

1 CCSP SAP 3.4

2 Abrupt Climate Change

3 Chapter 5. Potential for Abrupt Changes in Atmospheric Methane

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16 **Key Findings**

- 17 • The main concerns about abrupt changes in atmospheric methane stem from a)
18 the large quantity of methane believed to be stored in clathrate hydrates in the
19 sea floor and to a lesser extent in permafrost soils and b) climate driven changes
20 in emissions from northern high latitude and tropical wetlands.
21
- 22 • The size of the hydrate reservoir is uncertain, perhaps by up to a factor of 10.
23 Because the size of the reservoir is directly related to the perceived risks, it is
24 difficult to make certain judgment about those risks.
25
- 26 • There are a number of suggestions in the literature about the possibility of
27 catastrophic release of methane to the atmosphere based on both the size of the
28 hydrate reservoir and indirect evidence from paleoclimatological studies.
29 However, modeling and detailed studies of ice core methane so far do not
30 support catastrophic methane releases to the atmosphere in the last 650,000 years
31 or near future. Previous suggestions of a large release of methane at the
32 Paleocene-Eocene boundary (about 55 million years ago) face a number of
33 objections, but may still be viable.
34
- 35 • The current network of atmospheric methane (CH₄) monitoring sites is sufficient
36 for capturing large-scale changes in emissions, but it is insufficient for attributing
37 changes in emissions to one specific source sector.
38
- 39 • Observations show that there have not yet been significant increases in CH₄
40 emissions from high northern latitude hydrates and wetlands resulting from
41 increasing Arctic temperatures.
42
- 43 • While the risk of catastrophic release of methane to the atmosphere appears
44 remote, it is very likely that climate change will accelerate the pace of chronic
45 emissions from both hydrate sources and wetlands. Existing models suggest that
46 wetland emissions could double in the next century, and this could be an

1 underestimate primarily because of uncertainties in the evolution of Northern
2 Hemisphere wetlands as climate changes. Acceleration of chronic release from
3 hydrate reservoirs is expected, but the magnitude of the release is difficult to
4 estimate.

7 **Recommendations (Boxed Item)**

- 8 • Monitoring of atmospheric methane abundance and its isotopic composition
9 should be maintained and expanded to allow detection of change in net emissions
10 from northern and tropical wetland regions. Specifically, systematic
11 measurements of CH₄ mole fractions from tall towers and aircraft in the Arctic
12 and sub-Arctic regions would allow detection of changes in emissions from these
13 sparsely monitored but important regions.
- 14
- 15 • The feasibility of monitoring methane in the ocean water column near marine
16 hydrate deposits, or in the atmosphere near terrestrial hydrate deposits, should be
17 investigated.
- 18
- 19 • Efforts should be made to increase certainty in the size of the global methane
20 hydrate reservoirs. The level of concern about catastrophic release of methane to
21 the atmosphere is directly linked to the size of these reservoirs.
- 22
- 23 • The size and location of hydrate reservoirs that are most vulnerable to climate
24 change (for example stratigraphic type deposits in shallow water, the Siberian ice
25 complex, and regions of potential large submarine landslides) should be
26 identified and their potential impact on future methane concentrations should be
27 evaluated.
- 28
- 29 • Improvement in process-based modeling of methane release from marine
30 hydrates is needed. The transport of bubbles is particularly important, as are the
31 migration of gas through the stability zone and the mechanisms controlling
32 methane release from submarine landslides.
- 33
- 34 • Modeling efforts should establish the current and future climate driven
35 acceleration of chronic release of methane from wetlands and terrestrial hydrate
36 deposits. This should include development of improved representations of
37 wetland hydrology and biogeochemistry, and permafrost dynamics, in earth
38 system and global climate models.
- 39

40 **1. Background: Why are abrupt changes in methane a potential concern?**

41 **1.1 Introduction**

42 Methane (CH₄) is the second most important greenhouse gas that humans directly
43 influence. Concerns about methane's role in abrupt climate change stem primarily from
44 1) the large quantities of methane stored as solid methane hydrate on the seafloor and to
45 a lesser degree in terrestrial sediments, and the possibility that these reservoirs could be
46

1 unstable in the face of future global warming, and 2) the possibility of large-scale
2 conversion of frozen soil in the high latitude Northern Hemisphere to methane
3 producing wetland, due to accelerated warming at high latitudes. This chapter
4 summarizes the current state of knowledge about these reservoirs and their potential for
5 forcing abrupt climate change.

6 7 **1.2 Methane and Climate**

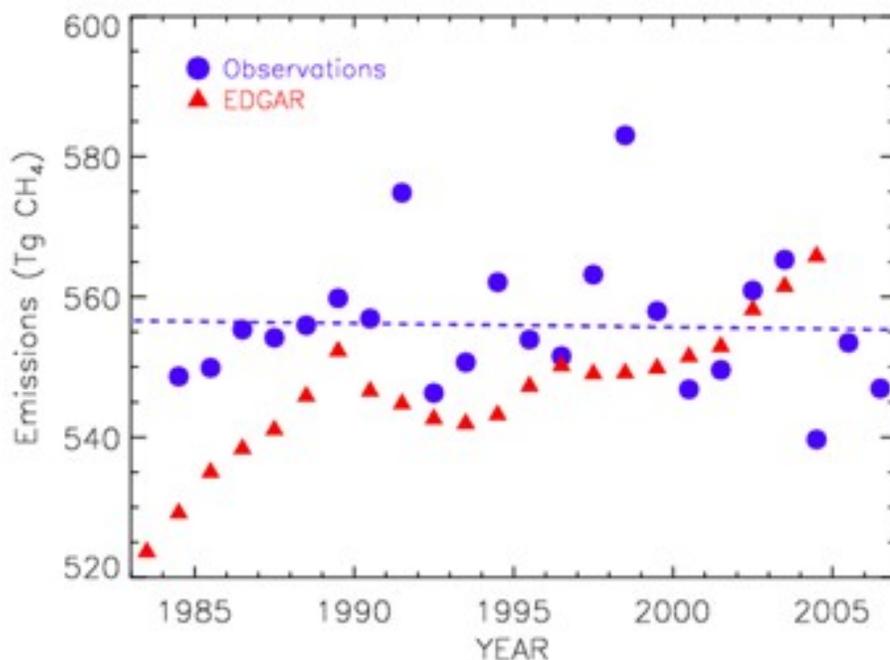
8 A spectral window exists between ~7 and 12 micrometers (μm) where the
9 atmosphere is somewhat transparent to terrestrial infrared (IR) radiation. Increases in
10 the atmospheric abundance of molecules that absorb IR radiation in this spectral region
11 contribute to the greenhouse effect. Methane is a potent greenhouse gas because it
12 strongly absorbs terrestrial IR radiation near 7.66 μm and its atmospheric abundance has
13 more than doubled since the start of the Industrial Revolution. Radiative forcing (RF) is
14 used to assess the contribution of a perturbation (in this case, the increase in CH_4 since
15 1750 AD) to the net irradiance at the top of the tropopause after allowing the
16 stratosphere to adjust to radiative equilibrium. The direct radiative forcing of
17 atmospheric methane determined from an increase in its abundance from its pre-
18 industrial value of 700 parts per billion (ppb) (*MacFarlane-Meure et al., 2006*;
19 *Etheridge et al., 1998*) to its 2006 globally-averaged abundance of 1775 ppb in 2006 is
20 $0.49 \pm 0.05 \text{ W m}^{-2}$ (*Hofmann et al., 2006*). Methane oxidation products, stratospheric
21 water (H_2O) vapor and tropospheric ozone (O_3), contribute indirectly to radiative
22 forcing, increasing methane's total contribution to $\sim 0.7 \text{ W m}^{-2}$ (e.g., *Hansen and Sato,*
23 *2001*), nearly half of that for carbon dioxide (CO_2) since the Industrial Revolution.
24 Increases in methane emissions can also increase the methane lifetime and the lifetimes
25 of other gases oxidized by the hydroxyl radical (OH). Assuming the abundances of all
26 other parameters that affect OH stay the same, the lifetime for an additional pulse of
27 CH_4 added to the atmosphere would be $\sim 40\%$ larger than the current value.
28 Additionally, CH_4 is oxidized to CO_2 ; CO_2 produced by CH_4 oxidation is equivalent to
29 $\sim 6\%$ of CO_2 emissions from fossil fuel combustion. Over a 100-year time horizon, the
30 direct and indirect effects on RF of emission of 1 kilogram (kg) CH_4 are 25 times greater
31 than for emission of 1 kg CO_2 (*IPCC Working Group I Fourth Assessment Report,*
32 *2007*).

33 The atmospheric abundance of CH_4 increased with human population because of
34 increased demand for energy and food. Beginning in the 1970s, as CH_4 emissions from
35 natural gas venting and flaring at oil production sites declined and rice agriculture
36 stabilized, the growth rate of atmospheric CH_4 decoupled from population growth.
37 Since 1999, the global atmospheric CH_4 abundance has been nearly stable; globally
38 averaged CH_4 in 1999 was only 3 ppb less than the 2006 global average of 1775 ppb.
39 Potential contributors to this stability are decreased emissions from the Former Soviet
40 Union after their economy collapsed in 1992 (*Dlugokencky et al., 2003*), decreased
41 emissions from natural wetlands because of widespread drought (*Bousquet et al., 2006*),
42 decreased emissions from rice paddies due to changes in water management (*Li et al.*
43 *2002*), and an increase in the chemical sink because of changing climate (*Fiore et al.,*
44 *2006*). Despite attempts to explain this surprising observation, the exact causes remain
45 unknown, which shrouds predictions of future CH_4 levels in significant uncertainties.
46 *Hansen et al. (2000)* have suggested that, because methane has a relatively short

1 atmospheric lifetime (see below) and reductions in emissions are often cost effective, it
2 is an excellent gas to target to counter increasing RF of CO₂ in the short term.

4 1.3 The Modern Methane Budget

5 The largest individual term in the global methane budget is the removal (removal
6 terms are referred to as “sinks”) from the atmosphere by oxidation of methane initiated
7 by reaction with hydroxyl radical (OH); smaller sinks occur from oxidation by chlorine
8 (troposphere and stratosphere), oxidation by electronically excited oxygen atoms
9 [O(¹D)] in the stratosphere, and oxidation in soils. The combination of these sink terms
10 results in an atmospheric CH₄ lifetime of ~9 yr (±10%). When combined with global
11 observations in a 1-box mass balance model of the atmosphere (that is, considering the
12 entire atmosphere to be a well-mixed uniform box), total global emissions can be
13 calculated with reasonable certainty. Using a lifetime of 8.9 years and NOAA (National
14 Oceanic and Atmospheric Administration) Earth System Research Laboratory (ESRL)
15 global observations of the CH₄ burden and trend gives average emissions of 556±10
16 teragrams (Tg) CH₄ yr⁻¹, with no significant trend (-0.05±0.31 Tg CH₄ yr⁻²) for 1984-
17 2006 (Figures 5.1 and 5.7). (1 Tg = 10¹²g = 0.001Gt, gigaton). The uncertainty on total
18 emissions is 1 standard deviation (s.d.) of the interannual variability; total uncertainty is
19 on order of ±10%. The total methane burden is ~5000 Tg or 5 Gt.



21 *Figure 1 about here. Methane emissions as function of time calculated with constant*
22 *lifetime; emissions from EDGAR inventory with constant natural emissions shown as*
23 *red triangles. EDGAR, Emission Database for Global Atmospheric Research.*
24
25

1 Methane is produced by a variety of natural and anthropogenic sources. Estimates of
 2 emissions from individual source terms are made using bottom-up and top-down
 3 methods. Bottom up inventories use emission factors (e.g., average emissions of CH₄
 4 per unit area for a specific wetland type) and activity levels (e.g., total area of that
 5 wetland type) to calculate emissions. Because the relatively few measurements of
 6 emission factors are typically extrapolated to large spatial scales, uncertainties in
 7 emissions estimated with the bottom-up approach are typically quite large. An example
 8 of the top-down method applied to the global scale is given above using a simple 1-box
 9 model, but it can also be applied using a three-dimensional chemical transport model to
 10 optimize emissions based on a comparison between model-derived mixing ratios and
 11 observations. Bottom-up inventories are normally used as initial guesses in this
 12 approach. This approach is used to estimate emissions by source and region. Table 5.1
 13 shows optimized CH₄ emissions calculated from an inverse modeling study
 14 (Bergamaschi et al., 2007; scenario 3) that was constrained by in situ surface
 15 observations and satellite retrievals of column-averaged CH₄ mixing ratios. It should be
 16 noted that optimized emissions from inverse model studies depend on the a priori
 17 estimates of emissions and the observational constraints, and realistic estimates of
 18 uncertainties are still a challenge. For example, despite the small uncertainties given in
 19 the table for termite emissions, emissions from this sector varied from ~31 to 67 Tg yr⁻¹
 20 over the range of scenarios tested, which is a larger range than the uncertainties in the
 21 table would imply. While total global emissions are fairly well constrained by this
 22 combination of measurements and lifetime, individual source terms still have relatively
 23 large uncertainties.

24
 25 Table 5.1. Annual CH₄ emissions by source type (from scenario 3 of *Bergamaschi et al.*,
 26 *2007*).

Source	Emissions (Tg/yr)
Coal	35.6±4.4
Oil and gas	41.8±5.5
Enteric fermentation	82.0±9.6
Rice agriculture	48.7±5.1
Biomass burning	21.9±2.6
Waste	67.0±10.7
Wetlands	208.5±7.6
Wild animals	6.8±2.0
Termites	42.0±6.7
Soil	-21.3±5.8
Oceans	-1.3±2.9
Total	531.6±3.7

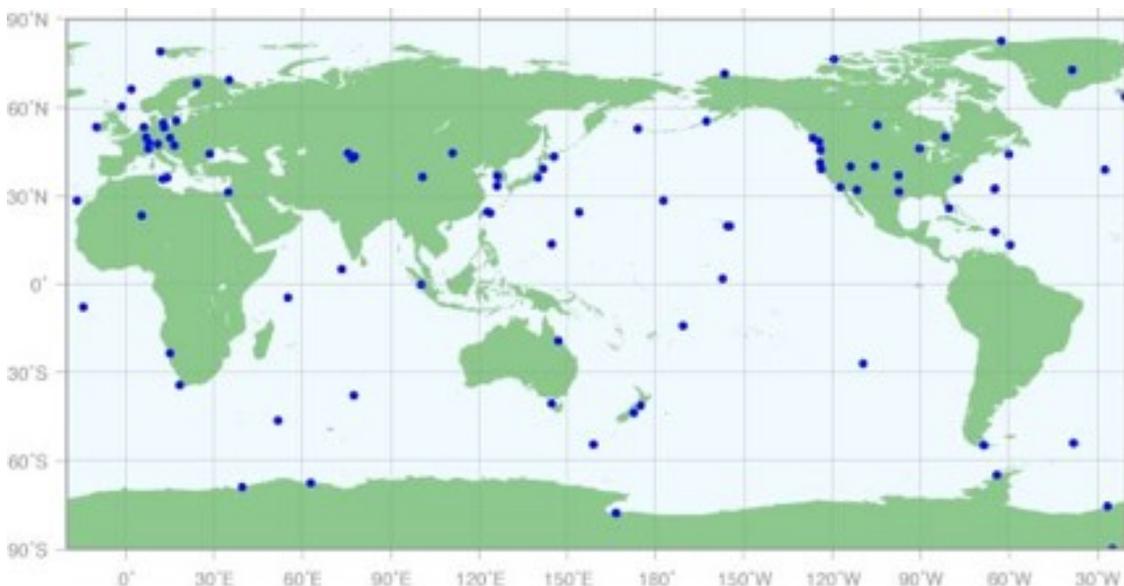
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 28 The constraint on the total modern source strength is important because any new
 29 proposed source (for example a larger than previously identified steady state marine
 30 hydrate source) would have to be balanced by a decrease in the estimated magnitude of
 31 another source. The budget presented in Table 5.1 refers to net fluxes to the atmosphere
 32 only. The gross production of methane is extremely likely to be significantly larger, but
 33 substantial quantities of methane are consumed in soils, oxic freshwater, and the ocean

1 before reaching the atmosphere (Reeburgh, 2004). (The soil sink in Table 5.1 refers
2 only to removal of atmospheric methane by oxidation in soils).

3
4 Given the short CH₄ lifetime (~9 yr), short term changes in methane emissions from
5 climatically sensitive sources such as biomass burning and wetlands, or in sinks, are
6 seen immediately in surface observations of atmospheric methane. As implied above,
7 reaction with methane is one of the major sinks for OH radical (the main methane sink),
8 and therefore increases in methane levels should increase the lifetimes of methane and
9 other long-lived greenhouse gases consumed by OH. Higher methane emissions mean
10 increased methane lifetimes, which in turn means that the impact of any short-term
11 increase in methane emissions will last longer.

12 13 **1.4 Observational network and its current limitations, particularly relative to the** 14 **hydrate, permafrost and arctic wetland sources**

15 The network of air sampling sites where atmospheric methane mixing ratios are
16 measured can be viewed on the World Meteorological Organization (WMO), World
17 Data Centre for Greenhouse Gases (WDCGG) Web site
18 (<http://gaw.kishou.go.jp/wdcgg/>) and is reproduced in Figure 5.2. Methane data have
19 been reported to the WDCGG for ~130 sites. Relatively few measurements are reported
20 for the Arctic, and sites are typically far from potential permafrost, hydrate, and wetland
21 sources. Existing Arctic sites have been used to infer decreased emissions from the
22 fossil-fuel sector of the Former Soviet Union (Dlugokencky et al., 2003) and provide
23 boundary conditions for model studies of emissions, but they are too remote from source
24 regions to accurately quantify emissions, so uncertainties on northern emissions will
25 remain large until more continuous measurement sites are added close to sources. The
26 optimal strategy would include continuous measurements from tall towers and vertical
27 profiles collected from aircraft. Measurements from tall towers are influenced by
28 emissions from much larger areas than eddy-correlation flux techniques, which have
29 footprints on the order of 1 km² (one square kilometer). When combined with global- or
30 regional-scale models, these measurements can be used to quantify fluxes; the vertical
31 profiles would be used to assess the quality of the model results through the troposphere.
32



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2 **Figure 5.2. Global network of monitoring sites (blue dots) for long-term observations**
3 **of atmospheric methane** (<http://gaw.kishou.go.jp/wdcgg/>).
4

5 **1.5 Abrupt Changes in Atmospheric Methane?**

6 Concern about abrupt changes in atmospheric methane stem largely from the
7 massive amounts of methane present as solid methane hydrate in ocean sediments and
8 terrestrial soils, which may become unstable in the face of future warming. Methane
9 hydrate is a solid substance that forms at low temperatures and high pressures in the
10 presence of sufficient methane, and is found primarily in marine continental margin
11 sediments and some arctic terrestrial sedimentary deposits (see Box 1). Warming or
12 release of pressure can destabilize methane hydrate, forming free gas that may ultimately
13 be released to the atmosphere. The processes controlling hydrate stability and gas
14 transport are complex, and only partly understood. Estimates of the total amount of
15 methane hydrate vary widely, from 500 to 10,000 gigatons of carbon (GtC) total stored
16 as methane in hydrates in marine sediments, and 7.5 to 400 GtC in permafrost (both
17 figures are uncertain, see section 4 below). The total amount of carbon in the modern
18 atmosphere is ~730 GtC, but the total methane content of the atmosphere is only ~5 GtC
19 (Dlugokencky et al., 1998). Therefore, even a release of a small portion of the methane
20 hydrate reservoir to the atmosphere could have a substantial impact on radiative forcing.
21

22 **Box 1: Chemistry, physics, and occurrence of methane hydrate**

23 A clathrate is a substance in which a chemical lattice of one type of molecule
24 traps another type of molecule. A clathrate hydrate is a solid gas hydrate in which gas
25 molecules are trapped in a lattice of water molecules (Figure 5.3). The potential
26 importance of methane hydrate to abrupt climate change results from the fact that large
27 amounts of methane can be stored in a relatively small volume of solid hydrate. For
28 example, 1 cubic meter (m^3) of gas hydrate is equivalent to 164 m^3 of free gas (and 0.8
29 m^3 of water) at standard temperature and pressure (*Kvenvolden, 1993*). Naturally
30 occurring clathrate hydrate on Earth is primarily methane hydrate and forms under high
31 pressure – low temperature conditions in the presence of sufficient methane. These

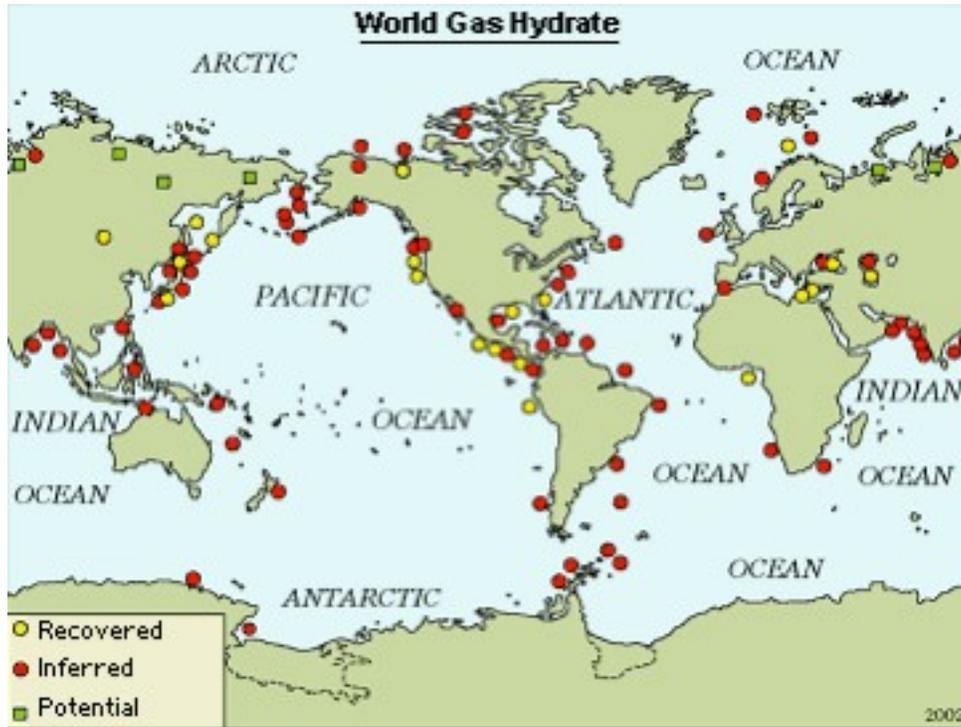
1 conditions are most often found in relatively shallow marine sediments on continental
2 margins but also in some high latitude soils (Figure 5.4). Although the amount of
3 methane stored as hydrate in geological reservoirs is not known, it is clear that very
4 large amounts are sequestered, particularly when compared to the present total
5 atmospheric methane burden.

6
7 The right combination of pressure and temperature conditions forms what is
8 known as the hydrate stability zone, shown schematically in Figure 5.5. In marine
9 sediments pressure and temperature both increase with depth, creating a relatively
10 narrow region where methane hydrate is stable. Whether or not methane hydrate forms
11 depends not only on temperature and pressure but on the amount of methane present.
12 The latter constraint limits methane hydrate formation to locations of significant
13 biogenic or thermogenic methane (*Kvenvolden, 1993*). When ocean bottom water
14 temperatures are near 0°C hydrates can form at shallow depths, below ~200 m water
15 depth, if sufficient methane is present. The upper limit of the hydrate stability zone can
16 therefore be at the sediment surface, or deeper in the sediment, depending on pressure
17 and temperature. The stability zone thickness increases with water depth in typical ocean
18 sediments. It is important to note, however, that most marine methane hydrates are
19 found in shallower water near continental margins, in areas where the organic carbon
20 content of the sediment is sufficient to fuel methanogenesis. In soils hydrate can form at
21 depths of ~200 m and deeper, in regions where surface temperatures are cold enough
22 that temperatures at 200 m are within the hydrate stability zone.



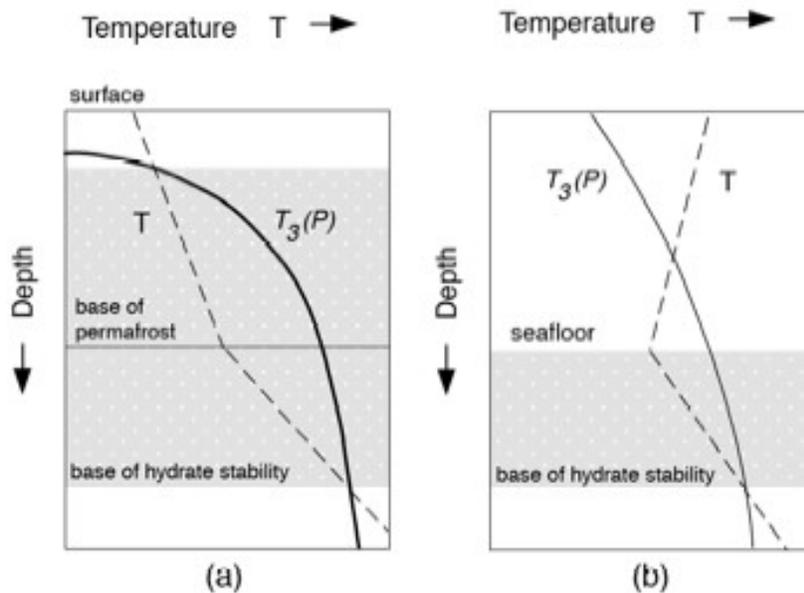
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25 **Figure 5.3. Photograph of methane hydrate as nodules, veins, and laminae in**
26 **sediment. Source:**
27 **http://geology.usgs.gov/connections/mms/joint_projects/methane.htm.**

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



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Figure 5.5. Schematic diagram of hydrate stability zone from Buffet (2000). Dashed lines show temperature profiles with depth, and $T_3(P)$ bounds the region where hydrate is stable in three phase equilibrium (Buffet, 2000). The gray shading indicates the hydrate stability zone. Figure from Buffet (2000).

1 Massive releases of methane from marine or terrestrial hydrates have not been
2 observed. Evidence from the ice core record indicates that abrupt shifts in methane
3 concentration have occurred in the past 110,000 years (Chappellaz et al., 1993; Brook et
4 al., 1996; 2000), although the concentration changes during these events were relatively
5 small. Farther back in geologic time, an abrupt warming at the Paleocene-Eocene
6 boundary about 55 million years ago has been attributed by some to a large release of
7 methane to the atmosphere, although other explanations may fit the data better (see
8 discussion in section 4). These past abrupt changes are discussed in detail below, but
9 their existence provides further motivation for considering the potential for future abrupt
10 changes in methane.

11
12 The large impact of a substantial release of methane hydrates to the atmosphere, if it
13 were to occur, coupled with the potential for a more steady increase in methane
14 production from melting hydrates and from wetlands in a warming climate, motivates
15 several questions this chapter attempts to address:

- 16
17 1) What is the volume of methane in terrestrial and marine sources and how much of it
18 is likely to be released if climate warms in the near future?
- 19 2) What is the impact on the climate system of the release of varying quantities of
20 methane over varying intervals of time?
- 21 3) What is the evidence in the past for abrupt climate change caused by massive
22 methane release?
- 23 4) What conditions (in terms of sea level rise and warming of bottom waters) would
24 allow methane release from hydrates locked up in sea floor sediments?
- 25 5) How much methane is likely to be released by warming of northern high-latitude
26 soils, sea level rise, and other climate driven changes in wetlands?
- 27 6) What are the observational and modeling requirements necessary to understand
28 methane storage and its release under various future scenarios of abrupt climate change?

29 30 **2. History of Atmospheric Methane**

31 Over the last ~300 years the atmospheric methane mixing ratio increased from
32 ~700-750 ppb (parts per billion) in 1700 AD to a global average of ~1775 ppb in 2006.
33 Direct atmospheric monitoring has been conducted in a systematic way only since the
34 late-1970s, and data for previous times come primarily from ice cores (Figure 6).
35 Current levels of methane are anomalous with respect to the long-term ice core record,
36 which now extends back to 650,000 years (*Spahni et al., 2005*). There are no direct
37 constraints on methane levels beyond 800,000 years, the age at the bottom of the oldest
38 ice core now available (European Project for Ice Coring in Antarctica (EPICA) Dome C
39 ice core). New international plans to drill at a very low accumulation rate site in
40 Antarctica may in the future extend the record to 1.5 million years (Brook and Wolff,
41 2005).
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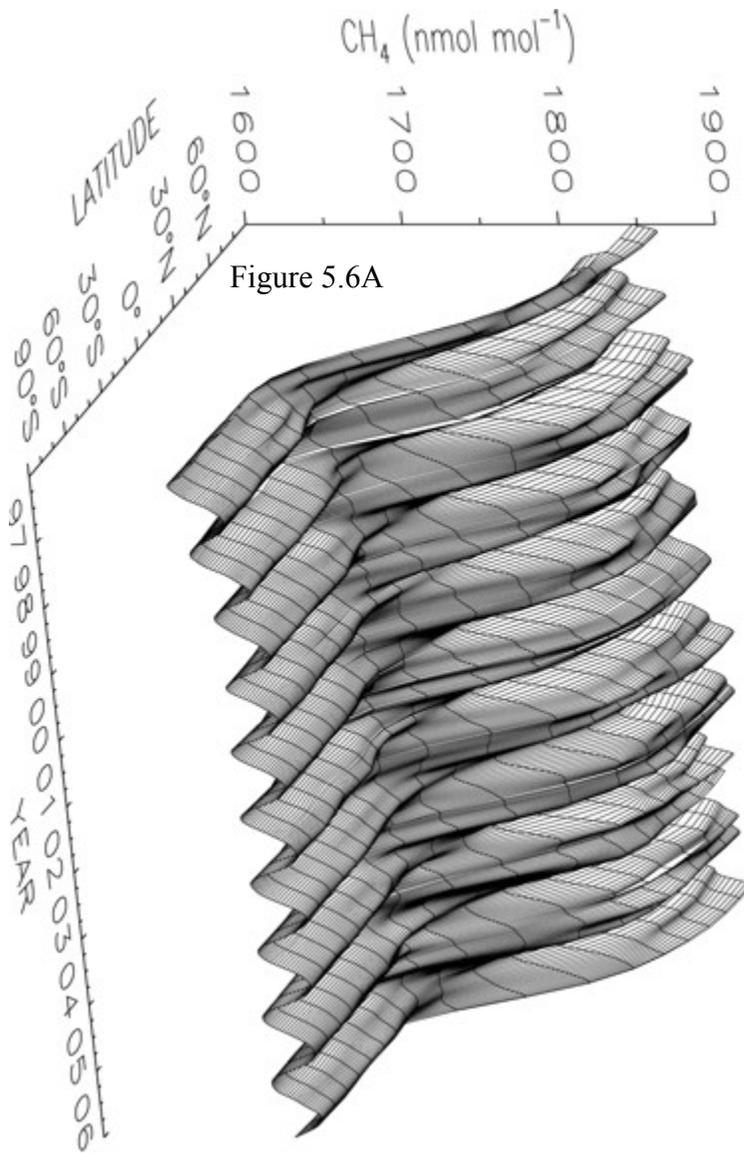
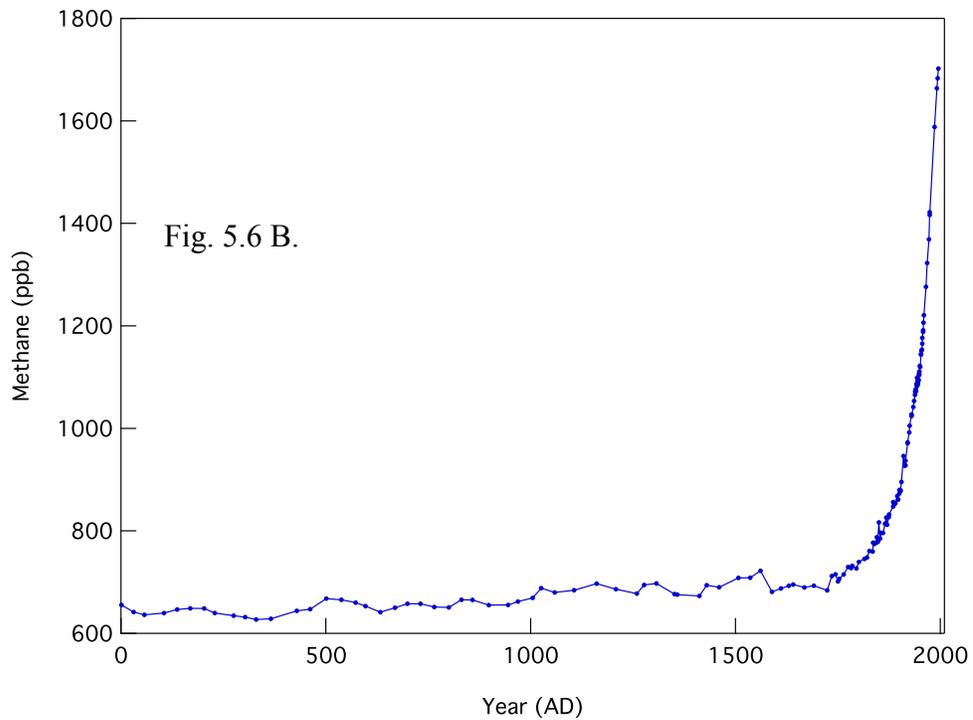


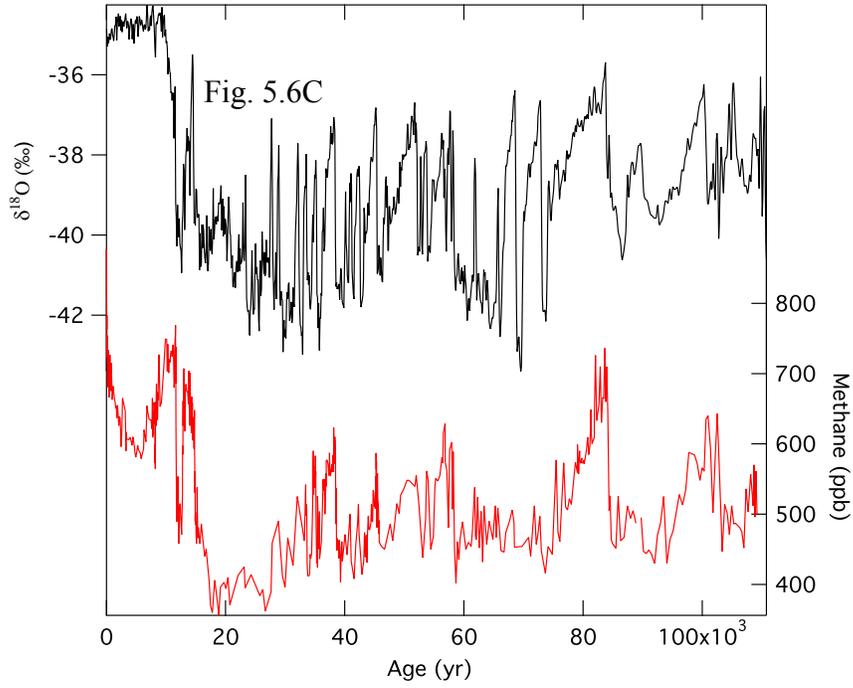
Figure 5.6A

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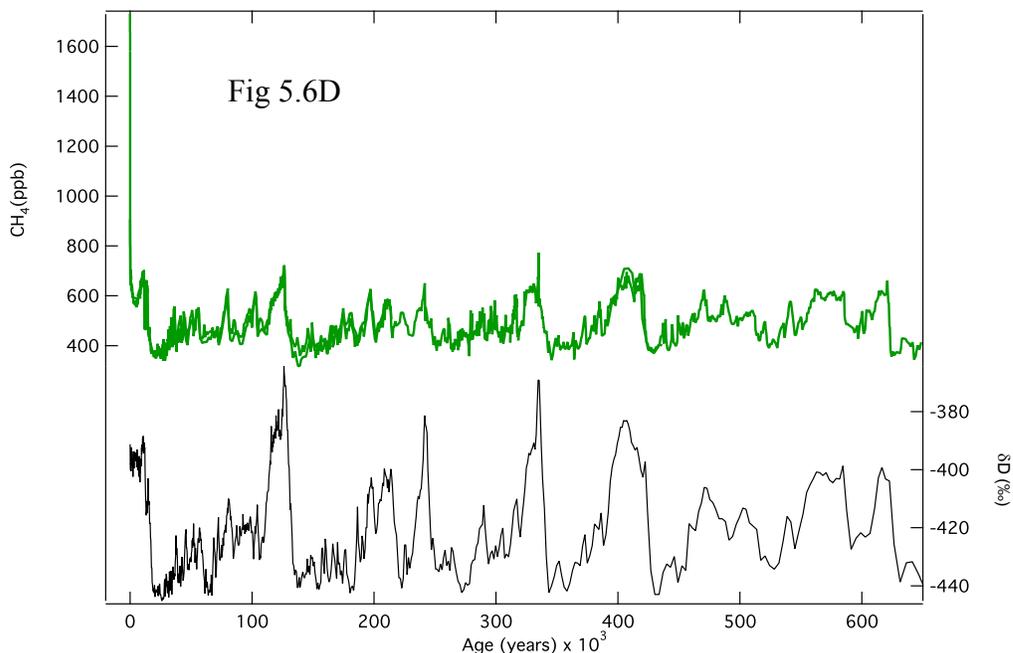


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Figure 5.6. The history of atmospheric methane from ice cores and direct measurements. A. Global representation of seasonal and interannual trends in tropospheric methane and interhemispheric gradient over the last decade from NOAA Global Monitoring Division (GMD) data. B. The last 1000 years from ice cores and direct measurements (MacFarling-Meure et al. (2006) and NOAA GMD 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 for the last 650,000 years from Spahni et al. (2005). Abbreviations: nmol mol⁻¹, nanomoles per mole; ppb, parts per billion by mole (same as nanomoles per mole); ‰, per mil.

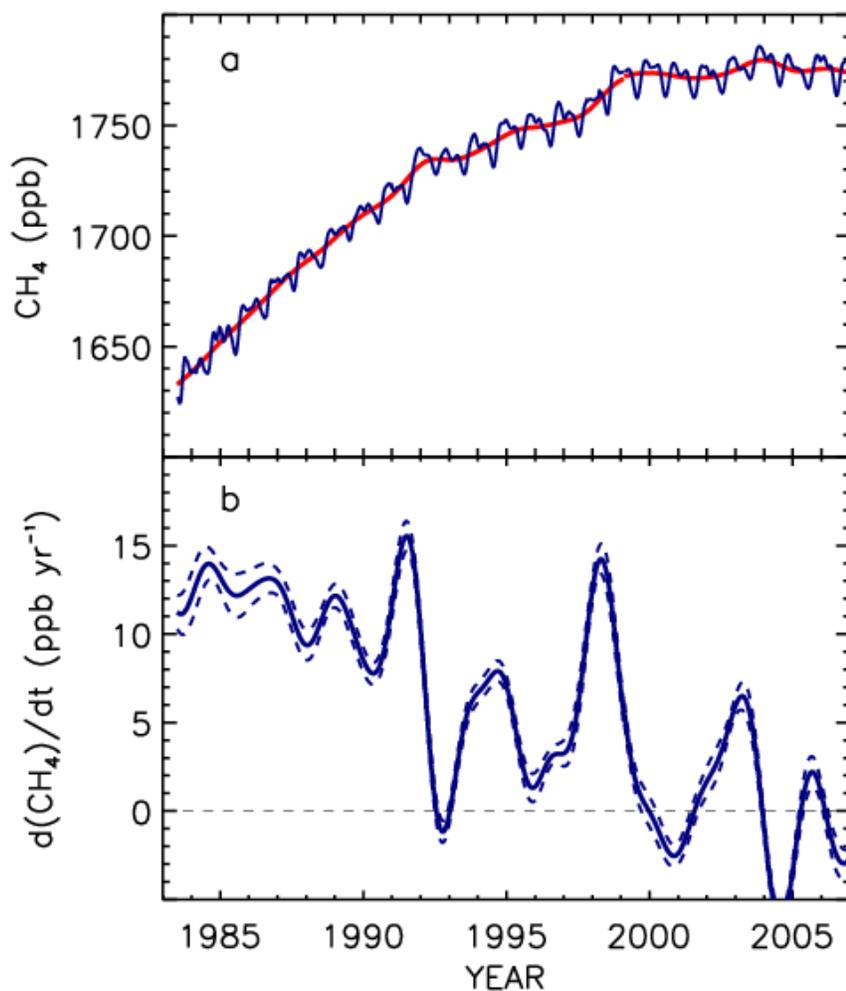
2.1 Direct observations

Early systematic measurements of the global distribution of atmospheric CH₄ 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 CH₄ growth rate was decreasing (Steele et al., 1992), and that, if the CH₄ lifetime were constant, atmospheric CH₄ was approaching steady state where emissions were approximately constant (Dlugokencky et al., 1998). Superimposed on this declining growth rate are significant variations that 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

1 changes in the chemical sink after the eruption of Mt. Pinatubo (Dlugokencky et al.,
 2 1996). Recent measurements show that the global atmospheric CH₄ burden has been
 3 nearly constant since 1999 (Fig. 5.7). This observation is not well understood,
 4 underscoring our lack of understanding of how individual methane sources are changing.

5 Recently published column-averaged CH₄ mixing ratios determined from a
 6 satellite sensor greatly enhance the spatial coverage of CH₄ observations (Frankenberg
 7 et al., 2006). Coverage in the tropics greatly increases measurements there, but coverage
 8 in the Arctic remains poor because of the adverse impact of clouds on the retrievals.
 9 Use of these retrievals in inverse model studies will reduce uncertainties in emissions
 10 estimates, particularly in the tropics.

11



12

13 **Figure 5.7. Recent trends in atmospheric methane from global monitoring data**
 14 **(NOAA, Earth System Research Laboratory, ESRL). A: Global average atmospheric**
 15 **methane mixing ratios (blue line) determined using measurements from the GMD**
 16 **cooperative air sampling network. The red line represents the long term trend. B:**
 17 **Global average growth rate for methane.**

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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 on these time scales 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.

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., 1993; 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 at the onset of abrupt warming in Greenland lags, or is coincident with, the warming, with lags of several decades at most (*Severinghaus et al., 1998; Severinghaus and Brook, 1999; Huber et al., 2006*). Methane closely follows the Greenland ice isotopic record (Figure 5.6C) to the extent that methane variations in Antarctic ice cores provide stratigraphic markers for the timing of abrupt warming in Greenland, allowing precise comparison of climate records from both polar regions (e.g., *Blunier and Brook, 2001; Brook et al., 2005; EPICA Members, 2006*). 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 *Fliückiger 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. 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, and marine and lake sediment records support enhanced monsoon rainfall in some tropical and subtropical regions, apparently associated with 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*).

1 The wetland hypothesis has been challenged by authors calling attention to the large
2 marine and terrestrial hydrate reservoir, and uncertainty about the extent of wetland
3 regions during the ice age (*Kennett et al., 2003; Nisbet, 2002*). The challenge was most
4 extensively developed by *Kennett et al. (2003)* who postulated that the abrupt shifts in
5 methane were in fact caused by abrupt release of methane from methane hydrates in sea
6 floor sediments on continental margins. This hypothesis originated from observations
7 of negative carbon isotope excursions in marine sediment records in the Santa Barbara
8 basin, which appear to have coincided with the onset of abrupt warming in Greenland
9 and increases in atmospheric methane in the ice core record. The “clathrate gun
10 hypothesis” postulates that millennial scale abrupt warming during the last ice age was
11 actually driven by atmospheric methane from hydrate release, and further speculates on
12 a central role for methane in causing late Quaternary climate change. Proponents of the
13 clathrate gun hypothesis maintain that wetlands were not extensive enough during the
14 ice age to be the source of the abrupt variations in methane in the ice core record. The
15 clathrate gun hypothesis is important for understanding the future potential for abrupt
16 changes in methane – concern for the future would be warranted if it could be
17 demonstrated that the clathrate reservoir was unstable on the time scale of abrupt late
18 Quaternary climate change.

19
20 The clathrate gun hypothesis as an explanation for late Quaternary methane cycles
21 faces several challenges, elaborated further in section 4. First, the radiative forcing of
22 the small variations in atmospheric methane burden during the ice age should have been
23 quite small (*Brook et al., 2000*) although it has been suggested that impacts on
24 stratospheric water vapor may have increased the greenhouse power of these small
25 methane variations (*Kennett et al., 2003*). Second, the ice core record clearly shows that
26 the abrupt changes in methane lagged the abrupt temperature changes in the Greenland
27 ice core record, albeit by only decades (*Severinghaus et al., 1998; Severinghaus and
28 Brook, 1999; Huber et al., 2006; Grachev et al., 2007*). These observations imply that
29 methane is a feedback rather than a cause of warming, ruling out one aspect of the
30 clathrate gun hypothesis (hydrates as trigger), but they do not constrain the cause of the
31 abrupt shifts in methane. Third, isotopic studies of ice core methane do not support
32 methane hydrates as a source for abrupt changes in methane (*Sowers, 2006; Schaefer et
33 al., 2006*). The strongest constraints come from hydrogen isotopes (*Sowers, 2006*) and
34 are described further in section 4. Fourth, recent work indicates that previous
35 assumptions about the development of wetlands, particularly in the circum-arctic region,
36 were hampered by a lack of data. It was previously believed that peatlands did not
37 develop until some time in the early Holocene, making it difficult to explain abrupt
38 changes in methane with emissions from northern wetlands. A recent compilation of
39 basal peat ages in the circum-arctic by *MacDonald et al. (2006)* clearly shows, however,
40 that peatland development started at ~16,000 years ago, supporting a role for wetlands in
41 abrupt changes in methane between 16,000 and 10,000 years ago (Fig. 5.6C). The
42 coincidence of peatland development and the higher Northern Hemisphere summer
43 insolation of late glacial and early Holocene time supports the hypothesis that such
44 wetlands were methane sources at previous times of higher Northern Hemisphere
45 summer insolation (*MacDonald et al., 2006*), for example during the last ice age or at
46 previous glacial-interglacial transitions (*Brook et al., 1996; 2000*).

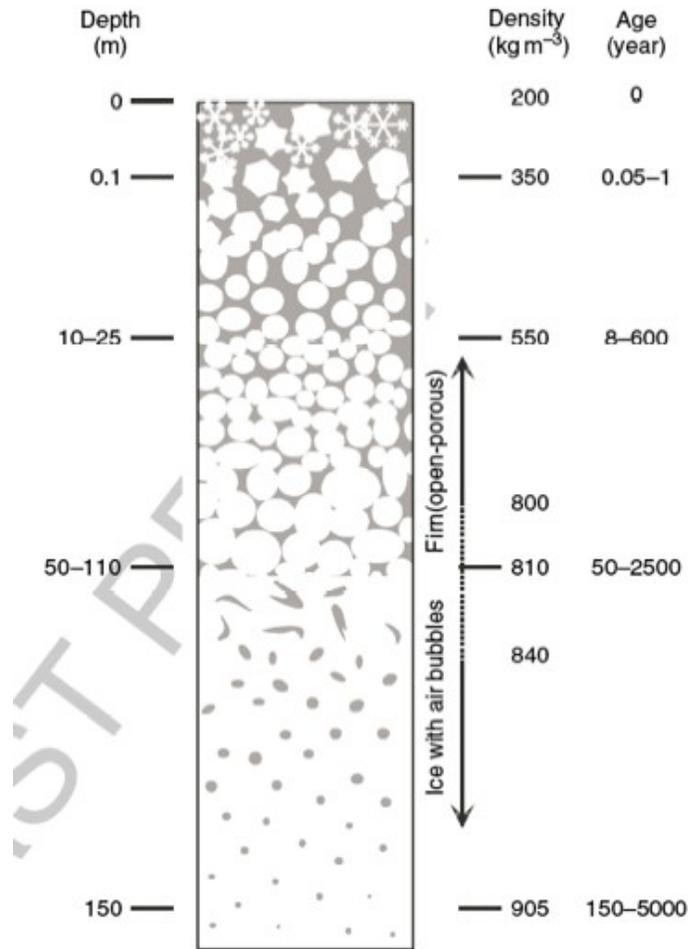
1 Box 2: The ice core record and its fidelity in capturing abrupt events.

2 Around the time of discovery of the abrupt, but small, changes in methane in the
3 late Quaternary ice core records (Fig. 5.6C) (*Chappellaz et al., 1993*) some authors
4 suggested that large releases of methane to the atmosphere might be consistent with the
5 ice core record, given the limits of time resolution of ice core data at that time, and the
6 smoothing of atmospheric records due to diffusion in the snowpack (*e.g., Thorpe et al.,*
7 *1994*). Since that time a large number of abrupt changes in methane in the Greenland
8 ice core record (which extends to ~120,000 years before present) have been sampled in
9 great detail, and no changes greatly exceeding those shown in Fig. 5.6C have been
10 discovered (*Brook et al., 1996; 2000; 2005; Blunier et al., 1998; Blunier and Brook,*
11 *2001; Chappellaz et al., 1997; Severinghaus et al. 1998; Severinghaus and Brook, 1999;*
12 *Huber et al. 2006; EPICA Members, 2006*).

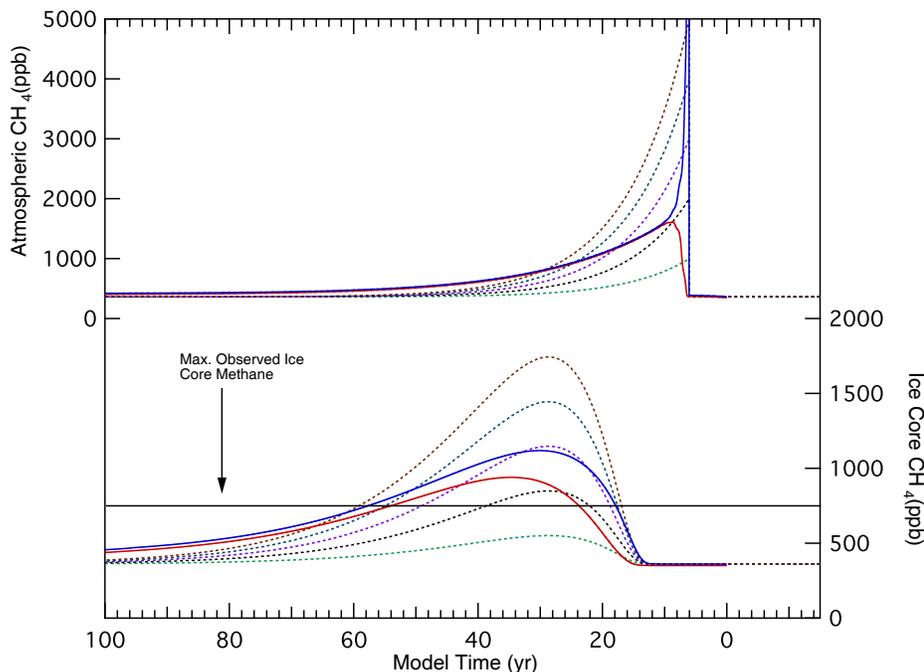
13
14 Could diffusion in the snowpack mask much larger changes? Air is trapped in
15 polar ice at the base of the firn (snowpack) where the weight of the overlying snow
16 transforms snow to ice, and air between the snow grains is trapped in bubbles (Fig. 5.8).
17 The trapped air is therefore younger than the ice it is trapped in (this offset is referred to
18 as the gas age-ice age difference. It is also mixed by diffusion, such that the air trapped
19 at an individual depth interval is a mixture of air of different ages. In addition, bubbles
20 do not close off all at the same depth, so there is additional mixing of air with different
21 ages due to this variable bubble close-off effect. The overall smoothing is somewhat
22 analogous to a Gaussian digital filter, and the width of the filter depends on the
23 parameters that control firn thickness, densification, and diffusion – primarily
24 temperature and snow accumulation rate.

25
26 *Spahni et al. (2003)* used the firn model of *Schwander et al. (1993)* to obtain a
27 smoothing function for the Greenland Ice Core Project (GRIP) ice core in Greenland for
28 the late Holocene, which has a Gaussian shape with width at half-height of about 20
29 years. This result is consistent with previous work by *Brook et al. (2000)* for the
30 Greenland Ice Sheet Project (GISP2) ice core who examined the impact of smoothing on
31 abrupt changes in methane in the Greenland ice core record. (GISP2 and GRIP are in
32 similar glaciological environments and their firn characteristics are very similar). *Brook*
33 *et al. (2000)* examined a variety of scenarios for abrupt changes in methane, including
34 those proposed by *Thorpe et al. (1994)* and compared what the ice core record would
35 record of those events with high resolution data for several abrupt shifts in methane (Fig.
36 5.9).

37
38 Two aspects of the ice core record argue against abrupt, catastrophic releases of
39 methane to the atmosphere as an explanation of the ice core record. First, the abrupt
40 shifts in methane concentration take place on time scales of centuries, whereas
41 essentially instantaneous releases would be recorded in the Greenland ice core record as
42 more abrupt events (Fig. 5.9). While this observation says nothing about the source of
43 the methane, it does indicate that the ice core record is not recording an essentially
44 instantaneous atmospheric change (*Brook et al., 2000*). Second, the maximum levels of
45 methane reached in the ice core record are not consistent with extremely large changes
46 in the atmospheric methane concentration.



1
 2 *Figure 5.8 about here. The firn column of a typical site on a polar ice sheet, from*
 3 *Schwander (2006).*
 4



1
2 **Figure 5.9.** Model simulations of smoothing instantaneous release of methane from
3 clathrates to the atmosphere and the ice core response to those events. The ice core
4 response was calculated by convolving the atmospheric histories in the top panel
5 with a smoothing function appropriate for the GISP2 ice core. The solid lines are the
6 atmospheric history and smoothed result for the model of a 4,000 teragram release of
7 methane from Thorpe et al. (2004). The heavy solid line represents release in the
8 Northern Hemisphere, and the thin solid line is the Southern Hemisphere history for
9 that event. From Brook et al. (2000).

10 3. Potential Mechanisms for future abrupt changes in atmospheric methane

11 Three categories of mechanism are considered here as potential causes of abrupt
12 changes in atmospheric methane in the near future large enough to cause abrupt climate
13 change. We focus on the following climate driven processes that could in principle
14 increase methane emissions from natural sources on time scales of decades to centuries.
15 Sections 4-6 discuss these processes in more detail.
16

17 3.1 Destabilization of marine methane hydrates

18 This issue is probably the most well known due to extensive research on the
19 occurrence of methane hydrates in marine sediments, and the large quantities of methane
20 apparently present in this solid phase in primarily continental margin marine sediments.
21 Destabilization of this solid phase requires mechanisms for warming the deposits and/or
22 reducing pressure on the appropriate time scale, transport of free methane gas to the
23 sediment-water interface, and transport to the atmosphere (see Box 5.1). There are a
24 number of physical impediments to abrupt release, in addition to the fact that bacterial
25

1 methanotrophy consumes methane in oxic sediments and the ocean water column.
2 Warming of bottom waters, slope failure, and their interaction are the most commonly
3 discussed mechanisms for abrupt release.
4

5 **3.2 Destabilization of permafrost hydrates**

6 Hydrate deposits at depth in permafrost soils are known to exist, and although
7 their extent is uncertain, the total amount of methane in permafrost hydrates appears to
8 be much smaller than in marine sediments. Surface warming eventually would increase
9 melting rates of permafrost hydrates. Inundation of some deposits by warmer seawater
10 and lateral invasion of the coastline are also concerns and may be mechanisms for more
11 rapid change.
12

13 **3.3 Changes in wetland extent and methane productivity**

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

23 In addition, although northern high-latitude wetlands seem particularly sensitive
24 to climate change, the largest natural source of methane to the atmosphere is from
25 tropical wetlands, and methane emissions there may also be sensitive to future changes
26 in temperature and precipitation. Modeling studies addressing this issue are therefore
27 also included in our discussion.
28

29 **4.2 Impact of Temperature Change on Marine Methane Hydrates**

30 **4.2.1 Propagation of temperature change to the hydrate stability zone**

31 The time dependence of changes in the inventory of methane in the hydrate
32 reservoir depends on the time scale of warming and chemical diffusion. There is
33 evidence from paleotracers (*Martin et al.*, 2005) and from modeling (*Archer et al.*,
34 2004) that the temperature of the deep sea is sensitive to the climate of the Earth's
35 surface. In general, the time scale for changing the temperature of the ocean increases
36 with depth, reaching a maximum of about a thousand years for the abyssal ocean. This
37 means that abrupt changes in temperature at the surface ocean would not be transmitted
38 immediately to the deep sea. There are significant regional variations in the ventilation
39 time of the ocean, and in the amount of warming that might be expected in the future.
40 The Arctic is expected to warm particularly strongly, because of the albedo feedback
41 from the melting Arctic ice cap. Temperatures in the North Atlantic appear to be
42 sensitive to changes in ocean circulation such as during rapid climate change during the
43 last ice age (*Dansgaard et al.*, 1989).
44
45

1 The top of the hydrate stability zone is at 200 to 600 m water depth, depending
2 mainly on the temperature of the water column. Within the sediment column,
3 temperature increases with depth along the geothermal temperature gradient, 30-50° C /
4 km (*Harvey and Huang, 1995*). The shallowest sediments that could contain hydrate
5 only have a thin hydrate stability zone, and the stability zone thickness increases with
6 water depth. A change in the temperature of the deep ocean will act as a change in the
7 upper boundary condition of the sediment temperature profile. Warming of the
8 overlying ocean may not put surface sediments into undersaturation, but the warmer
9 overlying temperature propagates downward until a new profile with the same
10 geothermal temperature gradient can be established. How long this takes is a strong
11 (second order) function of the thickness of the stability zone, but the time scales are in
12 general long. In 1,000 years the temperature signal should have propagated about 180 m
13 in the sediment. In steady state, an increase in ocean temperature will decrease the
14 thickness of the stability zone. *Dickens (2001b)* calculated that the volume of the
15 stability zone ought to decrease by about half with a temperature increase of 5° C.
16

17 **4.2.2 Impact on stratigraphic-type deposits**

18 After an increase in temperature of the overlying water causes hydrate to melt at
19 the base of the stability zone, the fate of the released methane is difficult to predict. The
20 increase in pore volume and pressure could provoke gas migration through the stability
21 zone or a landslide, or the bubbles could remain enmeshed in the sediment matrix.
22 Hydrate moves down to the base of the stability zone by the accumulation of overlying
23 sediment at the sea floor, so melting of hydrate at the stability zone takes place
24 continuously, not just in association with ocean warming.
25

26 When hydrate melts, most of the released methane goes into the gas phase to
27 form bubbles, assuming that the porewaters were already saturated in dissolved
28 methane. The fate of the new bubbles could be to remain in place, to migrate, or to
29 diffuse away and react chemically, and it is difficult to predict which will occur. The
30 potential for gas migration through the stability zone is one of the more significant
31 uncertainties in forecasting the ocean hydrate response to anthropogenic warming
32 (*Harvey and Huang, 1995*).
33

34 In cohesive sediments, bubbles expand by fracturing the sediment matrix,
35 resulting in elongated shapes (*Boudreau et al., 2005*). Bubbles tend to rise because they
36 are less dense than the water they are surrounded by, even at the 200+ atmosphere
37 pressures in sediments of the deep sea. If the pressure in the gas phase exceeds the
38 lithostatic pressure in the sediment, fracture and gas escape can occur (*Flemings et al.,*
39 *2003*). Modeled and measured (*Dickens et al., 1997*) porewater pressures in the
40 sediment column at Blake Ridge approach lithostatic pressures, indicating that new gas
41 bubbles added to the sediment might be able to escape to the overlying water by this
42 mechanism.
43

44 There is a differential-pressure mechanism which begins to operate when the
45 bubbles occupy more than about 10% of the volume of the pore spaces (*Hornbach et al.,*
46 *2004*). If a connected bubble spans a large enough depth range, the pressure of the

1 porewater will be higher at the bottom of the bubble than it is at the top, because of the
2 weight of the porewater over that depth span. The pressure inside the bubble will be
3 more nearly constant over the depth span, because the compressed gas is not as dense as
4 the porewater is. This will result in a pressure gradient at the top and the bottom of the
5 bubble, tending to push the bubble upward. *Hornbach et al.* (2004) postulated that this
6 mechanism might be responsible for allowing methane to escape from the sediment
7 column, and calculated the maximum thickness of an interconnected bubble zone, before
8 the bubbles would break through the overlying sediment column. In their calculations,
9 and in stratigraphic deposits (they refer to them as “basin settings”) the thickness of the
10 bubble column increases as the stability zone gets thicker. It takes more pressure force
11 to break through a thicker stability zone, so a taller column of gas is required. In
12 compressional settings, where the dominant force is directed sideways by tectonics,
13 rather than downward by gravity, the bubble layer is never as thick, reflecting an easier
14 path to methane escape.

15
16 Multiple lines of evidence indicate that gas can be transported through the
17 hydrate stability zone, without freezing into hydrate. Seismic studies at Blake Ridge
18 have observed the presence of bubbles along faults in the sediment matrix (*Taylor et al.*,
19 2000). Faults have been correlated with sites of methane gas emission from the sea floor
20 (*Aoki et al.*, 2000; *Zuhlsdorff and Spiess*, 2004; *Zuhlsdorff et al.*, 2000). Seismic studies
21 often show “wipeout zones” where the bubble zone beneath the hydrate stability zone is
22 missing, and all of the layered structure of the sediment column within the stability zone
23 is smoothed out. These are interpreted to be areas where gas has broken through the
24 structure of the sediment to escape to the ocean (*Hill et al.*, 2004; *Riedel et al.*, 2002;
25 *Wood et al.*, 2002). Bubbles associated with seismic wipeout zones are observed within
26 the depth range which should be within the hydrate stability zone, assuming that the
27 temperature of the sediment column is the steady-state expression of the local average
28 geothermal gradient (*Gorman et al.*, 2002). This observation has been explained by
29 assuming that upward migration of the fluid carries with it heat, maintaining a warm
30 channel where gas can be transported through what would otherwise be
31 thermodynamically hostile territory (*Taylor et al.*, 2000; *Wood et al.*, 2002).

32
33 The sediment surface of the world’s ocean has holes in it called pockmarks (*Hill*
34 *et al.*, 2004; *Hovland and Judd*, 1988), interpreted to be the result of catastrophic or
35 continuous escape of gas to the ocean. Pockmarks off Norway are accompanied by
36 authigenic carbonate deposits associated with anaerobic oxidation of methane (*Hovland*
37 *et al.*, 2005). Pockmarks range in size from meters to kilometers (*Hovland et al.*, 2005),
38 with one 700-km² example on the Blake Ridge (*Kvenvolden*, 1999). If the Blake Ridge
39 pockmark is the result of a catastrophic explosion, it might have released less than 1GtC
40 as methane (assuming a 500-m-thick layer of 4% methane yields 1 GtC). Since each
41 individual pockmark releases a small amount of methane relative to the atmospheric
42 inventory, pockmark methane release could impact climate as part of the ongoing
43 “chronic” methane source to the atmosphere, if the frequency of pockmark eruptions
44 increased. Pockmarks do not represent “catastrophic” methane releases.

45

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

15
16 Warming temperatures or sea level changes may trigger the melting of hydrate
17 deposits, provoking landslides (*Driscoll et al.*, 2000; *Kvenvolden*, 1999; *Vogt and Jung*,
18 2002). *Paul* (1978) calculates that landslides can release up to about 5 GtC as methane,
19 enough to alter the radiative forcing by about 0.2 watts per square meter (W/m^2). The
20 origin of these estimates is discussed in the section on the Storegga Landslide.

21 22 **4.2.3 Impact on structural-type hydrate deposits**

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

32
33 The Gulf of Mexico is basically a leaky oil field (*MacDonald et al.*, 2004;
34 *Macdonald et al.*, 1994; *MacDonald et al.*, 2002; *Milkov and Sassen*, 2000; *Milkov and*
35 *Sassen*, 2001; *Milkov and Sassen*, 2003; *Sassen et al.*, 2001a; *Sassen and MacDonald*,
36 1994; *Sassen et al.*, 2003). Natural oil seeps leave slicks on the sea surface that can be
37 seen from space. Large chunks of methane hydrate have been found on the sea floor in
38 contact with seawater (*Macdonald et al.*, 1994). One of the three chunks they saw had
39 vanished when they returned a year later; presumably it had detached and floated away.

40
41 *Collett and Kuuskraa* (1998) estimate that 500 GtC might reside as hydrates in
42 the Gulf sediments, but *Milkov* (2001) estimates only 5 GtC. In the Community Climate
43 System Model (CCSM) under doubled CO_2 (after 80 years of 1%/year CO_2 increase,
44 from C. Bitz, personal communication, [year]), waters at 500 m depth in the Gulf warm
45 about 0.75° C, and 0.2° at 1,000 m. In situ temperatures at 500 m are much closer to the
46 hydrate melting temperature, so the relative change in the saturation state is much more

1 significant at 500 m than deeper. The equilibrium temperature change in the deep ocean
2 to a large, 5,000 GtC fossil fuel release could be 3° C (*Archer et al.*, 2004). *Milkov and*
3 *Sassen* (2003) subjected a two-dimensional model of the hydrate deposits in the Gulf to
4 a 4°C temperature increase and predicted that 2 GtC from hydrate would melt.
5 However, there are no observations to suggest that methane emission rates are currently
6 accelerating. *Sassen et al.* (2001b) find no molecular fractionation of gases in near-
7 surface hydrate deposits that would be indicative of partial dissolution, and suggest that
8 the reservoir may in fact be growing.

9
10 Other examples of structural deposits include the summit of Hydrate Ridge
11 (*Torres et al.*, 2004; *Trehu et al.*, 2004b) and the Niger Delta (*Brooks et al.*, 2000). The
12 distribution of hydrate at Hydrate Ridge indicates up-dip flow along sand layers
13 (*Weinberger et al.*, 2005). Gas is forced into sandy layers where it accumulates until the
14 gas pressure forces it to vent to the surface (*Trehu et al.*, 2004a). *Trehu et al.* (2004b)
15 estimate that 30-40% of pore space is occupied by hydrate, while gas fractions are 2-4%.
16 Methane emerges to the sea floor with bubble vents and subsurface flows of 1 meter per
17 second, and in regions with bacterial mats and vesicomid clams (*Torres et al.*, 2002).
18 Further examples of structural deposits include the Peru Margin (*Pecher et al.*, 2001)
19 and Nankai Trough (*Nouze et al.*, 2004).

20
21 Mud volcanoes are produced by focused upward fluid flow into the ocean. Mud
22 volcanoes often trap methane in hydrate deposits that encircle the channels of fluid flow
23 (*Milkov*, 2000; *Milkov et al.*, 2004). The fluid flow channels associated with mud
24 volcanoes are ringed with the seismic images of hydrate deposits, with authigenic
25 carbonates, and with pockmarks (*Dimitrov and Woodside*, 2003) indicative of anoxic
26 methane oxidation. *Milkov* (2000) estimates that mud volcanoes contain at most 0.5 GtC
27 of methane in hydrate; about 100 times his estimate of the annual supply.

28 29 **4.2.4 Fate of Methane Released as Bubbles**

30 Methane released from sediments in the ocean may reach the atmosphere
31 directly, or it may dissolve in the ocean. Bubbles are not generally a very efficient
32 means of transporting methane through the ocean to the atmosphere. *Rehder et al.*
33 (2002) compared the dissolution kinetics of methane and argon and found enhanced
34 lifetime of methane bubbles below the saturation depth in the ocean, about 500 m,
35 because a hydrate film on the surface of the methane bubbles inhibited gas exchange.
36 Bubbles dissolve more slowly from petroleum seeps, where oily films on the surface of
37 the bubble inhibit gas exchange, also changing the shapes of the bubbles (*Leifer and*
38 *MacDonald*, 2003). On a larger scale, however, *Leifer et al.* (2000) diagnosed that the
39 rate of bubble dissolution is limited by turbulent transport of methane-rich water out of
40 the bubble stream into the open water column. The magnitude of the surface dissolution
41 inhibition seems small; in the *Rehder et al.* (2002) study, a 2-cm bubble dissolves in 30
42 m above the stability zone, and only 110 m below the stability zone. Acoustic imaging
43 of the bubble plume from Hydrate Ridge showed bubbles surviving from 600-700 m
44 water depth where they were released to just above the stability zone at 400 m
45 (*Heeschen et al.*, 2003). One could imagine hydrate-film dissolution inhibition as a

1 mechanism to concentrate the release of methane into the upper water column, but not
2 really as a mechanism to get methane through the ocean directly to the atmosphere.

3
4 Methane can reach the atmosphere if the methane bubbles are released in waters
5 that are only a few tens of meters deep, as in the case of melting the ice complex in
6 Siberia (*Shakhova et al.*, 2005; *Washburn et al.*, 2005; *Xu et al.*, 2001) or during time
7 periods of lower sea level (*Luyendyk et al.*, 2005). If the rate of methane release is large
8 enough, the rising column of seawater in contact with the bubbles may saturate with
9 methane, or the bubbles can be larger, potentially increasing the escape efficiency to the
10 atmosphere.

11 12 **4.2.5 Fate of Methane Hydrate in the Water Column**

13 Pure methane hydrate is buoyant in seawater, so floating hydrate is another
14 potential way to deliver methane from the sediment to the atmosphere (*Brewer et al.*,
15 2002). In sandy sediment, the hydrate tends to fill the existing pore structure of the
16 sediment, potentially entraining sufficient sediment to prevent the hydrate/sediment
17 mixture from floating, while in fine-grained sediments, bubble and hydrate grow by
18 fracturing the cohesion of the sediment, resulting in irregular blobs of bubbles
19 (*Boudreau et al.*, 2005; *Gardiner et al.*, 2003) or pure hydrate. Brewer et al. (2002) and
20 Paull et al. (2003) stirred surface sediments from Hydrate Ridge using the mechanical
21 arm of a submersible remotely operated vehicle and found that hydrate did manage to
22 shed its sediment load enough to float. Hydrate pieces of 0.1 m survived a 750-m ascent
23 through the water column. Paull et al. (2003) described a scenario for a submarine
24 landslide in which the hydrates would gradually make their way free of the turbidity
25 current comprised of the sediment/seawater slurry.

26 27 **4.2.6 Fate of Dissolved Methane in the Water Column**

28 Methane is unstable to bacterial oxidation in oxic seawater. *Rehder et al.* (1999)
29 inferred a methane oxidation lifetime in the high-latitude North Atlantic of 50 years.
30 Clark et al. (2000) correlated methane emission from Coal Point in California with a
31 methane maximum in the water column extending into the Pacific Ocean. Methane
32 oxidation is faster in the deep ocean near a particular methane source where its
33 concentration is higher (turnover time 1.5 years), than in the surface ocean (turnover
34 time of decades) (*Valentine et al.*, 2001). Water column concentration and isotopic
35 measurements indicate complete water-column oxidation of the released methane at
36 Hydrate Ridge (*Grant and Whiticar*, 2002; *Heeschen et al.*, 2005).

37
38 An oxidation lifetime of 50 years leaves plenty of time for transport of methane gas
39 to the atmosphere. Typical gas-exchange time scales for gas evasion from the surface
40 ocean would be about 3-5 meters per day. A surface mixed layer 100 m deep would
41 approach equilibrium (degas) in about a month. Even a 1,000-m-thick winter mixed
42 layer would degas about 30% during a 3-month winter window. The ventilation time of
43 subsurface waters depends on the depth and the fluid trajectories in the water (*Luyten et*
44 *al.*, 1983), but 50 years is enough time that a significant fraction of the dissolved
45 methane from bubbles might reach the atmosphere before it is oxidized.

46 **4.3 Geologic data relevant to past hydrate release**

4.3.1 Evidence for climate impact of hydrate release in the geologic record

The Storegga Landslide. One of the largest exposed submarine landslides in the ocean is the Storegga Slide in the Norwegian continental margin (*Bryn et al.*, 2005; *Mienert et al.*, 2000; *Mienert 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. 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 BSR (*Bunz and Mienert*, 2004; *Mienert et al.*, 2005; *Zillmer et al.*, 2005a; *Zillmer et al.*, 2005b) corresponding to the base of the hydrate stability zone (HSZ) at 200-300 m, and pockmarks (*Hovland et al.*, 2005) indicating gas expulsion from the sediment.

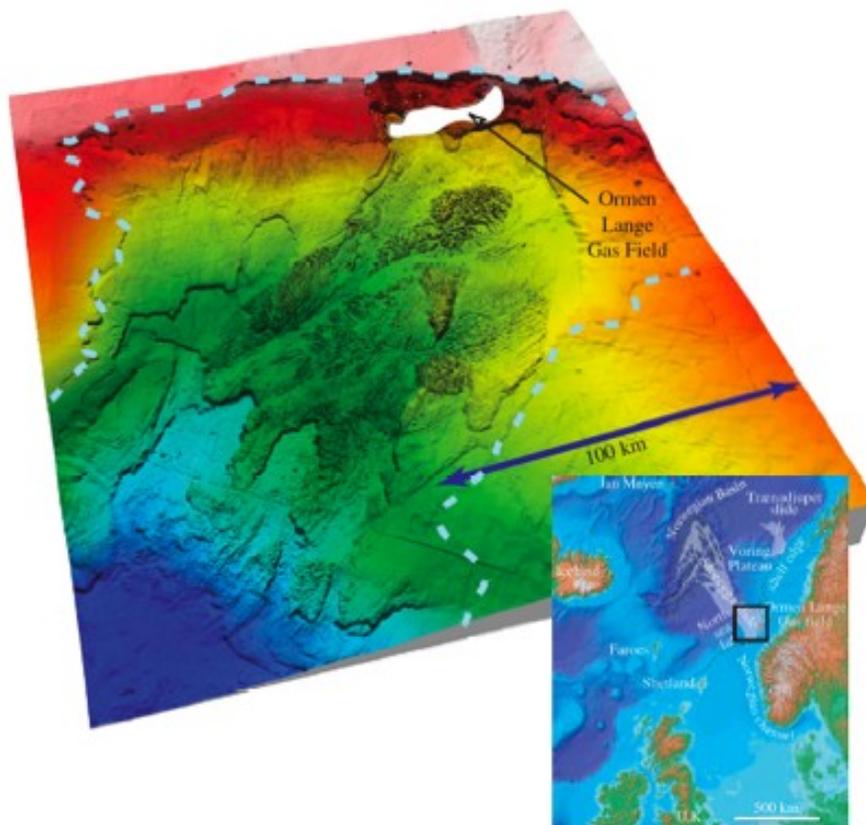


Figure 5.10. Image and map of the Storegga Landslide from Masson et al.(2006). The slide excavated on average the top 250 m of sediment over a swath hundreds of kilometers wide.

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.*,

1 2005). As explained above, rapid sediment loading traps pore water in the sediment
2 column faster than it can be expelled by the increasing sediment load. At some point,
3 the sediment column floats in its own porewater (*Dugan and Flemings, 2000*). This
4 mechanism has the capacity to explain why the Norwegian continental margin, of all
5 places in the world, should have landslides synchronous with climate change.

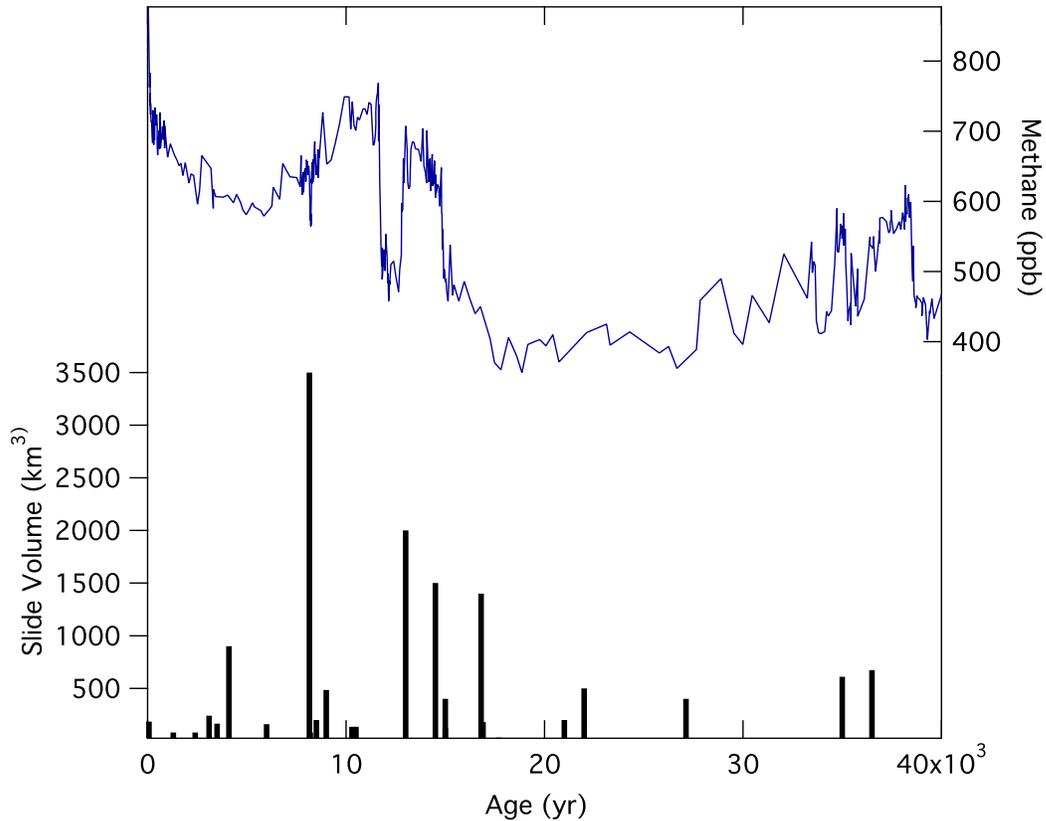
6 The other possibility is the dissociation of methane hydrate deposits by rising
7 ocean temperatures. Rising sea level is also a player in this story, but a smaller one.
8 Rising sea level tends to increase the thickness of the stability zone by increasing the
9 pressure. A model of the stability zone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

23
24 The amount of methane released by the slide can be estimated from the volume
25 of the slide and the potential hydrate content. Hydrate just outside the slide area has
26 been estimated by seismic methods to fill as much as 10% of the porewater volume, in a
27 layer about 50 m thick near the bottom of the stability zone (*Bunz and Mienert, 2004*).
28 If these results were typical of the entire 10^4 km² area of the slide, the slide could have
29 released 1-2 GtC of methane in hydrate. *Paul (1978)* assumed 10% hydrate fraction and
30 predicted 5 GtC methane released.

31
32 If 5 GtC CH₄ reached the atmosphere all at once, it would raise the atmospheric
33 concentration by about 2.5 parts per million (ppm) of methane, relative to a present-day
34 concentration of about 1.7 ppm, trapping about 0.2 W/m² of greenhouse heat, or more
35 considering indirect feedbacks. The methane radiative forcing would subside over a
36 time scale of a decade or so, as the pulse of released methane is oxidized to CO₂, and the
37 atmospheric methane concentration relaxes toward the long-term steady state value. The
38 radiative impact of the Storegga Landslide would then be comparable in magnitude but
39 opposite in sign to the eruption of a large volcano, such as the Mt. Pinatubo eruption (-2
40 W/m²), but it would last for longer (10 years for methane and 2 for a volcano).

41
42 It is tantalizing to wonder if there could be any connection between the Storegga
43 Landslide and the 8.2 kyr climate event (*Alley and Agustsdottir, 2005*), which is
44 presumed to have been triggered by fresh water release to the North Atlantic. However,
45 ice cores record a 0.075 ppm drop in methane concentration during the 8.2 kyr event
46 (*Kobashi et al., 2007*), not a rise. The shutdown of convection in the North Atlantic

1 would have, if anything, cooled the overlying waters. *Maslin et al. (2004)* suggested
 2 that an apparent correlation between the ages of submarine landslides in the North
 3 Atlantic region and methane variations during the deglaciation supported the hypothesis
 4 that clathrate release by this mechanism influenced atmospheric methane. The lack of
 5 response for Storegga, by far the largest landslide known, and a relatively weak
 6 association of other large slides with increased methane levels, however, make this a
 7 fairly tentative argument (Fig. 5.11).
 8

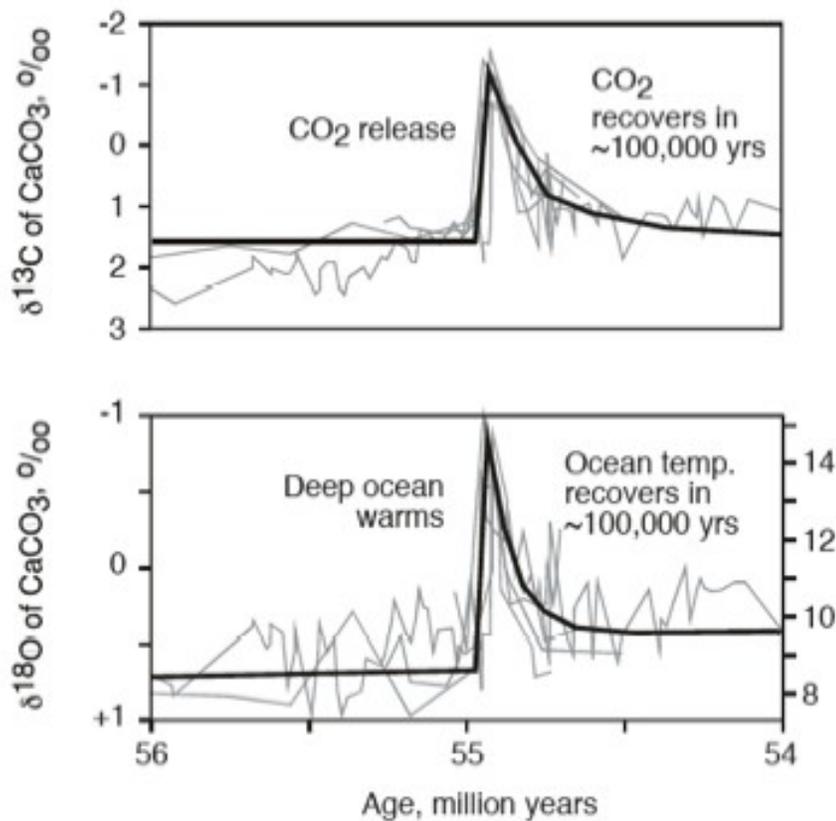


9
 10 **Figure 5.11. Timing of submarine landslides in the North Atlantic region and pre-**
 11 **industrial ice core methane variations. Landslide data from Maslin et al. (2004).**
 12 **Methane data from Brook et al. (2000) and Kobashi et al. (2007). Abbreviations: km³,**
 13 **cubic kilometers; yr, year; ppb, parts per billion.**
 14

15 Much of our knowledge of the Storegga Landslide is due to research sponsored
 16 by the Norwegian oil industry, which is interested in tapping the Ormen Lange gas field
 17 within the headlands of the Storegga slide but is concerned about the geophysical hazard
 18 of gas extraction (*Bryn et al., 2005*). The Norwegians do not want to trigger another
 19 Storegga Landslide. The conclusion that rapid glacial sediment loading is a cause of the
 20 slides would seem to indicate that drilling should be safe until another ice age were to
 21 start depositing new sediment on the sea floor. On the other hand, the modeling results
 22 of *Mienert et al. (2005)* indicate that it is plausible that warming and melting of hydrates
 23 had something to do with the slide. Several thousand years elapsed between the
 24 warming and the landslide. Estimates of potential methane emission range from 1—to 5

1 GtC, which is significant but not apocalyptic. As far as can be determined, the Storegga
 2 Landslide had no impact on climate.

3
 4 **The Paleocene-Eocene Thermal Maximum.** About 55 million years ago, the
 5 $\delta^{13}\text{C}$ signature of carbon in the ocean and on land decreased by 2.5-5 per mil (‰) on a
 6 time scale of less than 10 kyr, then recovered in parallel on a time scale of ~120-220 kyr
 7 (*Kennett and Stott, 1991; Zachos et al., 2001*). Associated with this event, commonly
 8 called the Paleocene-Eocene Thermal Maximum (PETM), the $\delta^{18}\text{O}$ of CaCO_3 from
 9 intermediate depths in the ocean decreased by 2-3‰, indicative of a warming of about
 10 5°C (Fig. 5.12). The timing of the spikes is to a large extent synchronous. Planktonic
 11 foraminifera and terrestrial carbon records show a $\delta^{13}\text{C}$ perturbation a bit earlier than
 12 benthic foraminifera do, suggesting that the carbon spike invaded the deep ocean from
 13 the atmosphere (*Thomas et al., 2002*). Similar events, also associated with transient
 14 warmings, although less well documented, have been described from other times in
 15 geologic history (*Hesselbo et al., 2000; Jenkyns, 2003*).
 16



17 *Figure*
 18 **5.12. Carbon (top) and oxygen (bottom) isotope record for benthic foraminifera from**
 19 **sites in the south Atlantic and western Pacific Oceans for the Paleocene-Eocene**
 20 **Thermal Maximum (PETM), from Zachos et al. (2001), modified by Archer (2007). ‰,**
 21 **per mil.**
 22

1 The benthic $\delta^{18}\text{O}$ record is most easily interpreted as a temperature change, at a
2 depth of several kilometers in the ocean, from about 8° to about 14° C, in a few
3 thousand years. Warming is also implied by Mg/Ca ratios in CaCO_3 (Zachos et al.,
4 2003). Planktonic $\delta^{18}\text{O}$ can also be fractionated by changes in freshwater forcing,
5 reflected in salinity, but salinity can be assumed to be regionally more homogeneous in
6 the deep ocean than at the surface. There is usually an offset between the $\delta^{18}\text{O}$ recorded
7 by foraminifera and the true equilibrium value, called a vital effect, but single-species
8 reconstructions of $\delta^{18}\text{O}$ tend to reduce the impact of these vital effects. The $\delta^{18}\text{O}$ of the
9 whole ocean changes when ice sheets grow, but there were no ice sheets at this time.
10 The seawater $\delta^{18}\text{O}$ can be influenced by chemical reactions with rocks, but not on short
11 time scales such as seen here.

12
13 The change in isotopic composition of the carbon in the ocean is attributed to the
14 release of some amount of isotopically light carbon to the atmosphere. However, it is
15 not clear where the carbon came from, or how much of it there was. The magnitude of
16 the carbon shift depends on where it was recorded. The surface change recorded in
17 CaCO_3 in soils (Koch et al., 1992) and in some planktonic foraminifera (Thomas et al.,
18 2002) is twice as large a change as is reported for the deep sea. Land records may be
19 affected by changes in plant fractionation, driven by changing hydrological cycle
20 (Bowen et al., 2004). Ocean records may be affected by CaCO_3 dissolution (Zachos et
21 al., 2005), resulting in diagenetic imprints on the remaining CaCO_3 , a necessity to use
22 multiple species, or simple inability to find CaCO_3 at all.

23
24 We can estimate the change in the carbon inventory of the ocean by specifying
25 an atmospheric partial pressure of CO_2 value, a mean ocean temperature, and insisting
26 on equilibrium with CaCO_3 [Zeebe and Westbroek, 2003]. The ocean was warmer, prior
27 to the PETM event, than it is today. Atmospheric pCO_2 was probably at least 560 ppm
28 at this time (Huber et al., 2002). The present-day inventory of CO_2 in the ocean is about
29 40,000 GtC. According to simple thermodynamics, neglecting changes in the biological
30 pump or circulation of the ocean, the geological steady-state inventory for late
31 Paleocene, pre-PETM time could have been on the order of 50,000 GtC.

32
33 The lighter the isotopic value, the smaller the amount of carbon that must be
34 released to explain the isotopic shift (Fig. 5.12, top). Candidate sources include
35 methane, which can range in its isotopic composition from -30 to -110‰ . If the ocean
36 $\delta^{13}\text{C}$ value is taken at face value, and the source was methane at -60‰ , then 2,000 GtC
37 would be required to explain the isotopic anomaly. If the source were thermogenic
38 methane or organic carbon at $\delta^{13}\text{C}$ of about -25‰ , then 10,000 GtC would be required.

39
40 *Buffett and Archer* (2004) find that the steady-state hydrate reservoir size in the
41 ocean is extremely sensitive to the temperature of the deep sea. At the temperature of
42 Paleocene time but with everything else as in the present-day ocean, they predict less
43 than a thousand GtC of methane in steady state. As the ocean temperature decreases, the
44 stability zone gets thinner and covers less area. Their model was able to fit 6,000 GtC in
45 the Arctic Ocean, however, using 6° temperatures from CCSM (Huber et al., 2002)

1 (which may be too cold) and assuming that the basin had been anoxic (Sluijs et al.,
2 2006).

3
4 Marine organic matter has an isotopic composition of -20‰, and would require
5 6,000 GtC to explain the isotopic anomaly. *Svensen et al.* (2004) proposed that lava
6 intrusions into organic-rich sediments could have caused the isotopic shift. They cite
7 evidence that the isotopic composition of methane produced from magma intrusion
8 should be -35 to -50‰, requiring therefore 2,500-3,500 GtC to explain the isotope
9 anomaly in the deep ocean. If CO₂ were also released, from metamorphism of CaCO₃,
10 the average isotopic composition of the carbon spike would be lower, and the mass of
11 carbon greater. *Storey et al.* (2007) showed that the opening of the North Atlantic
12 Ocean corresponds in time with the PETM. However, volcanic activity continued for
13 hundreds of thousands of years, leaving still unexplained the reason for the fast (<10,000
14 years) carbon isotope excursion.

15
16 A comet impact might have played a role in the PETM, and while the isotopic
17 composition of comets is not well constrained, carbon in cometary dust tends to be about
18 -45‰ (*Kent et al.*, 2003). *Kent et al.* (2003) calculate that an 11 km comet containing
19 20-25% organic matter, a rather large icy tarball, could deliver 200 GtC, enough to
20 decrease the δ¹³C of the atmosphere and upper ocean by 0.4‰. It is unlikely that a
21 comet could deliver thousands of GtC however. An impact strike to a carbonate
22 platform or an organic-rich sediment of some sort could release carbon, but it would
23 take a very large crater to release thousands of gigatons of carbon.

24
25 Volcanic carbon has an isotopic composition of -7‰, requiring a huge carbon
26 release of 20,000 GtC to explain the PETM. Excess carbon emissions have been
27 attributed to superplume cycles in the mantle and flood basalt volcanic activity (*Larson*,
28 1991). However, these events tend to take millions of years to play out (*Dickens et al.*,
29 1995). *Bralower et al.* (1997) and *Schmitz et al.* (2004) find evidence of increased
30 volcanic activity during the PETM interval but view the activity as rearranging ocean
31 circulation, triggering methane release, rather than being a major primary source of
32 carbon itself, presumably because the potential volcanic carbon source is too slow.

33
34 Acidification of the ocean by invasion of CO₂ drove a shoaling of the depth of
35 CaCO₃ preservation in the Atlantic (*Zachos et al.*, 2005) although, curiously, not in the
36 Pacific (*Zachos et al.*, 2003). The magnitude of the carbonate compensation depth
37 (CCD) shift in the Atlantic, if taken as representative of the whole ocean, would be
38 suggestive of a large carbon addition, on the order of 5,000 GtC or more (*Archer et al.*,
39 1997).

40
41 A large carbon release is also supported by the warming inferred from the δ¹⁸O
42 spike. The temperature can be altered by both CH₄ and CO₂. *Schmidt and Shindell*
43 (2003) calculated that the steady-state atmospheric CH₄ concentration during the period
44 of excess emission (ranging from 500-20,000 years) would be enough to explain the
45 temperature change. However, the atmospheric methane concentration anomaly would
46 decay away a few decades after the excess emission ceased. At this point the

1 temperature anomaly would die away also. Hence, as soon as the carbon isotopic
2 composition stopped plunging negative, the oxygen isotopic composition should recover
3 as the ocean cools. The carbon isotopic composition meanwhile should remain light for
4 hundreds of thousands of years (*Kump and Arthur, 1999*) until the carbon reservoir
5 isotopic composition reapproached a steady-state value. The record shows instead that
6 the oxygen and carbon isotopic anomalies recovered in parallel (Fig. 5.12). This
7 suggests that CO₂ is the more likely greenhouse warmer rather than CH₄. It could be
8 that the time scale for the pCO₂ to reach steady state might be different than the time
9 scale for the isotopes to equilibrate, analogous to the equilibration of the surface ocean
10 by gas exchange: isotopes take longer. However, in the *Kump and Arthur (1999)* model
11 results, pCO₂ seems to take longer to equilibrate than δ¹³C. The first-order result is that
12 the CO₂ and δ¹³C timescales are much more similar than the CH₄ and δ¹³C timescales
13 would be.

14
15 A warming of 5°C would require somewhere between one and two doublings of
16 the atmospheric CO₂ concentration, if the climate sensitivity is in the range of 2.5 – 5°C.
17 Beginning from 600 ppm, we would increase the pCO₂ of the atmosphere to somewhere
18 in the range of 1,200 – 2,400 ppm. The amount of carbon required to achieve this value
19 for hundreds of thousands of years (after equilibration with the ocean and with the
20 CaCO₃ cycle) would be of order 20,000 GtC. This would imply a mean isotopic
21 composition of the spike of mantle isotopic composition, not isotopically light methane.
22 The amount of carbon required to explain the observed δ¹⁸O would be higher if the
23 initial atmospheric pCO₂, were higher than the assumed 600 ppm. The only way that a
24 biogenic methane source could explain the warming is if the climate sensitivity were
25 much higher in the Paleocene than it seems to be today, which seems unlikely because
26 the ice albedo feedback amplifies the climate sensitivity today (*Pagani et al., 2006*).
27

28 The bottom line conclusion about the source of the carbon isotopic excursion is
29 that it is still not clear. There is no clear evidence in favor of a small, very isotopically
30 depleted source of carbon. Mechanistically, it is easier to explain a small release than a
31 large one, and this is why methane has been a popular culprit for explaining the δ¹³C
32 shift. Radiative considerations argue for a larger carbon emission, corresponding to a
33 less fractionated source than pure biogenic methane. Thermogenic methane might do,
34 such as the release of somewhat more thermogenic methane than in Gulf of Mexico
35 sediments, if there were a thermogenic deposit that large. Or perhaps it was some
36 combination of sources, an initial less-fractionated source such as marine organic matter
37 or a comet, followed by hydrate release.

38
39 The PETM is significant to the present day because it is a close analog to the
40 potential fossil fuel carbon release if we burn all the coal reserves. There are about
41 5,000 GtC in coal, while oil and traditional natural gas deposits are hundreds of Gton
42 each (*Rogner, 1997*). The recovery timescale from the PETM (140 kyr) is comparable
43 to the model predictions, based on the mechanism of the silicate weathering thermostat
44 (400 kyr timescale [*Berner et al., 1983*]).
45

1 The magnitude of the PETM warming presents something of a problem. A 5,000
2 GtC of fossil fuel release will warm the deep ocean by perhaps 2-4°C, based on
3 paleoclimate records and model results (*Martin et al.*, 2005). The warming during the
4 PETM was 5°C, and this was from an atmospheric CO₂ concentration higher than today,
5 (at least 600 ppm), so that a further spike of only 2,000 GtC (based on methane isotopic
6 composition) would have only a tiny radiative impact, not enough to warm the Earth by
7 5°C. One possibility is that our estimates for the climate sensitivity are too low by a
8 factor of 2 or more. However, as mentioned above, one might expect a decreased
9 climate sensitivity for an ice-free world rather than for the ice-age climate of today.

10
11 Another possibility is that the PETM was driven by two sources of carbon,
12 totaling maybe 10,000 GtC. At most 10% of this carbon could have had an initial $\delta^{13}\text{C}$
13 of -60‰, if the rest were volcanic carbon at -7‰. The implication would be that the
14 hydrate reservoir at that time did not amplify the initial carbon release (analogous to our
15 fossil fuel CO₂) by more than 10%. However, there are no strong ideas for where that
16 other 9,000 GtC could have come from.

17
18 Perhaps the global average $\delta^{13}\text{C}$ shift was as large as recorded in soils (*Koch et*
19 *al.*, 1992) and some planktonic foraminifera (*Thomas et al.*, 2002), and perhaps it was
20 thermogenic methane, so the hydrate release could have been 8,000 GtC. In this case we
21 can attribute all of the temperature change to the radiative effect of the released carbon,
22 mostly as the accumulated CO₂. The *Archer and Buffett* (2005) model predicted a
23 regime in model space where the hydrate reservoir would be unstable, periodically
24 melting down. The time period between meltdowns was determined by the timescale of
25 methane accumulation in the reservoir. The critical parameters to the model are the
26 timescale for a melting relaxation to the equilibrium size, and the fraction of the
27 reservoir which melts at all. If most of the reservoir equilibrates quickly, then periodic
28 meltdowns result. Tauntingly, there are several tiny “aftershocks” of the PETM, all
29 about 2 million years apart, such as an Eocene layer of mysterious origin (ELMO) event
30 (*Lourens et al.*, 2005). The trouble then is that the model, tuned to periodic meltdowns
31 during the PETM, predicts that the hydrate reservoir today, larger because the ocean is
32 colder, should periodically melt down even more severely today.

33
34 Could some external agent of warming, not CO₂, have driven temperatures up?
35 The $\delta^{13}\text{C}$ could be showing us methane release, but the temperature would be attributed
36 to something else, something no one has thought of yet. The difficulty here would be
37 that the decay of the temperature spike follows so closely the decay of the $\delta^{13}\text{C}$ spike.
38 This tends to steer us back to the path of CO₂ as the proximate agent of temperature
39 change.

40
41 At present, the PETM serves as a cautionary tale about the long duration of a
42 release of new CO₂ to the atmosphere (*Archer*, 2005). However, our current
43 understanding of the processes responsible for the $\delta^{13}\text{C}$ spike is not strong enough to
44 provide any new constraint to the stability of the methane hydrate reservoir in the
45 immediate future.

46

1 **Santa Barbara Basin and the Clathrate Gun Hypothesis.** *Kennett et al.* (2003) and
2 *Nisbet* (2002) argue that methane from hydrates is responsible for the initial deglacial
3 rise in the Greenland methane record, and for abrupt changes in methane at other times.
4 *Kennett et al.* (2000) found episodic negative $\delta^{13}\text{C}$ excursions in benthic foraminifera in
5 the Santa Barbara Basin, which they interpret as reflecting release of hydrate methane
6 during warm climate intervals. Biomarkers for methanotrophy are found in greater
7 abundance and indicate greater rates of reaction, during warm intervals in the Santa
8 Barbara Basin (*Hinrichs et al.*, 2003) and in the Japanese coastal margin (*Uchida et al.*,
9 2004). *Cannariato and Stott* (2004), however, argued that these results could have
10 arisen from contamination or subsequent diagenetic overprints.

11
12 As discussed in section 1, there are several arguments against the hypothesis of a
13 clathrate role in controlling atmospheric methane during the last glacial period. Perhaps
14 the most powerful so far is that the isotopic ratio of D/H in ice core methane indicates a
15 freshwater source, rather than a marine source, apparently ruling out much of a role for
16 marine hydrate methane release (*Sowers*, 2006). The timing of the deglacial methane
17 rise was also more easily explained by wetland degassing than by catastrophic methane
18 release (*Brook et al.*, 2000). The interhemispheric gradient of methane tells us that the
19 deglacial increase in atmospheric methane arose in part from high northern latitudes
20 (*Dallenbach et al.*, 2000), although more work is needed to verify this conclusion
21 because constraining the gradient is analytically difficult. The deglacial methane rise
22 could therefore be attributed at least in part to methanogenesis from decomposition of
23 thawing organic matter or from high-latitude wetlands. Regardless of the source of the
24 methane, the climate forcing from the observed methane record (Fig. 5.6C and D) is too
25 weak to argue for a dominant role for methane in the glacial cycles (*Brook et al.*, 2000).

26 **4.4 Review of model results addressing past and future methane hydrate** 27 **destabilization**

28 **4.4.1 Quantity of methane potentially released**

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

1 **4.4.2 Climate impact of potential release**

2 *Schmidt and Shindell* (2003) showed that the chronic release of methane from a
3 large hydrate reservoir over thousands of years can have a significant impact on global
4 climate. The accumulating CO₂ from the oxidation of the methane also has a significant
5 climate impact. New CO₂ from methane oxidation accumulates in the atmosphere /
6 ocean / terrestrial biosphere carbon pool and persists to affect climate for hundreds of
7 thousands of years (*Archer*, 2005). If a pool of methane is released over a timescale of
8 thousands of years, the climate impact from the accumulating CO₂ concentration may
9 exceed that from the steady-state increase in the methane concentration (*Archer and*
10 *Buffett*, 2005; *Dickens*, 2001a; *Harvey and Huang*, 1995; *Schmidt and Shindell*, 2003).
11 After the emission stops, methane drops quickly to a lower steady state, while the CO₂
12 persists (*Schmidt and Shindell*, 2003).

13
14 If hydrates melt in the ocean, much of the methane would probably be oxidized
15 in the ocean rather than reaching the atmosphere directly as methane. This reduces the
16 century-timescale climate impact of melting hydrate, but on timescales of millennia and
17 longer the climate impact is the same regardless of where the methane is oxidized.
18 Methane oxidized to CO₂ in the ocean will equilibrate with the atmosphere within a few
19 hundred years, resulting in the same partitioning of the added CO₂ between the
20 atmosphere and the ocean regardless of its origin.

21
22 *Archer and Buffett* (2005) find an amplifying positive feedback among
23 atmospheric CO₂, the temperature of the deep ocean, and the release of carbon from
24 methane hydrate to more atmospheric CO₂. They find that if the melting kinetics of the
25 reservoir are assumed to be too fast, or the release fraction too high, then the reservoir
26 becomes unstable, melting down spontaneously in ways that are not seen in the δ¹³C
27 record.

28
29 The rate and extent to which methane carbon can escape the sediment column in
30 response to warming is very difficult to constrain at present. It depends on the stability
31 of the sediment slope to sliding, and on the permeability of the sediment and the hydrate
32 stability zone cold trap to bubble methane fluxes. *Archer and Buffett* (2005) find that in
33 a worst-case scenario, after thousands or hundreds of thousands of years, the methane
34 hydrate reservoir could release as much carbon as fossil fuel emissions.

35 **4.5 Conclusions about potential for abrupt release of methane from marine** 36 **hydrates**

37 On the timescale of the coming century, it appears likely that most of the marine
38 hydrate reservoir will be insulated from anthropogenic climate change. The exception is
39 in shallow ocean sediments where methane gas is focused by subsurface migration. The
40 most likely response of these deposits to anthropogenic climate change is an increased
41 background rate of chronic methane release, rather than an abrupt release. Methane gas
42 in the atmosphere is a transient species, its loss by oxidation continually replenished by
43 ongoing release. An increase in the rate of methane emission to the atmosphere from
44 melting hydrates would increase the steady-state methane concentration of the
45 atmosphere. The potential rate of methane emission from hydrates is more speculative
46 than the rate from other methane sources such as the decomposition of peat in thawing

1 permafrost deposits, or anthropogenic emission from agricultural, livestock, and fossil
2 fuel industries, but the potential rates appear to be comparable to these sources.

3 4 **5. TERRESTRIAL METHANE HYDRATES**

5 There are two sources for methane in hydrates, biogenic production by microbes
6 degrading organic matter in anaerobic environments, and thermogenic production at
7 temperatures above 110°C, typically at depths greater than about 15 km. Terrestrial
8 methane hydrates are primarily biogenic (*Archer, 2007*). They form and are stable
9 under ice sheets (thicker than ~250 m) and within permafrost soils at depths of about
10 150 to 2,000 m below the surface (*Kvenvolden 1993; Harvey and Huang 1995*). Their
11 presence is known or inferred from geophysical evidence (e.g., well logs) on Alaska's
12 North Slope, the Mackenzie River delta and Arctic islands of Canada, the Messoyakha
13 Gas field and two other regions of western Siberia, and two regions of northeastern
14 Siberia (*Kvenvolden and Lorenson 2001*). Samples of terrestrial methane hydrates have
15 been recovered from 900 to 1,110 m depth in the Mallik core in the Mackenzie River
16 delta, Northwest Territories, Canada (*Uchida et al 2002; Kvenvolden and Lorenson,*
17 *2001*).

18 19 **5.1 Terrestrial methane hydrate pool size and distribution**

20 While most methane hydrates are marine, the size of the contemporary terrestrial
21 methane hydrate pool, although unknown, may be large. Estimates range from less than
22 10 Gt CH₄ (Meyer, 1981) to more than 18,000 Gt CH₄ (*Dobrynin et al., 1981*) (both
23 cited in Harvey and Huang, 1995). More recent estimates are 400 Gt CH₄ (*MacDonald,*
24 *1990*), 800 Gt CH₄ (*Harvey and Huang, 1995*), and 4.5-400 GtC; this is a small fraction
25 of the ocean methane hydrate pool size (section4).

26 Terrestrial methane hydrates are a potential fossil energy source. Recovery can
27 come from destabilization of the hydrates by warming, reducing the pressure, or
28 injecting a substance (e.g., methanol) that shifts the stability line (see Box 5.1). The
29 Messoyakha Gas Field in western Siberia, at least some of which lies in the terrestrial
30 methane hydrate stability zone, began producing gas in 1969, and some production is
31 thought to have come from methane hydrates, though methanol injection made this
32 production very expensive (*Kvenvolden 1993; Krason, 2000*). A more recent review of
33 the geological evidence for methane production from hydrates at Messoyakha by *Collett*
34 *and Ginsburg (1998)* could not confirm unequivocally that hydrates contributed to the
35 produced gas. Due to low costs of other available energy resources, there had not been
36 significant international industrial interest in hydrate methane extraction during 1970-
37 2000 (*Kvenvolden 2000*), and the fraction of terrestrial methane hydrate that is or will be
38 technically and economically recoverable is not well established. In the U.S., the
39 Methane Hydrate Research and Development Act of 2000 and its subsequent 2005
40 Amendment have fostered the National Methane Hydrates R&D Program, supporting a
41 wide range of laboratory, engineering, and field projects with one focus being on
42 developing the knowledge and technology base to allow commercial production of
43 methane from domestic hydrate deposits by the year 2015, beginning with Alaska's
44 North Slope. Estimates of technically and economically recoverable methane in
45 hydrates are being developed (*Boswell, 2005; 2007*).

46

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 §7.4). *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 Section 7.3.1).

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 non-permafrost 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 not likely 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 CO₂.

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 section 4 have focused on methane emissions from the larger and more vulnerable marine hydrates. Emissions from terrestrial hydrates may have contributed to changes in methane observed in the ice core record, but there are so far no distinctive isotopic tracers of terrestrial hydrates, as is the case for marine hydrate (*Sowers, 2006*).

5.3.1. Quantity of methane released from terrestrial hydrates in the past

Weitemeyer and Buffett (2006) modeled the accumulation and release of biogenic methane from terrestrial hydrates below the Laurentide and Cordilleran ice sheets of North America during the last glaciation. Methane was generated under the ice sheet from anaerobic decomposition of buried, near-surface soil organic matter, and hydrates formed if the ice sheet was greater than ~250 m thick. Hydrate destabilization arose from pressure decreases with ice sheet melting/thinning. They simulated total releases for North America of about 40-100 Tg CH₄, with most of the deglacial emissions occurring during periods of glacial retreat during a 500-year interval around 14 kBP, and a 2000-year interval centered on about 10 kBP. The highest simulated emission rates (~15-35 Tg CH₄ yr⁻¹) occurred during the dominant period of ice sheet melting around 11-9 kBP.

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 CH₄ km⁻² y⁻¹ (or 0.4 g CH₄ m⁻² y⁻¹). They assume that the methane flux from the seafloor is of the same order of magnitude, and may reach 1-1.5 g CH₄ m⁻² y⁻¹. These fluxes are low compared to wetland fluxes (typically ~1-100 g CH₄ m⁻² y⁻¹; Bartlett and Harriss, 1993), but applied across the total area of shallow Arctic shelf, the annual flux may be as high as 1-5 Tg CH₄ 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 Section 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 atmospheric perturbation is equivalent to about 2-25% of pre-industrial Holocene atmospheric methane burdens, and roughly equivalent to a radiative forcing of 2-100 mW m⁻² (using contemporary values for methane radiative efficiency and indirect effects [*Ramaswamy et al., 2001*]).

1 Thermokarst erosion on the Arctic coast of Siberia is thought to cause hydrate
2 destabilization and emissions of methane that are at most 1% of total global methane
3 emissions, and so this process is not likely to be having a large climatic impact.
4

5 **5.4 Estimates of future terrestrial hydrate release and climatic impact**

6 *Harvey and Huang (1995)* modeled terrestrial methane hydrate release due to
7 global warming (step function temperature increases of 5°C, 10°C, and 15°C, and the
8 propagation of this heat into hydrate-bearing permafrost). Over the first few centuries
9 the methane release is very small, and after 1,000 years, the cumulative methane release
10 is <1%, 2%, and 5% of the total terrestrial methane hydrate pool size, respectively; by
11 5,000 years this cumulative release has increased to 3%, 15%, and 30%, respectively.
12 Even 5,000 years after a step function increase in temperature of 15°C, the radiative
13 forcing caused by terrestrial hydrate melting (direct effects of methane plus methane
14 converted to carbon dioxide) was only ~0.3 W/m².
15

16 Methane release from hydrate destabilization due to decaying ice sheets is not
17 likely to be substantial unless there are significant hydrate pools under Greenland and/or
18 Antarctica, which does not seem to be the case. Thermokarst erosion release is the only
19 known present terrestrial hydrate methane source. This process can be expected to
20 continue into the future, and it is likely that emissions will remain a small fraction of the
21 global methane budget and therefore have a small impact on radiative forcing.
22 However, most recent modeling analyses have focused on marine hydrates (e.g.,
23 Dickens, 2001; Archer and Buffett, 2004), and more work on the terrestrial hydrate
24 reservoir is clearly needed.
25

26 **5.5 Conclusions**

27 No mechanisms have been proposed for the abrupt release of significant
28 quantities of methane from terrestrial hydrates (*Archer, 2007*). Slow and perhaps
29 sustained release from permafrost regions may occur over decades to centuries from
30 mining extraction of methane from terrestrial hydrates in the arctic (*Boswell, 2007*),
31 over decades to centuries from continued thermokarst erosion of coastal permafrost in
32 Eurasia (*Shakova et al., 2005*), and over centuries to millennia from the propagation of
33 any warming 100-1,000 m down into permafrost hydrates (*Harvey and Huang, 1995*).
34

35 **6. CHANGES IN METHANE EMISSIONS FROM NATURAL WETLANDS**

36 **6.1 Introduction**

37 Natural wetlands are most extensive at high latitudes, where boreal and arctic
38 wetlands have substantial carbon in peat and are frequently associated with permafrost,
39 and in the tropics, often associated with river and lake floodplains. Annual methane
40 emissions from tropical wetlands are roughly twice that from boreal/arctic wetlands.
41 Globally, wetlands are the largest single methane source to the atmosphere, with recent
42 emission estimates ranging from 100 to 231 Tg CH₄ yr⁻¹ (*Denman et al., 2007*),
43 constituting more than 75% of the total estimated natural emissions. Variations in
44 wetland distribution and saturation, in response to long-term variations in climate, are
45 therefore thought to have been main determinants for variation in the atmospheric CH₄
46

1 concentration in the past (*Chappellaz et al., 1990; Chappellaz et al., 1993; Brook et al.,*
2 *1996; 2000; Delmotte et al., 2004*). Recent interannual variations in methane emissions
3 have been dominated by fluctuations in wetland emissions (*Bousquet et al., 2006*),
4 although biomass burning also plays a significant role.

5
6 Methane emissions from natural wetlands are sensitive to temperature and
7 moisture (see below), and thus to climate variability and change. Emissions can also be
8 influenced by anthropogenic activities that impact wetlands such as pollution loading
9 (e.g., *Gauci et al., 2004*), land management (e.g., *Minkinen et al., 1997*), and water
10 management (e.g., *St. Louis et al., 2000*). While these anthropogenic impacts can be
11 expected to change in the coming decades, they are not likely to be a source of abrupt
12 changes in methane emissions from natural wetlands, so this section will focus on
13 climate impacts.

14
15 Global climate model projections suggest that the tropics, on average, and the
16 northern high latitudes are likely to become warmer and wetter during the 21st century,
17 with greater changes at high latitudes (*Chapman and Walsh, 2007; Meehl et al., 2007*).
18 Temperatures in the tropics by 2100 are projected to increase by 2-4°C (*IPCC, 2007*).
19 Precipitation in the tropics is expected to increase in East Africa and Southeast Asia,
20 show little change in West Africa and Amazonia, and decrease in Central America and
21 northern South America (*IPCC, 2007*).

22
23 Warming in the northern high latitudes in recent decades has been stronger than
24 in the rest of the world (*Serreze and Francis 2006*), and that trend is projected to
25 continue, with multi-model projections indicating that Arctic land areas could warm by
26 between 3.5° and 8°C by 2100 (*Meehl et al., 2007*). The northern high latitudes are also
27 expected to see an increase in precipitation by more than 20% in winter and by more
28 than 10% in summer. Climate change of this magnitude is likely to have diverse
29 impacts on the Arctic climate system (*ACIA 2004*), including the methane cycle.
30 Principal among the projected impacts is that soil temperatures are expected to warm
31 and permafrost, which is prevalent across much of the northern high latitudes, is
32 expected to thaw and degrade. Permafrost thaw may alter the distribution of wetlands
33 and lakes through soil subsidence and changes in local hydrological conditions. Since
34 methane production responds positively to soil moisture and summer soil temperature,
35 the projected strong warming and associated landscape changes expected in the northern
36 high latitudes, coupled with the large carbon source (northern peatlands have ~250 GtC
37 as peat within 1 to a few meters of the atmosphere; *Turunen et al., 2002*), will likely lead
38 to a significant increase in methane emissions over the coming century.

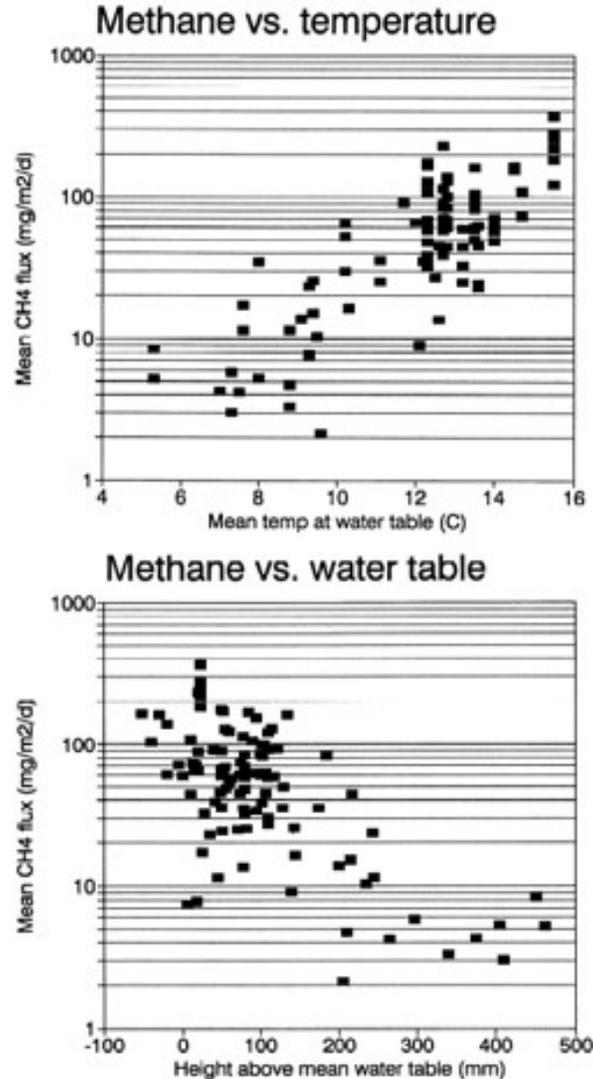
39 40 **6.2 Factors controlling methane emissions from natural wetlands**

41 Methane is produced as a byproduct of microbial decomposition of organic
42 matter under anaerobic conditions that are typical of saturated soils and wetlands. As
43 this methane migrates from the saturated soil to the atmosphere (via molecular diffusion,
44 ebullition (bubbling), or plant-mediated transport), it can be oxidized to carbon dioxide
45 by microbial methanotrophs in oxygenated sediment or soil. In wetlands, a significant
46 fraction of the methane produced is oxidized by methanotrophic bacteria before reaching

1 the atmosphere (*Reeburgh, 2004*). If the rate of methanogenesis is greater than the rate
2 of methanotrophy and pathways for methane to diffuse through the soil are available,
3 then methane is emitted to the atmosphere. Dry systems, where methanotrophy exceeds
4 methanogenesis, can act as weak sinks for atmospheric methane (see Table 5.1).
5 Methane emissions are extremely variable in space and time, and therefore it is difficult
6 to quantify regional-scale annual emissions (*Bartlett and Harriss, 1993; Melack et al.,*
7 *2004*). Recent reports of a significant source of methane from an aerobic process in
8 plants (*Keppeler et al., 2006*) appear to be in error (*Dueck et al., 2007*).
9

10 There have not been many field studies measuring methane fluxes from tropical
11 wetlands around the world, but work in the Amazon and Orinoco Basins of South
12 America has shown that methane emissions appear to be most strongly controlled in
13 aquatic habitats by inundation depth and vegetation cover (e.g., flooded forest, floating
14 macrophytes, open water) (*Devol et al., 1990; Bartlett and Harriss, 1993; Smith et al.,*
15 *2000; Melack et al., 2004*). Wet season (high water) fluxes are generally higher than dry
16 season (low water) fluxes (*Bartlett and Harriss, 1993*).
17

18 At high latitudes, the most important factors influencing methane fluxes are
19 water table depth, soil or peat temperature, substrate type and availability, and
20 vegetation type (Fig. 5.13). Water table depth determines both the fraction of the
21 wetland soil/peat that is anaerobic and the distance from this zone of methane
22 production to the atmosphere (i.e., the length of the oxidation zone) and is often the
23 single most important factor controlling emissions (*Bubier et al., 1995; Waddington et*
24 *al., 1996; MacDonald et al., 1998*). The strong sensitivity of CH₄ emissions to water
25 table position suggests that changing hydrology of northern wetlands under climate
26 change could drive large shifts in associated methane emissions.
27



1
2 **Figure 5.13. Relationships between water table height, temperature, and methane**
3 **emissions for northern wetlands from Bubier et al. (1995). Abbreviations: mg/m²/d,**
4 **milligrams per square meter per day; mm, millimeters; C, degrees Celsius.**

5
6 Vegetation type controls plant litter tissue quality/decomposability, methanogen
7 substrate input by root exudation (e.g., King and Reeburgh, 2002), and the potential for
8 plant-mediated transport of methane to the atmosphere (e.g., King et al., 1998; Joabsson
9 and Christensen, 2001). Substrate type and quality, generally related to quantity of root
10 exudation and to vegetation litter quality and degree of decomposition, can directly
11 affect potential methane production. Vegetation productivity controls the amount of
12 organic matter available for decomposition.

13
14 In wetland ecosystems, when the water table is near the surface and substantial
15 methane emissions occur, the remaining controlling factors rise in relevance.
16 Christensen et al. (2003) find that temperature and microbial substrate availability
17 together explain almost 100% of the variations in mean annual CH₄ emissions across a

1 range of sites across Greenland, Iceland, Scandinavia, and Siberia. *Bubier et al. (1995)*
2 find a similarly strong dependence on soil temperature at a northern peatland complex in
3 Canada. The observed strong relationship between CH₄ emissions and soil temperature
4 reflects the exponential increase in microbial activity as soil temperatures warm. The
5 strong warming expected across the northern high latitudes is likely to be a positive
6 feedback on methane emissions.

7
8 The presence or absence of permafrost can also have a direct influence on CH₄
9 emissions. Across the northern high latitudes, permafrost features such as ice wedges,
10 ice lenses, thermokarst, and ice heaving determine the surface microtopography. Small
11 variations in surface topography have a strong bearing on plant community structure and
12 evolution as well as soil hydrologic and nutritional conditions (*Jorgenson et al. 2001*;
13 *Jorgenson et al., 2006*), all of which are controlling factors for methane emission.
14 Projections of future methane emission are hampered by the difficulty of modeling
15 landscape/watershed hydrology well enough at large scales to realistically represent
16 small changes in wetland water table depth.

17 18 **6.3 Observed and projected changes in natural wetlands**

19 20 **6.3.1 Observed changes in Arctic wetlands and lakes**

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

27
28 In recent decades, lake area and count in discontinuous permafrost regions have
29 decreased in western Siberia (*Smith et al., 2005a*) and Alaska (*Riordan et al., 2006*) but
30 have increased in continuous permafrost regions in northwestern Siberia (*Smith et al.,*
31 *2005a*). The differing trends in discontinuous and continuous permafrost zones can be
32 understood if one considers that initial permafrost warming leads to development of
33 thermokarst and lake and wetland expansion as the unfrozen water remains trapped near
34 the surface by the icy soil beneath it. As the permafrost degrades more completely, lake
35 or wetland drainage follows, as water more readily drains through the more ice-free soil
36 to the ground-water system.

37
38 A strength of the Smith et al. (2005a) study is that lake abundance is determined
39 via satellite, permitting the study of thousands of lakes and evaluation of the net change
40 across a broad area, which can in turn be attributed to regional driving mechanisms such
41 as climate and permafrost degradation. A similar analysis for wetlands would be useful
42 but is presently intractable because wetlands are not easy to pinpoint from satellite, as
43 inundation, particularly in forested regions, cannot be easily mapped, and wetland-rich
44 landscapes are often very spatially heterogeneous. (Frey and Smith, 2007).

45
46 Present-generation global climate or large-scale hydrologic models do not

1 represent the thermokarst processes that appear likely to dictate large-scale changes in
2 wetland extent over the coming century. However, wetland area can also respond to
3 trends in precipitation minus evaporation (P–E). A positive P–E trend could lead, in the
4 absence of large increases in runoff, to an expansion of wetland area and more saturated
5 soil conditions, thereby increasing the area from which methane emission can occur.
6 Most climate models predict that both Arctic precipitation and evapotranspiration will
7 rise during the 21st century if greenhouse gas concentrations in the atmosphere continue
8 to rise. In at least one model, the NCAR CCSM3, the P–E trend is positive throughout
9 the 21st century (*Lawrence and Slater, 2005*).

10 6.3.2 Observed and projected changes in permafrost conditions

11 There is a considerable and growing body of evidence that soil temperatures are
12 warming, active layer thickness (ALT) is increasing, and permafrost is degrading at
13 unprecedented rates (*e.g., Osterkamp and Romanovsky, 1999; Romanovsky et al., 2002;*
14 *Smith et al., 2005b; Osterkamp and Jorgenson, 2006*). Continuous permafrost in
15 Alaska, which has been stable over hundreds, or even thousands, of years, has suffered
16 an abrupt increase in degradation since 1982 that “appears beyond normal rates of
17 change in landscape evolution” (*Jorgenson et al., 2006*). Similarly, discontinuous
18 permafrost in Canada has shown a 200-300% increase in the rate of thawing over the
19 1995-2002 period relative to that of 1941-91 (*Camill, 2005*). *Payette et al. (2004)*
20 present evidence of accelerated thawing of subarctic peatland permafrost over the last 50
21 years. An example of permafrost degradation and transition to wetlands in the Tanana
22 Flats region of central Alaska is shown in Figure 5.14.



25
26 **Figure 5.14. Transition from permafrost (left) to wetlands (right) over the last 20**
27 **years (*Jorgensen et al., 2001*). Photos from [http://www.arctic.noaa.gov/detect/land-](http://www.arctic.noaa.gov/detect/land-tundra.shtml)**
28 **[tundra.shtml](http://www.arctic.noaa.gov/detect/land-tundra.shtml).**

29
30 Model projections of soil temperature warming and permafrost degradation in
31 response to the strong anticipated high-latitude warming vary considerably, although
32 virtually all of them indicate that a significant amount of permafrost degradation will
33 occur if the Arctic continues to warm (*Anisimov and Nelson, 1997; Stendel and*
34 *Christensen, 2002; Zhang et al., 2003; Sazonova et al., 2004*). *Buteau et al. (2004)* find
35 downward thawing rates of up to 13 cm yr⁻¹ in ice-rich permafrost for a 5°C warming
36 over 100 years. A collection of process-based models, both global and regional, all with
37 varying degrees of completeness in terms of their representation of permafrost, indicates

1 widespread large-scale degradation of permafrost (and by extension thermokarst
2 development), sharply increasing ALTs, and a contraction of the area where permafrost
3 can be found near the Earth's surface during the 21st century (*Lawrence and Slater,*
4 *2005; Euskirchen et al., 2006; Lawrence et al., 2007; Saito et al., 2007; Zhang et al.,*
5 *2007*).
6

7 **Box 5.3: High-latitude terrestrial feedbacks**

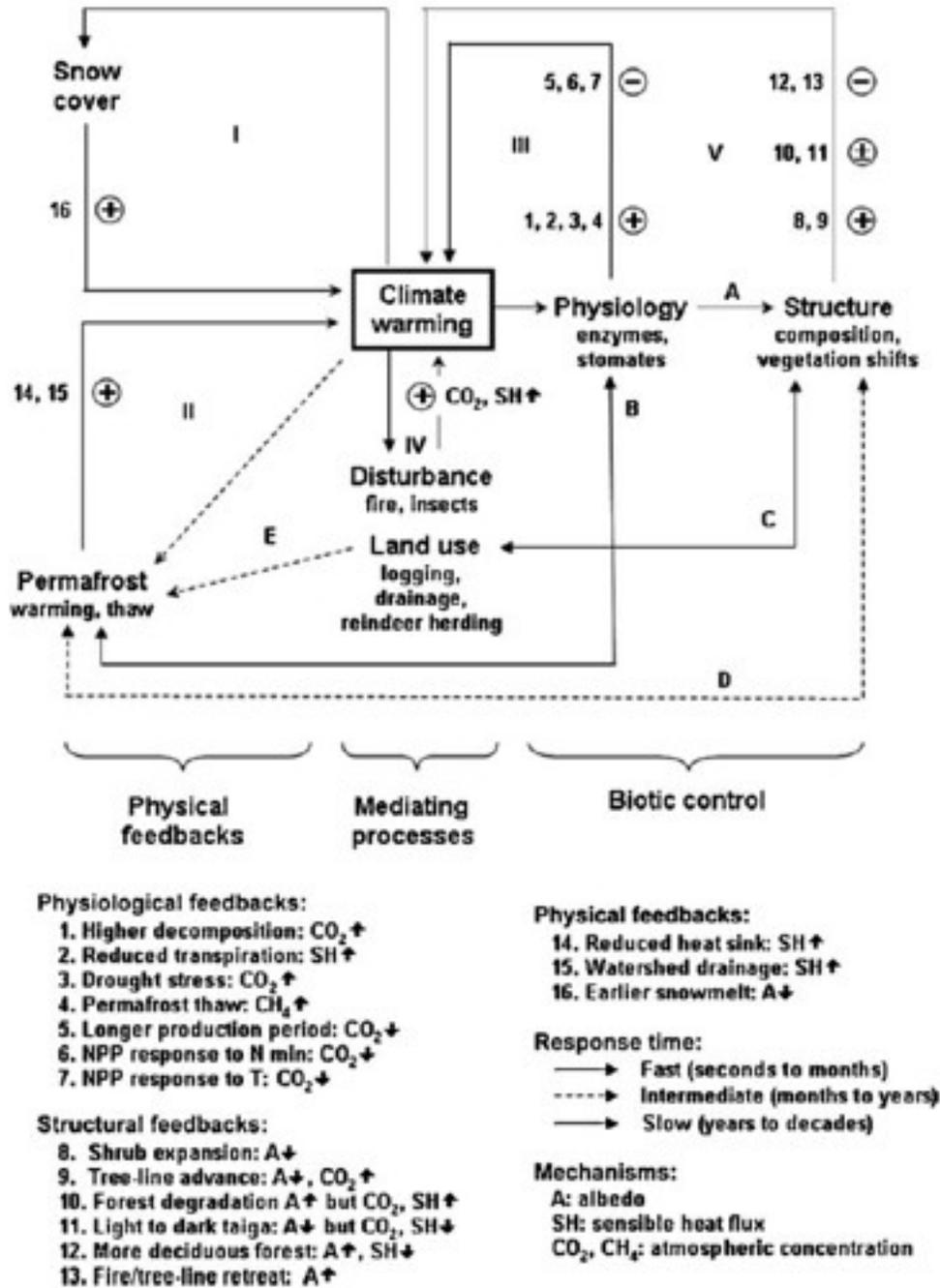
8 In recent decades, the Arctic has witnessed startling environmental change. The
9 changes span many facets of the Arctic system including rapidly decreasing sea ice
10 extent, melting glaciers, warming and degrading permafrost, increasing runoff to the
11 Arctic Ocean, expanding shrub cover, and important changes to the carbon balance
12 (*Serreze et al., 2000; Hinzman et al., 2005*). The observed environmental trends are
13 driven largely by temperatures that are increasing across the Arctic at roughly twice the
14 rate of the rest of the world (*Serreze and Francis, 2006*). If the Arctic warming
15 continues and accelerates, as is predicted by all global climate models (*Chapman and*
16 *Walsh, 2007*), it may invoke a number of feedbacks that have the potential to alter and
17 possibly accelerate Arctic and global climate change. If the feedbacks operate
18 constructively, even relatively small changes in the Arctic could conspire to amplify
19 global climate change. Continued environmental change, especially if it occurs rapidly,
20 is likely to have adverse consequences for highly vulnerable Arctic and global
21 ecosystems and negative impacts on human activities, particularly in the Arctic,
22 including costly damage to infrastructure and marginalization of many Arctic
23 communities.
24

25 The Arctic can influence global climate through both positive and negative
26 feedbacks (Figure 5.15). For example, sea-ice retreat reduces surface albedo, enhances
27 absorption of solar radiation, and ultimately leads to greater pan-Arctic warming.
28 Large-scale thawing of permafrost alters soil structural (thermokarst) and hydrologic
29 properties (*Jorgenson et al., 2001*) with knock-on effects on the spatial extent of lakes
30 and wetlands (*Smith et al., 2005a; Riordan et al., 2006*), runoff to the Arctic ocean,
31 ecosystem functioning (*Jorgenson et al., 2001; Payette et al., 2004*), and the surface
32 energy balance. Warming is also expected to enhance decomposition of soil organic
33 matter, releasing carbon to the atmosphere (a positive feedback) (*Zimov et al., 2006*) and
34 also releasing nitrogen which, in nutrient limited Arctic ecosystems, may prompt shrub
35 growth (a negative feedback due to carbon sequestration) (*Sturm et al., 2001*). This
36 greening-of-the-Arctic negative feedback may itself be offset by a positive radiative
37 feedback related to lower summer and especially winter albedos of shrubs and trees
38 relative to tundra (*Chapin et al., 2005*), which promotes an earlier spring snowmelt that
39 among other things affects soil temperature and permafrost (*Sturm et al., 2001*).
40

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

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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 probably 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.



1
2 *Figure 5.15. Physical and biological feedbacks in high latitude terrestrial systems,*
3 *from McGuire et al. (2006).*
4

5 **6.4 Observed and modeled sensitivity of wetland methane emissions to climate**
6 **change**

7 Field studies indicate that methane emissions do indeed increase in response to
8 soil warming and permafrost thaw. *Christensen et al. (2003)* note that a steady rise in
9 soil temperature will enhance methane production from existing regions of

1 methanogenesis that are characterized by water tables at or near the surface. While this
2 aspect is important, changes in landscape-scale hydrology have the ability to drive a
3 more significant change in methane emissions. For example, at a mire in sub-Arctic
4 Sweden, permafrost degradation and associated vegetation changes have driven a 22-
5 66% increase in landscape-scale CH₄ emissions over the period 1970 to 2000
6 (*Christensen et al., 2004*). *Bubier et al. (2005)* estimated that in a Canadian boreal
7 landscape with discontinuous permafrost and ~30% wetland coverage, landscape-scale
8 methane fluxes increased by ~60% from a dry year to a wet year, due to changes in
9 wetland water table depth, particularly at the beginning and end of the summer.
10 *Nykänen et al. (2003)* also found higher methane fluxes during a wetter year at a sub-
11 Arctic mire in northern Finland. *Walter et al. (2006)* find that thawing permafrost along
12 the margins of thaw lakes in eastern Siberia accounts for most of the methane released
13 from the lakes. This emission, which occurs primarily through ebullition, is an order of
14 magnitude larger where there has been recent permafrost thaw and thermokarst
15 compared to where there has not. These hotspots have extremely high emission rates
16 but account for only a small fraction of the total lake area. Methane released from these
17 hotspots appears to be Pleistocene age, indicating that climate warming may be releasing
18 old carbon stocks previously stored in permafrost (*Walter et al., 2006*). At smaller
19 scales, there is strong evidence that thermokarst development substantially increases
20 CH₄ emissions from high-latitude ecosystems. Mean CH₄ emission rate increases
21 between permafrost peatlands and collapse wetlands of 13-fold (*Wickland et al., 2006*),
22 30-fold (*Turetsky et al., 2002*), and up to 19-fold (*Bubier et al., 1995*) have been
23 reported.

24
25 A number of groups have attempted to predict changes in natural methane
26 emissions on a global scale. These studies broadly suggest that natural methane
27 emissions from wetlands will rise as the world warms. *Shindell et al. (2004)* incorporate
28 a linear parameterization for methane emissions, based on a detailed process model, into
29 a global climate model and find that overall wetland methane emissions increased by
30 121 Tg CH₄ y⁻¹, 78% higher than their baseline estimate. They project a tripling of
31 northern high-latitude methane emissions, and a 60% increase in tropical wetland
32 methane emissions in a doubled CO₂ simulation. The increase is attributed to a rise in
33 soil temperature in combination with wetland expansion driven by a positive P-E trend
34 predicted by the model. About 80% of the increase was due to enhanced flux rates, and
35 20% due to expanded wetland area or duration of inundation. The predicted increase in
36 the atmospheric methane burden was 1,000 Tg, ~20% of the current total, equivalent to
37 an increase of ~430 ppb, assuming a methane lifetime of 8.9 years. Utilizing a similar
38 approach but with different climate and emission models, *Gedney et al. (2004)* project
39 that global wetland emissions (including rice paddies) will roughly double, despite a
40 slight reduction in wetland area. The northern wetland methane emissions, in particular,
41 increase by 100% (44 to 84 Tg CH₄ yr⁻¹) in response to increasing soil temperatures and
42 in spite of a simulated 10% reduction in northern wetland areal extent. Using a more
43 process-based ecosystem model, which includes parameterizations for methane
44 production and emission, *Zhuang et al. (2007)* model a doubling of methane emissions
45 over the 21st century in Alaska, once again primarily in response to the soil temperature
46 influence on methanogenesis, and secondarily to an increase in NPP (Net Primary

1 Productivity) of Alaskan ecosystems. These factors outweigh a negative contribution to
2 methane emissions related to a simulated drop in the water table. It is important to note
3 that these models simulate only the direct impacts of climate change (altered
4 temperature and moisture regimes, and in one case enhanced vegetation productivity)
5 but not indirect impacts, such as changing landscape hydrology with permafrost
6 degradation and changing vegetation distribution. At this time, it is not known whether
7 direct or indirect effects will have a stronger impact on net methane emissions. These
8 models all predict fairly smooth increases in annual wetland emissions, with no abrupt
9 shifts in flux.

10 **6.5 Conclusion about potential for abrupt release of methane from wetlands**

11 Tropical wetlands are a stronger methane source than boreal/arctic wetlands and
12 will likely continue to be over the next century, during which fluxes from both regions
13 are expected to increase. However, four factors differentiate northern wetlands from
14 tropical wetlands and make them more likely to experience a larger increase in fluxes:
15 (1) high-latitude amplification of climatic warming will lead to a stronger temperature
16 impact, (2) for regions with permafrost, warming-induced permafrost degradation could
17 make more organic matter available for decomposition and substantially change the
18 system hydrology, (3) the sensitivity of microbial respiration to temperature generally
19 decreases with increasing temperatures (e.g., *Davidson and Janssens, 2006*), and (4)
20 most northern wetlands have substantial carbon as peat. On the other hand, two
21 characteristics of northern peatlands counter this: (1) northern peatlands are complex,
22 adaptive ecosystems, with internal feedbacks and self-organizing structure (*Belyea and*
23 *Baird, 2007*) that allow them to persist in a relatively stable state for millennia and that
24 may reduce their sensitivity to hydrological change, and (2) much of the organic matter
25 in peat is well-decomposed (e.g., *Frolking et al. 2001*) and may not be good substrate
26 for methanogens.
27

28
29 The balance of evidence suggests that anticipated changes to northern wetlands
30 in response to large-scale permafrost degradation, thermokarst development, a positive
31 P-E trend in combination with substantial soil warming, enhanced vegetation
32 productivity, and an abundant source of organic matter will conspire to drive a chronic
33 increase in CH₄ emissions from the northern latitudes during the 21st century. Due to
34 the strong interrelationships between temperature, moisture, permafrost, and nutrient and
35 vegetation change, and the fact that negative feedbacks such as the draining/drying of
36 wetlands are also possible, it is difficult to establish how large the increase will be over
37 the coming century. A doubling of CH₄ emissions could be realized fairly easily. Much
38 larger increases cannot be discounted.
39

40 It is worth noting that our understanding of the northern high-latitude methane
41 cycle continues to evolve. For example, a recent field study suggests that prior estimates
42 of methane emissions from northern landscapes may be biased low due to an
43 underestimation of the contribution of ebullition from thermokarst hot spots in Siberian
44 thaw lakes (*Walter et al., 2006*). Another interesting recently discovered phenomena is
45 the cold adaptation of some methanogenic microorganisms that have been found in
46 permafrost deposits in the Lena River basin (*Wagner et al., 2007*). These microbes can

1 produce methane even in the very cold conditions of permafrost, often drawing on old
2 soil organic matter. The activity levels of these cold-adapted methanogens are sensitive
3 to temperature and even a modest soil warming can lead to an accumulation of methane
4 deposits which, under scenarios where permafrost degradation leads to thermokarst or
5 coastal erosion, could be quickly released to the atmosphere.

6
7 These recent studies highlight the fact that key uncertainties remain in our
8 understanding of natural methane emissions and their susceptibility to climate change as
9 well as in our ability to predict future emissions. Among the most important
10 uncertainties in our understanding and required improvements to process-based models
11 are: (1) the contribution of ebullition and changes in ebullition to total methane
12 emissions; (2) the rate of change in permafrost distribution and active layer thickness
13 and associated changes in distribution of wetlands and lakes as well as, more generally,
14 terrestrial ecosystems; (3) model representation of soil thermal and hydrologic processes
15 and their response to climate change; (4) the contribution that shifts in vegetation and
16 changes in peatland functioning will alter the methane cycle; and (5) representation of
17 the highly variable and regionally specific methane production and emission
18 characteristics. Even with resolution of these issues, all predictions of future methane
19 emissions are predicated on the accurate simulation and prediction of high-latitude
20 climate. Improvements of many facets critical to the high-latitude climate system are
21 required, including improvements to the treatment of snow, polar clouds, subsoil
22 processes, subpolar oceans, and sea-ice in global climate models.

23 24 **7. FINAL PERSPECTIVES**

25
26 Although the prospect of a catastrophic release of methane to the atmosphere as
27 a result of anthropogenic climate change over the next century appears highly unlikely,
28 the carbon stored as methane hydrate and as potential methane in the organic carbon
29 pool of northern (and tropical) wetland soils has a role to play in future climate change.
30 Changes in climate, including warmer temperatures and more precipitation in some
31 regions, will quite likely increase the chronic emissions of methane from both melting
32 hydrates and natural wetlands. The magnitude of this effect cannot be predicted with
33 great accuracy yet but is at least equivalent to the current magnitude of many
34 anthropogenic sources, which have already more than doubled the levels of methane in
35 the atmosphere since the start of the Industrial Revolution

36
37 On a longer time scale, the hydrate reservoir may be a major player in global
38 warming over the next 1000-100,000 years. *Archer and Buffet (2005)* show that melting
39 methane hydrates may be a large positive feedback to warming caused by anthropogenic
40 carbon dioxide. The significance of this effect depends on the magnitudes of fossil fuel
41 release and the clathrate reservoir, but in some scenarios an additional $\sim 1 \text{ W/m}^2$ of
42 radiative forcing results from including the melting of the clathrate reservoir in a long
43 term climate/biogeochemical model. These longer-term effects may ultimately be the
44 major impact of methane hydrates due to global warming.

1
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