent shifts in soil thermal dynamics on growing season length, productivity, and carbon sequestration in terrestrial high-latitude ecosystems. *Glob. Change Biol.*, **12**, 731-750.

Fiore A.M., L.W. Horowitz, E.J. Dlugokencky, and J.J. West, 2006: Impact of meteorology and emissions on methane trends, 1990\u20132004. *Geophys. Res. Lett.*, **33**, L12809, doi:10.1029/2006GL026199.

Flemings, B.P., X. Liu, and W.J. Winters, 2003: Critical pressure and multiphase flow in Blake Ridge gas hydrates. *Geology*, **31**, 1057-1060.

Forster, P., V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, J. Nganga, R. Prinn, G. Raga, M. Schulz and R. Van Dorland, 2007: Changes in atmospheric constituents and in radiative forcing. *In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom, and New York.

Flückiger, J., T. Blunier, B. Stauffer, J. Chappellaz, R. Spahni, K. Kawamura, J. Schwander, T.F. Stocker, and D. Dahl-Jensen, 2004: N_2O and CH_4 variations during the last glacial epoch: Insight into global processes. *Glob. Biogeochem. Cycles*, **18(1)**, GB1020, doi:10.1029/2003GB002122.

Frankenberg, C., J.F. Meirink, P. Bergamaschi, A.P.H. Goede, M. Heimann, S. Körner, U. Platt, M. van Weele, and T. Wagner, 2006: Satellite chartography of atmospheric methane from SCIAMACHY on board ENVISAT: Analysis of the years 2003 and 2004. *J. Geophys. Res.*, **111**, D07303, doi:10.1029/2005JD006235.

Frey, K.E., and L.C. Smith, 2007: How well do we know northern land cover? Comparison of four global vegetation and wetland products with a new ground-truth database for West Siberia. *Glob. Biogeochem. Cyc.*, **21**, GB1016, doi:10.1029/2006GB002706.

Friborg, T., H. Soegaard, T.R. Christensen, C.R. Lloyd, and N.S. Panikov, 2003: Siberian wetlands: Where a sink is a source. *Geophys. Res. Lett.*, **30**.

Frolking S, N.T. Roulet, T.R. Moore, P.J.H. Richard, M. Lavoie, and S.D. Muller, 2001: Modeling northern peatland decomposition and peat accumulation. *Ecosystems*, **4**, 479-498.

Gardiner, B.S., B.P. Boudreau, and B.D. Johnson, 2003: Growth of disk-shaped bubbles in sediments, *Geochimica et Cosmochimica Acta*, **67(8)**, 1485-1494.

Gauci,V., E. Matthews, N. Dise, B. Walter, D. Koch, G. Granberg, and M. Vile, 2004: Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries. *Proc. Nat. Acad. Sci.*, **101**, 12583-12587.

Gedney, N., P.M. Cox, and C. Huntingford, 2004: Climate feedback from wetland methane emissions. *Geophys. Res. Lett.*, **31**, L20503, doi:10.1029/2004GL020919.

Gorman, A.R., W.S. Holbrook, M.J. Hornbach, K.L. Hackwith, D. Lizarralde, and I. Pecher, 2002: Migration of methane gas through the hydrate stability zone in a low-flux hydrate province. *Geology*, **30(4)**, 327-330.

Grachev A.M., E.J. Brook, and J.P. Severinghaus, 2007: Abrupt changes in atmospheric methane at the MIS 5b-5a transition. *Geophys. Res. Lett.*, **34**, L20703, doi:10.1029/2007GL029799.

Grant, N.J., and M.J. Whiticar, 2002: Stable carbon isotopic evidence for methane oxidation in plumes above Hydrate Ridge, Cascadia Oregon margin. *Global Biogeochemical Cycles*, **16(4)**, 1124.

Hampton, M.A., H.J. Lee, and J. Locat, 1996: Submarine landslides. *Reviews of Geophysics*, **34(1)**, 33-59.

Hansen, J., and M. Sato, 2001: Trends of measured climate forcing agents. *Proc. Natl. Acad. Sci.*, **98**, 14778-14783, doi:10.1073/pnas.261553698.

Hansen, J., M. Sato, R. Ruedy, A. Lacis, and V. Oinas, 2000: Global warming in the twenty-first century: An alternative scenario. *Proc. Natl. Acad. Sci.*, **97**, 9875-9880, doi:10.1073/pnas.170278997.

Hansen, J., and M. Sato, 2001: Trends of measured climate forcing agents. *Proc. Natl. Acad. Sci.*, **98**, 14778-14783, doi:10.1073/pnas.261553698.

Harvey, L.D.D., and Z. Huang, 1995: Evaluation of the potential impact of methane clathrate destabilization on future global warming. *J. Geophysical Res.*, **100**, 2905-2926.

Heeschen, K.U., R.W. Collier, M.A. de Angelis, E. Suess, G. Rehder, P. Linke, and G.P. Klinkhammer, 2005: Methane sources, distributions, and fluxes from cold vent sites at Hydrate Ridge, Cascadia margin. *Global Biogeochemical Cycles*, **19(2)**.

Heeschen, K.U., A.M. Trehu, R.W. Collier, E. Suess, and G. Rehder, 2003: Distribution and height of methane bubble plumes on the Cascadia margin characterized by acoustic imaging. *Geophysical Research Letters*, **30(12)**.

Hesselbo, S.P., D.R. Grocke, H.C. Jenkyns, C.J. Bjerrum, P. Farrimond, H.S.M. Bell, and O.R. Green, 2000: Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature*, **406(6794)**, 392-395.

Hill, J.C., N.W. Driscoll, J.K. Weissel, and J.A. Goff, 2004: Large-scale elongated gas blowouts along the US Atlantic margin. *Journal of Geophysical Research-Solid Earth*, **109(B9)**.

Hill, T.M., J.P. Kennett, D.L. Valentine, Z. Yang, C.M. Reddy, R.K. Nelson, R.J. Behl, C. Robert, and L. Beaufort, 2006: Climatically driven emissions of hydrocarbons from marine sediments during deglaciation. *Proc. Natl. Acad. Sci.*, **103**, 13570-13574.

Hinrichs K.-U., J.M. Hayes, S.P. Sylva, P.G. Brewer, and E.F. Delong. 1999: Methane-consuming archaebacteria in marine sediments. *Nature*, **398**, 802-805.

Hinrichs, K.U., L.R. Hmelo, and S.P. Sylva, 2003: Molecular fossil record of elevated methane levels in late pleistocene coastal waters. *Science*, *299(5610)*, 1214-1217.

Hinzman, L.D., N.D. Bettez, W.R. Bolton, F.S. Chapin, M.B. Dyurgerov, C.L. Fastie, B. Griffith, R.D. Hollister, A. Hope, H P. Huntington, A M. Jensen, G.J. Jia, T. Jorgenson, D.L. Kane, D.R. Klein, G. Kofinas, A H. Lynch, A.H. Lloyd, A.D. McGuire, F.E. Nelson, W.C. Oechel, T.E. Osterkamp, C.H. Racine, V.E. Romanovsky, R.S. Stone, D.A. Stow, M. Sturm, C.E. Tweedie, G.L. Vourlitis, M.D. Walker, D.A. Walker, P.J. Webber, J.M. Welker, K. Winker, and K. Yoshikawa, 2005: Evidence and implications of recent climate change in northern Alaska and other arctic regions. *Clim. Change*, **72**, 251-298.

Hofmann, D.J., J.H. Butler, E.J. Dlugokencky, J.W. Elkins, K. Masarie, S.A. Montzka, and P. Tans, 2006: The role of carbon dioxide in climate forcing from 1979 to 2004: Introduction of the annual greenhouse gas index. *Tellus B*, **58**, 614-619.

Hornbach, M.J., D.M. Saffer, and W.S. Holbrook, 2004: Critically pressured free-gas reservoirs below gas-hydrate provinces. *Nature*, **427(6970)**, 142-144.

Hovland, M., and A.G. Judd, 1998: Seabed pockmarks and seepages. Graham & Trotman, London.

Hovland, M., H. Svensen, C.F. Forsberg, H. Johansen, C. Fichler, J.H. Fossa, R. Jonsson, and H. Rueslatten, 2005: Complex pockmarks with carbonate-ridges off mid-Norway: Products of sediment degassing. *Marine Geology*, **218(1-4)**, 191-206.

Huber, C., M. Leuenberger, R. Spahni, J. Flükiger, J. Schwander, T.F. Stocker, S. Johnsen, A. Landais, and J. Jouzel, 2006: Isotope calibrated Greenland temperature record over Marine Isotope Stage 3 and its relation to CH_4. *Earth and Planet. Sci. Lett.*, **243**, 504-519.

Huber, M., L. Sloan, and C. Shellito, 2002: Early Paleogene oceans and climate: A fully coupled modeling approach using the National Center for Atmospheric Research Community Climate System Model. In: *Causes and consequences of globally warm climates in the Early Paleogene*. [Wing, S.L., P.D. Gingerich, B. Schmitz, and E. Thomas (eds.)]. Geological Society of America, Boulder, CO, 25-47.

Jenkyns, H.C, 2003: Evidence for rapid climate change in the Mesozoic-Palaeogene greenhouse world. *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences*, **361(1810)**, 1885-1916.

Joabsson, A., and T.R. Christensen, 2001: Methane emissions from wetlands and their relationship with vascular plants: An Arctic example. *Global Change Biol.*, **7**, 919-932.

Jorgenson, M.T., Y.L. Shur, and E.R. Pullman, 2006: Abrupt increase in permafrost degradation in Arctic Alaska. *Geophys. Res. Lett.*, **33**, L02503, doi:10.1029/2005GL024960

Jorgenson, M.T., C.H. Racine, J.C. Walters, and T.E. Osterkamp, 2001: Permafrost degradation and ecological changes associated with a warming climate in central Alaska. *Clim. Change*, **48**, 551-579.

Jorgenson, M.T., Y.L. Shur, and E.R. Pullman, 2006: Abrupt increase in permafrost degradation in Arctic Alaska. *Geophys. Res. Lett.*, **33**, L02503, doi:10.1029/2005GL024960

Kaplan, J.O., 2002, Wetlands at the last glacial maximum: Distribution and methane emissions. *Geopysical Research Letters*, **29**, doi: 10.1029/2001GL013366.

Kaplan. J.O., G. Folberth and D.A. Hauglustaine, 2006. Role of methane and volatile biogenic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations. *Global Biogeochemical Cycles*, **20**, GB2016, doi:10.1029/2005GB002590.

Kelly, M., R.L. Edwards, H. Cheng, D. Yuan, Y. Cai, M. Zhang, Y. Lin, and Z. An, 2006: High resolution characterization of the Asian Monsoon between 146,000 and 99,000 years B.P. from Dongge Cave, China and correlation of events surrounding Termination II. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **236**, 20-38.

Kennett, J.P., K.G. Cannariato, I.L. Hendy, and R.J. Behl, 2000: Carbon isotopic evidence for methane hydrate instability during quaternary interstadials. *Science*, **288(5463)**, 128-133.

Kennett, J.P., K.G. Cannariato, I.L. Hendy, and R.J. Behl, 2003: Methane hydrates in Quaternary climate change: The clathrate gun hypothesis. AGU Press.

Kennett, J.P., and L.D. Stott. 1991. Abrupt deep sea warming, paleoceanographic changes and benthic extinctions at the end of the Paleocene. *Nature*, **353**, 319-322.

Keppler, F., J. Hamilton, M. Braß, and T. Rockman, 2006, Methane emissions from terrestrial plants under aerobic conditions. *Nature*, **439**, 187-191.

Kent, D.V., B.S. Cramer, L. Lanci, D. Wang, J.D. Wright, and R. Van der Voo, 2003: A case for a comet impact trigger for the Paleocene/Eocene thermal maximum and carbon isotope excursion. *Earth and Planetary Science Letters*, **211(1-2)**, 13-26.

King, J.Y., and W.S. Reeburgh, 2002: A pulse-labeling experiment to determine the contribution of recent plant photosynthates to net methane emission in arctic wet sedge tundra. *Soil Biology & Biochemistry*, **34**, 173-180.

King, J.Y., W.S. Reeburgh, and S.K. Regli, 1998: Methane emission and transport by arctic sedges in Alaska: Results of a vegetation removal experiment. *J. Geophys. Res.*, **103**, 29083-29092.

Klauda, J.B., and S.I. Sandler, 2005: Global distribution of methane hydrate in ocean sediment. *Energy & Fuels*, **19(2)**, 459-470.

Kobashi, T., J. Severinghaus, E. Brook, J.M. Barnola and A. Grachev, 2007: Precise timing and characterization of abrupt climate change at 8.2k B.P. from air trapped in polar ice. *Quaternary Science Reviews*, **26**, 1212-1222.

Koch, P.L., J.C. Zachos, and P.D. Gingerich. 1992. Coupled isotopic change in marine and continental carbon reservoirs near the Paleocene/Eocene boundary. *Nature*, **358**, 319-322.

Krason J, 2000: Messoyakh gas field (W. Siberia): A model for development of the methane hydrate deposits of Mackenzie Delta. In: Gas Hydrates: Challenges for the Future. [Holder, G.D., and P.R. Bishnoi (eds.)]. New York Academy of Sciences, 173-188.

Kump, L.R., and M.A. Arthur, 1999: Interpreting carbon-isotope excursions: Carbonates and organic matter. *Chem. Geol.*, **161**, 181-198.

Kvenvolden, K.A. 1993. Gas hydrates—Geological perspective and global change. *Reviews of Geophysics*, **31**, 173-187.

Kvenvolden, K.A., 1999: Potential effects of gas hydrate on human welfare. *Proc. Natl. Acad. Sci.*, **96**, 3420-3426.

Kvenvolden, K.A, 2000: Gas hydrate and humans. In: *Gas Hydrates: Challenges for the Future*. [Holder, G.D., and P.R. Bishnoi (eds.)]. New York Academy of Sciences, 17-22.

Kvenvolden, K.A., and T.D. Lorenson, 2001: The global occurrence of natural gas hydrates. In: Natural Gas Hydrates: Occurrence, Distribution, and Detection. [Paull, C.K., and W.P. Dillon (eds.)]. *American Geophysical Union Geophysical Monographs 124*, 3-18.

Larson, R.L., 1991: Geological consequences of superplumes. *Geology*, **19**, 963-966.

Lawrence, D.M., and A.G. Slater, 2005: A projection of severe near-surface permafrost degradation during the 21st century. *Geophys. Res. Lett.*, **24,** L24401, doi:10.1029/2005GL025080.

Lawrence, D.M., A.G. Slater, and V.E. Romanovsky, 2007: The sensitivity of a model projection of near-surface permafrost degradation to soil column depth and inclusion of soil organic matter. Submitted to *J. Geophys. Res.*

Leifer, I., J.F. Clark, and R.F. Chen, 2000: Modifications of the local environment by natural marine hydrocarbon seeps. *Geophysical Research Letters*, **27(22)**, 3711-3714.

Leifer, I., and I. MacDonald, 2003: Dynamics of the gas flux from shallow gas hydrate deposits: interaction between oily hydrate bubbles and the oceanic environment. *Earth and Planetary Science Letters*, **210(3-4)**, 411-424.

Li, C., J.J. Qiu, S. Frolking, X. Xiao, W. Salas, B. Moore, S. Boles, Y. Huang, and R. Sass, 2002: Reduced methane emissions from large-scale changes in water management of China's rice paddies during 1980-2000. *Geophys. Res. Lett.,* **29(20)**, doi:10.1029/2002GL015370.

Luyendyk, B., J. Kennett, and J.F. Clark, 2005: Hypothesis for increased atmospheric methane input from hydrocarbon seeps on exposed continental shelves during glacial low sea level. *Marine and Petroleum Geology*, **22(4)**, 591-596.

Luyten, J.R., J. Pedlosky, and H. Stommel, 1983: The ventilated thermocline, *J. Phys. Ocean.*, **13**, 292-309.

MacDonald, G.J., 1990: Role of methane clathrates in past and future climates. *Clim. Change*, **16**, 247-281.

MacDonald, G.M., D.W. Berilman, K.V. Kremenetski, Y. Sheng, L. Smith, and A. Velichko, 2006: Rapid development of circumarctic peatlands and atmospheric CH_4 and CO_2 variations. *Science*, **314**, 285-288.

MacDonald, I.R., G. Bohrmann, E. Escobar, F. Abegg, P. Blanchon, V. Blinova, W. Bruckmann, M. Drews, A. Eisenhauer, X. Han, K. Heeschen, F. Meier, C. Mortera, T. Naehr, B. Orcutt, B. Bernard, J. Brooks, and M. de Farago, 2004:

Asphalt volcanism and chemosynthetic life in the Campeche Knolls, Gulf of Mexico. *Science*, **304(5673)**, 999-1002.

MacDonald, I.R., I. Leifer, R. Sassen, P. Stine, R. Mitchell, and N. Guinasso, 2002: Transfer of hydrocarbons from natural seeps to the water column and atmosphere. *Geofluids*, **2(2)**, 95-107.

MacDonald, I.R., N.L. Guinasso, R. Sassen, J.M. Brooks, L. Lee, and K.T. Scott, 1994: Gas hydrate that breaches the sea-floor on the continental-slope of the Gulf of Mexico. *Geology*, **22(8)**, 699-702.

MacDonald, J.A., D. Fowler, K.J. Hargreaves, U. Skiba, I.D. Leith, and M.B. Murray, 1998: Methane emission rates from a northern wetland; response to temperature, water table and transport. *Atmospheric Environment*, **32,** 3219.

MacFarling-Meure, C., D. Etheridge, C. Trudinger, P.S. Steele, R. Langenfelds, T. van Ommen, A. Smith, and J. Elkins, 2006: Law dome CO_2, CH_4, and N_2O records extended to 2000 years BP. *Geophysical Research Letters*, **33**, L14810, doi:10.1029/2006GL026152.

Martin, P., D. Archer, and D. Lea, 2005: Role of deep sea temperatures in the carbon cycle during the last glacial. *Paleoceanography*, doi:10.1029/2003PA000914.

Maslin, M., M. Owen, S. Day, and D. Long, 2004: Linking continental-slope failures and climate change: Testing the clathrate gun hypothesis. *Geology*, **32(1)**, 53-56.

Masson, D.G., C.B. Harbitz, R.B. Wynn, G. Pedersen, and F. Løvholt, 2006: Submarine landslides: processes, triggers, and hazard prediction. *Philosophical Transactions of the Royal Society*, **364**, 2009-2039.

McGuire, A.D., F.S. Chapin, J.E. Walsh, and C. Wirth, 2006: Integrated regional changes in arctic climate feedbacks: Implications for the global climate system. *Annual Review of Environment and Resources*, **31**, 61-91.

Meehl, G.A., T.F. Stocker, W.D. Collins, P. Friedlingstein, A.T. Gaye, J.M. Gregory, A. Kitoh, R. Knutti, J.M. Murphy, A. Noda, S.C.B. Raper, I.G. Watterson, A.J. Weaver, and Z.-C. Zhao, 2007: Global climate projections. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom, and New York.

Melack, J.M., L.L. Hess, M. Gastil, B.R. Forsberg, S.K. Hamilton, I.B.T. Lima, and E.M.L.M. Novo, 2004: Regionalization of methane emissions in the Amazon Basin with microwave remote sensing. *Global Change Biology*, **10**, 530-544.

Meyer, R.F., 1981, Speculations on oil and gas resources in small fields and unconventional deposits. In: Long-term Energy Resources, v. 1, 49-72 [Meyer, R.F., and J.C. Olson (eds.)]. Pitman, Boston.

Mienert, J., K. Andreassen, J. Posewang, and D. Lukas, 2000: Changes of the hydrate stability zone of the Norwegian margin from glacial to interglacial times. *Gas Hydrates: Challenges for the Future*, 200-210.

Mienert, J., M. Vanneste, S. Bunz, K. Andreassen, H. Haflidason, and H.P. Sejrup, 2005: Ocean warming and gas hydrate stability on the mid-Norwegian margin at the Storegga slide. *Marine and Petroleum Geology*, **22(1-2)**, 233-244.

Milkov, A.V., 2000: Worldwide distribution of submarine mud volcanoes and associated gas hydrates. *Marine Geology*, **167(1-2)**, 29-42.

Milkov, A.V., 2004: Global estimates of hydrate-bound gas in marine sediments: How much is really out there? *Earth-Science Reviews*, **66(3-4)**, 183-197.

Milkov, A.V., and R. Sassen, 2000: Thickness of the gas hydrate stability zone, Gulf of Mexico continental slope. *Marine and Petroleum Geology*, **17(9)**, 981-991.

Milkov, A.V., and R. Sassen, 2001: Estimate of gas hydrate resource, northwestern Gulf of Mexico continental slope. *Marine Geology*, **179(1-2)**, 71-83.

Milkov, A.V., and R. Sassen, 2002: Economic geology of offshore gas hydrate accumulations and provinces. *Marine and Petroleum Geology*, **19(1)**, 1-11.

Milkov, A.V., and R. Sassen, 2003: Two-dimensional modeling of gas hydrate decomposition in the northwestern Gulf of Mexico: Significance to global change assessment. *Global and Planetary Change*, **36(1-2)**, 31-46.

Milkov, A.V., P.R. Vogt, K. Crane, A.Y. Lein, R. Sassen, and G.A. Cherkashev, 2004: Geological, geochemical, and microbial processes at the hydrate-bearing Hakon Mosby mud volcano: A review. *Chemical Geology*, **205(3-4)**, 347-366.

Minkkinen, K., J. Laine, H. Nykanen, P.J. Marikainen, 1997: Importance of drainage ditches in emissions of methane from mires drained for forestry. *Can. J. For. Res.*, **27**, 949-952.

Nisbet, E.G, 2002: Have sudden large releases of methane from geological reservoirs occurred since the last glacial maximum, and could such releases occur again? *Philosophical Transactions of the Royal Society of London Series A—Mathematical Physical and Engineering Sciences*, **360(1793)**, 581-607.

Nisbet, E.G., and D.J.W. Piper, 1998: Giant submarine landslides. *Nature*, **392(6674)**, 329-330.

Nouze, H., P. Henry, M. Noble, V. Martin, and G. Pascal, 2004: Large gas hydrate accumulations on the eastern Nankai Trough inferred from new high-resolution 2-D seismic data. *Geophysical Research Letters*, **31(13)**, L13308, doi:10.1029/2004GL019848.

Nykänen, H., J.E.P. Heikkinen, L. Pirinen, K. Tiilikainen, and P.J. Martikainen, 2003: Annual CO_2 exchange and CH_4 fluxes on a subarctic palsa mire during climatically different years. *Global Biogeochem. Cycles*, **17(1)**, 1018, doi:10.1029/2002GB001861.

Osterkamp, T.E., and J.C. Jorgenson, 2006: Warming of permafrost in the Arctic National Wildlife Refuge. *Alaska. Permafr. Periglac. Proc.*, **17**, 65-69.

Osterkamp, T.E., and V.E. Romanovsky, 1999: Evidence for warming and thawing of discontinuous permafrost in Alaska. *Permafr. Periglac. Proc.*, **10**, 17-37.

Pagani, M., K. Caldeira, D. Archer, and J.C. Zachos, 2006: An ancient carbon mystery. *Science*, **314(5805)**, 1556-1557.

Paull, C.K., P.G. Brewer, W. Ussler, E.T. Peltzer, G. Rehder, and D. Clague, 2003: An experiment demonstrating that marine slumping is a mechanism to transfer methane from seafloor gas-hydrate deposits into the upper ocean and atmosphere. *Geo-Marine Letters*, **22(4)**, 198-203.

Paull, C.K., W. Ussler, and W.P. Dillon, 1991: Is the extent of glaciation limited by marine gas hydrates? *Geophys. Res. Lett.*, **18**, 432-434.

Payette, S., A. Delwaide, M. Caccianiga, and M. Beauchemin, 2004: Accelerated thawing of subarctic peatland permafrost over the last 50 years. *Geophys. Res. Lett.*, **31,** L18208, doi:10.1029/2004GL020358.

Pecher, I.A., N. Kukowski, C. Huebscher, J. Greinert, and J. Bialas, 2001: The link between bottom-simulating reflections and methane flux into the gas hydrate stability zone—New evidence from Lima basin, Peru margin. *Earth and Planetary Science Letters*, **185(3-4)**, 343-354.

Peterson, L.C., G.H. Haug, K.A. Hughen, and U. Rohl, 2000: Rapid changes in the hydrologic cycle of the tropical Atlantic during the last glacial. *Science*, **290**, 1947-1951.

Ramaswamy, V., O. Boucher, J. Haigh, et al, 2001: Radiative forcing of climate change. In: *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change.* [Houghton J.T., Y. Ding, D.J. Griggs, et al. (eds.)]. Cambridge University Press, Cambridge, United Kingdom, 350-416.

Reeburgh, W.S., 2004: Global methane biogeochemistry. In: *Treatise on Geochemistry. The Atmosphere.* [Keeling, R.F. (ed.)]. Elsevier, Amsterdam, v. 4, 65-89.

Rehder, G., P.W. Brewer, E.T. Peltzer, and G. Friederich, 2002: Enhanced lifetime of methane bubble streams within the deep ocean. *Geophysical Research Letters*, **29(15)**, 1731, doi:10.1029/2001GL013966.

Rehder, G., R.S. Keir, E. Suess, and M. Rhein, 1999: Methane in the northern Atlantic controlled by microbial oxidation and atmospheric history. *Geophysical Research Letters*, **26(5)**, 587-590.

Riedel, M., G.D. Spence, N.R. Chapman, and R.D. Hyndman, 2002: Seismic investigations of a vent field associated with gas hydrates, offshore Vancouver Island. *Journal of Geophysical Research-Solid Earth*, **107(B9)**.

Riordan, B., D. Verbyla, and A.D. McGuire, 2006: Shrinking ponds in subarctic Alaska based on 1950-2002 remotely sensed images. *Journal of Geophysical Research-Biogeosciences*, **111,** G04002, doi:10.1029/2005JG000150.

Rogner, H.-H, 1997: An assessment of world hydrocarbon resources. *Annu. Rev. Energy Environ.*, **22**, 217-262.

Romanovsky, V.E., M. Burgess, S. Smith, K. Yoshikawa, and J. Brown, 2002: Permafrost temperature records: Indicator of climate change. *Eos*, **589**, 593-594.

Rothwell, R.G., M.S. Reeder, G. Anastasakis, D.A.V. Stow, J. Thomson, and G. Kahler 2000. Low sea-level stand emplacement of megaturbidites in the western and eastern Mediterranean Sea. *Sedimentary Geology*, **135(1-4)**, 75-88.

Saito, K., M. Kimoto, T. Zhang, K. Takata, and S. Emori, 2007: Evaluating a high-resolution climate model: Simulated hydrothermal regimes in frozen ground regions and their change under the global warming scenario. *J. Geophys. Res.*, **112,** F02S11, doi:10.1029/2006JF000577.

Sassen, R., S.L. Losh, L. Cathles, H.H. Roberts, J.K. Whelan, A.V. Milkov, S.T. Sweet, and D.A. DeFreitas, 2001a: Massive vein-filling gas hydrate: relation to ongoing gas migration from the deep subsurface in the Gulf of Mexico. *Marine and Petroleum Geology*, **18(5)**, 551-560.

Sassen, R., and I.R. MacDonald, 1994: Evidence of structure H hydrate, Gulf of Mexico continental slope. *Org. Geochem.*, **22**, 1029-1032.

Sassen, R., A.V. Milkov, H.H. Roberts, S.T. Sweet, and D.A. DeFreitas, 2003: Geochemical evidence of rapid hydrocarbon venting from a seafloor-piercing mud diapir, Gulf of Mexico continental shelf. *Marine Geology*, **198(3-4)**, 319-329.

Sassen, R., S.T. Sweet, A.V. Milkov, D.A. DeFreitas, and M.C. Kennicutt, 2001b: Thermogenic vent gas and gas hydrate in the Gulf of Mexico slope: Is gas hydrate decomposition significant? *Geology*, **29(2)**, 107-110.

Sazonova, T.S., V.E. Romanovsky, J.E. Walsh, and D.O. Sergueev, 2004: Permafrost dynamics in the 20th and 21st centuries along the East Siberian transect. *J. Geophys. Res.*, **109**, D01108, doi:10.1029/2003JD003680

Schaefer, H., M. Whiticar, E. Brook, V. Petrenko, D. Ferretti, and J. Severinghaus, 2006: Ice record of $\delta^{13}C$ for atmospheric methane across the Younger Dryas-Pre Boreal Transition. *Science*, **313**, 1109-1112.

Schlesinger, W., 1997: Biogeochemistry: An analysis of global change. Academic Press.

Schmidt, G.A., and D.T. Shindell, 2003: Atmospheric composition, radiative forcing, and climate change as a consequence of a massive methane release from gas hydrates. *Paleoceanography*, **18(1)**.

Schmitz, B., B. Peucker-Ehrenbrink, C. Heilmann-Clausen, G. Aberg, F. Asaro, and C.T.A. Lee, 2004: Basaltic explosive volcanism, but no comet impact, at the Paleocene-Eocene boundary: high-resolution chemical and isotopic records from Egypt, Spain and Denmark. *Earth and Planetary Science Letters*, **225(1-2)**, 1-17.

Schwander, J., 2006: Ice core chronologies. In: *Encyclopedia of Quaternary Science*. [Elias, S. (ed.)]. Elsevier, Amsterdam.

Schwander, J., J.-M. Barnola, C. Andrie, M. Leuenberger, A. Ludin, D. Raynaud, and B. Stauffer, 1993: The age of the air in the firn and the ice at Summit, Greenland. *J. Geophys. Res.*, **98**, 2831-2838.

Serreze, M.C., and J.A. Francis, 2006: The arctic amplification debate. *Clim. Change*, **76**, 241-264.

Serreze, M.C., J.E. Walsh, F.S. Chapin, T. Osterkamp, M. Dyurgerov, V. Romanovsky, W.C. Oechel, J. Morison, T. Zhang, and R.G. Barry, 2000: Observational evidence of recent change in the northern high-latitude environment. *Clim. Change*, **46**, 159-207.

Severinghaus, J., and E. Brook, 1999: Simultaneous tropical-abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice. *Science*, **286**, 930-934.

Severinghaus, J.P., T. Sowers, E. Brook, R.B. Alley, and M.L. Bender, 1998: Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice. *Nature*, **391**, 141-148.

Shakhova, N., I. Semiletov, and G. Panteleev, 2005: The distribution of methane on the Siberian Arctic shelves: Implications for the marine methane cycle. *Geophys. Res. Lett.*, **32(9)**, L09601, doi:10.1029/2005GL022751.

Shindell, D.T., B.P. Walter, and G. Faluvegi, 2004: Impacts of climate change on methane emissions from wetlands. *Geophys. Res. Lett.*, **31**, L21202, doi:10.1029/2004GL021009.

Sluijs, A., S. Schouten, M. Pagani, M. Woltering, H. Brinkhuis, J.S. Sinninghe Damsté, G.R. Dickens, M. Huber, G.-J. Reichart, R. Stein, J. Matthiessen, L.J. Lourens, N. Pedentchouk, J. Backman, K. Moran, and the Expedition 302 Scientists, 2006: Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum. *Nature*, **441**, 610-613.

Smith, D.E., S. Shi, R.A. Cullingford, A.G. Dawson, S. Dawson, C.R. Firth, I.D.L. Foster, P.T. Fretwell, B.A. Haggart, L.K. Holloway, and D. Long, 2004: The holocene storegga slide Tsunami in the United Kingdom. *Quaternary Science Reviews*, **23(23-24)**, 2291-2321.

Smith, L.C., Y. Sheng, G.M. MacDonald, and L.D. Hinzman, 2005: Disappearing Arctic lakes. *Science*, **308,** 1429-1429.

Smith, L.K., W.M. Lewis, J.P. Chanton, G. Cronin, and S.K. Hamilton, 2000: Methane emissions from the Orinoco River floodplain, Venezuela. *Biogeochemistry*, **51**, 113-140.

Solheim, A., K. Berg, C.F. Forsberg, and P. Bryn, 2005: The Storegga slide complex: Repetitive large scale sliding with similar cause and development. *Marine and Petroleum Geology*, **22(1-2)**, 97-107.

Sowers, T., 2006: Late quaternary atmospheric CH_4 isotope record suggests marine clathrates are stable. *Science*, **311(5762)**, 838-840.

Spahni, R., J. Schwander, J. Flückiger., B. Stauffer, J. Chappellaz, and D. Raynaud, 2003: The attenuation of fast atmospheric CH_4 variations recorded in polar ice cores. *Geophys. Res. Lett.*, **30**, doi:10.1029/2003GL017093.

Spahni, R., et al., 2005: Atmospheric methane and nitrous oxide of the late Pleistocene from Antarctic ice cores. *Science*, **310**, 1317-1321.

St. Louis, V.I., C.A. Kelly, E. Duchemin, J.W.M. Rudd, and D.M. Rosenberg, 2000: Reservoir surfaces as sources of greenhouse gases to the atmosphere: A global estimate. *BioScience*, **50**, 766–775.

Steele, L.P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin, and K.A. Masarie, 1992: Slowing down of the global accumulation of atmospheric methane during the 1980s. *Nature*, **358(6384)**, 313-316.

Stendel, M., and J.H. Christensen, 2002: Impact of global warming on permafrost conditions in a coupled GCM. *Geophys. Res. Lett.*, **13**, doi:10.1029/2001GL014345.

Storey, M., R. Duncan, and C.C. Swisher, 2007: Paleocene-Eocene thermal maximum and the opening of the northeast Atlantic. *Science*, **316**, 587-589.

Sturm, M., J.P. McFadden, G.E. Liston, F.S. Chapin III, C.H. Racine, and J. Holmgren, 2001: Snow-shrub interactions in Arctic tundra: A hypothesis with climatic implications. *J. Clim.*, **14,** 336-344.

Sultan, N., P. Cochonat, J.P. Foucher, and J. Mienert, 2004: Effect of gas hydrates melting on seafloor slope instability. *Marine Geology*, **213(1-4)**, 379-401.

Svensen, H., S. Planke, A. Malthe-Sorenssen, B. Jamtveit, R. Myklebust, T.R. Eidem, and S.S. Rey, 2004: Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. *Nature*, **429(6991)**, 542-545.

Taylor, M.H., W.P. Dillon, and I.A. Pecher, 2000: Trapping and migration of methane associated with the gas hydrate stability zone at the Blake Ridge Diapir: New insights from seismic data. *Marine Geology*, **164(1-2)**, 79-89.

Thomas, D.J., J.C. Zachos, T.J. Bralower, E. Thomas, and S. Bohaty, 2002: Warming the fuel for the fire: Evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene thermal maximum. *Geology*, **30(12)**, 1067-1070.

Thorpe, R.B., K.S. Law, S. Bekki, J.A. Pyle, E.G. Nisbet, 1996: Is methane-driven deglaciation consistent with the ice core record? *Journal of Geophysical Research*, **101**, 28627-28635.

Torres, M.E., J. McManus, D.E. Hammond, M.A. de Angelis, K.U. Heeschen, S.L. Colbert, M.D. Tryon, K.M. Brown, and E. Suess, 2002: Fluid and chemical fluxes in and out of sediments hosting methane hydrate deposits on Hydrate Ridge, OR, I: Hydrological provinces. *Earth and Planetary Science Letters*, **201(3-4)**, 525-540.

Torres, M.E., K. Wallmann, A.M. Trehu, G. Bohrmann, W.S. Borowski, and H. Tomaru, 2004: Gas hydrate growth, methane transport, and chloride enrichment at the southern summit of Hydrate Ridge, Cascadia margin off Oregon. *Earth and Planetary Science Letters*, **226(1-2)**, 225-241.

Trehu, A.M., P.B. Flemings, N.L. Bangs, J. Chevallier, E. Gracia, J.E. Johnson, C.S. Liu, X.L. Liu, M. Riedel, and M.E. Torres, 2004: Feeding methane vents and gas hydrate deposits at south Hydrate Ridge. *Geophysical Research Letters*, **31(23)**.

Trehu, A.M., P.E. Long, M.E. Torres, G. Bohrmann, F.R. Rack, T.S. Collett, D.S. Goldberg, A.V. Milkov, M. Riedel, P. Schultheiss, N.L. Bangs, S.R. Barr, W.S. Borowski, G.E. Claypool, M.E. Delwiche, G.R. Dickens, E. Gracia, G. Guerin, M. Holland, J.E. Johnson, Y.J. Lee, C.S. Liu, X. Su, B. Teichert, H. Tomaru, M. Vanneste, M. Watanabe, and J.L. Weinberger, 2004b: Three-dimensional distribution of gas hydrate beneath southern Hydrate Ridge: Constraints from ODP Leg 204. *Earth and Planetary Science Letters*, **222(3-4)**, 845-862.

Turetsky, M.R., R.K. Wieder, and D.H. Vitt, 2002: Boreal peatland C fluxes under varying permafrost regimes. *Soil Biology & Biochemistry*, **34**, 907-912.

Turunen, J., E. Tomppo, K. Tolonen, and A. Reinikainen, 2002: Estimating carbon accumulation rates of undrained mires in Finland—Application to boreal and subarctic regions. *The Holocene*, **1**, doi:10.1191/0959683602hl522rp.

Uchida, T., S. Dallimore, and J. Mikami, 2002: Occurrences of natural gas hydrates beneath the permafrost zone in Mackenzie Delta: Visual and x-ray CT imagery. In: *Gas Hydrates: Challenges for the Future*. [Holder, G.D., and P.R. Bishnoi (eds.)]. New York Academy of Sciences, 1021-1033.

Uchida, M., Y. Shibata, K. Ohkushi, N. Ahagon, and M. Hoshiba, 2004: Episodic methane release events from Last Glacial marginal sediments in the western North Pacific. *Geochemistry Geophysics Geosystems*, **5**.

Valdes, P.J., D.J. Beerling, and C.E. Johnson, 2005. The ice age methane budget. *Geophysical Research Letters*, **32**, L02704, doi.10.1029/2004GL021004.

Valentine, D.L., D.C. Blanton, W.S. Reeburgh, and M. Kastner, 2001: Water column methane oxidation adjacent to an area of active hydrate dissociation, Eel River Basin. *Geochimica et Cosmochimica Acta*, **65(16)**, 2633-2640.

van der Werf, G.R., J.T. Randerson, G.J. Collatz, L. Giglio, P.S. Kasibhatla, A.F. Arellano, Jr., S.C. Olsen, and E.S. Kasischke, 2004: Continental-scale partitioning of fire emissions during the 1997 to 2001 El Nino/La Nina period. *Science*, **303**, 73-74.

Vogt, P.R., and W.Y. Jung, 2002: Holocene mass wasting on upper non-Polar continental slopes - due to post-Glacial ocean warming and hydrate dissociation? *Geophysical Research Letters*, **29(9)**, 1341, doi:10.1029/2001GL013488.

von Huissteten, J., 2004: Methane emission from northern wetlands in Europe during oxygen isotope stage 3. *Quaternary Science Reviews*, **23**, 1989-2005.

Waddington, J.M., N.T. Roulet, and R.V. Swanson, 1996: Water table control of CH_4 emission enhancement by vascular plants in boreal peatlands. *J. Geophys. Res.*, **101**, 22775-22785.

Wagner, D., A. Gattinger, A. Embacher, E.M. Pfeiffer, M. Schloter, and A. Lipski, 2007: Methanogenic activity and biomass in Holocene permafrost deposits of the Lena Delta, Siberian Arctic and its implication for the global methane budge. *Glob. Change Biol.*, **13**, 1089-1099.

Wakeham, S.G., C.M. Lewis, E.C. Hopmans, S. Schouten, and J.S. Sinninghe Damsté, 2003: Archaea mediate anaerobic oxidation of methane in deep euxinic waters of the Black Sea. *Geochimica et Cosmochimica Acta*, **67**, 1359-1374.

Walter, B.P., M. Heimann, and E. Matthews, 2001: Modeling modern methane emissions from natural wetlands 2. Interannual variations 1982-1993. *J. Geophys. Res.*, **106(D24)**, 34207-34220.

Walter, K.M., S.A. Zimov, J.P. Chanton, D. Verbyla, and F.S. Chapin, 2006: Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. *Nature*, **443**, 71-75.

Wang, X.-F., A.S. Auler, R.L. Edwards, H. Cheng, H., P.S. Cristalli, P.L. Smart, D.A. Richards, and C.-C. Shen, 2004: Wet periods in northeastern Brazil over the past 210 kyr linked to distant climate anomalies. *Nature*, **432**, 740-744.

Wang, Z.-P., X.-G. Han, G.G. Wang, Y. Song, and J. Gulledge, 2008: Aerobic methane emission from plants in the Inner Mongolia Steppe. *Environ. Sci. Technol.*, **42**, 62-68, 10.1021/es071224l.

Washburn, L., J.F. Clark, and P. Kyriakidis, 2005: The spatial scales, distribution, and intensity of natural marine hydrocarbon seeps near Coal Oil Point, California. *Marine and Petroleum Geology*, **22(4)**, 569-578.

Weinberger, J.L., K.M. Brown, and P.E. Long, 2005: Painting a picture of gas hydrate distribution with thermal images. *Geophysical Research Letters*, **32(4)**.

Weitemeyer, K.A., and B.A. Buffett, 2006: Accumulation and release of methane from clathrates below the Laurentide and Cordilleran ice sheets. *Global & Planetary Change*, **53**, 176-187.

Wickland, K.P., R.G. Striegl, J.C. Neff, and T. Sachs, 2006: Effects of permafrost melting on CO_2 and CH_4 exchange of a poorly drained black spruce lowland. *Journal of Geophysical Research-Biogeosciences*, **111**, G02011, doi:10.1029/2005JG000099.

Wood, W.T., J.F. Gettrust, N.R. Chapman, G.D. Spence, and R.D. Hyndman, 2002: Decreased stability of methane hydrates in marine sediments owing to phase-boundary roughness. *Nature*, **420(6916)**, 656-660.

Xu, W.Y., R.P. Lowell, and E.T. Peltzer, 2001: Effect of seafloor temperature and pressure variations on methane flux from a gas hydrate layer: Comparison between current and late Paleocene climate conditions. *Journal of Geophysical Research-Solid Earth*, **106(B11)**, 26413-26423.

Yuan, D.X., H. Cheng, R.L. Edwards, C. Dykoski, M.J. Kelly, M.L. Zhang, J.M. Qing, Y.S. Lin, Y.G. Wang, J.A. Dorale, Z.S. An, and, Y.J. Cai, 2004: Timing, duration, and transitions of the Last Interglacial Asian Monsoon. *Science*, **304**, 575-578.

Zachos, J.C., M. Pagani, L. Sloan, E. Thomas, and K. Billups, 2001: Trends, rhythms, and abberations in global climate 65 Ma to present. *Science*, **292**, 686-693.

Zachos, J.C., U. Rohl, S.A. Schellenberg, A. Sluijs, D.A. Hodell, D.C. Kelly, E. Thomas, M. Nicolo, I. Raffi, L.J. Lourens, H. McCarren, and D. Kroon, 2005: Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science*, **308(5728)**, 1611-1615.

Zachos, J.C., M.W. Wara, S. Bohaty, M.L. Delaney, M.R. Petrizzo, A. Brill, T.J. Bralower, and I. Premoli-Silva, 2003: A transient rise in tropical sea surface temperature during the Paleocene-Eocene thermal maximum. *Science*, **302(5650)**, 1551-1554.

Zeebe, R.E., and P. Westbroek, 2003: A simple model for the $CaCO_3$ saturation state of the ocean: The "Strangelove", the "Neritan", and the "Cretan" Ocean *Geochemistry Geophysics Geosystems*, **4**.

Zhang, Y., W.J. Chen, and J. Cihlar, 2003: A process-based model for quantifying the impact of climate change on permafrost thermal regimes. *J. Geophys. Res.*, **D22**, doi:10.1029/2002JD003354.

Zhang, Y., W.J. Chen, and D.W. Riseborough, 2007: Temporal and spatial changes of permafrost in Canada in the 21st century. *J. Geophys. Res.*

Zhuang, Q., J.M. Melillo, A.D. McGuire, D.W. Kicklighter, R.G. Prinn, P.A. Steudler, B.S. Felzer, and S. Hu, 2007: Net emissions of CH_4 and CO_2 in Alaska: Implications for the region's greenhouse gas budget. *Ecological Applications*, **17**, 203-212.

Zillmer, M., E.R. Flueh, and J. Petersen, 2005a: Seismic investigation of a bottom simulating reflector and quantification of gas hydrate in the Black Sea. *Geophysical Journal International*, **161(3)**, 662-678.

Zillmer, M., T. Reston, T. Leythaeuser, and E.R. Flueh, 2005b: Imaging and quantification of gas hydrate and free gas at the Storegga slide offshore Norway. *Geophysical Research Letters*, **32(4)**, L04308, doi:10.1029/2004GL021535.

Zimov, S., E.A.G. Schuur, and F.S. Chapin, 2006: Permafrost and the global carbon budget. *Science*, **312**, 1612-1613.

Zuhlsdorff, L., and V. Spiess, 2004: Three-dimensional seismic characterization of a venting site reveals compelling indications of natural hydraulic fracturing. *Geology*, **32(2)**, 101-104.

Zuhlsdorff, L., V. Spiess, C. Hubscher, H. Villinger, and A. Rosenberger, 2000: Implications for focused fluid transport at the northern Cascadia accretionary prism from a correlation between BSR occurrence and near-sea-floor reflectivity anomalies imaged in a multi-frequency seismic data set. *International Journal of Earth Sciences*, **88(4)**, 655-667.