



## REVIEW ARTICLE

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## Key Points:

- Gas hydrates are widespread, sequester large amounts of methane at shallow depths, and have a narrow range of stability conditions
- Warming climate conditions destabilize hydrates, but sediment and water column sinks mostly prevent methane emission to the atmosphere
- Gas hydrate is dissociating at some locations now, but the impacts are primarily limited to ocean waters, not the atmosphere

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## The interaction of climate change and methane hydrates

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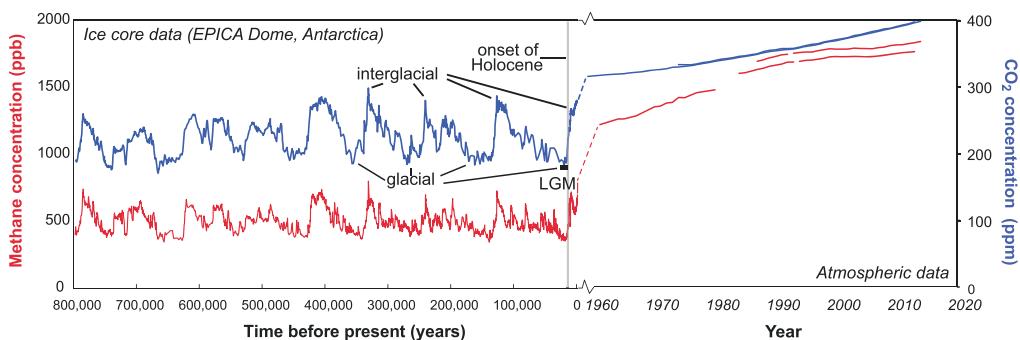
**Abstract** Gas hydrate, a frozen, naturally-occurring, and highly-concentrated form of methane, sequesters significant carbon in the global system and is stable only over a range of low-temperature and moderate-pressure conditions. Gas hydrate is widespread in the sediments of marine continental margins and permafrost areas, locations where ocean and atmospheric warming may perturb the hydrate stability field and lead to release of the sequestered methane into the overlying sediments and soils. Methane and methane-derived carbon that escape from sediments and soils and reach the atmosphere could exacerbate greenhouse warming. The synergy between warming climate and gas hydrate dissociation feeds a popular perception that global warming could drive catastrophic methane releases from the contemporary gas hydrate reservoir. Appropriate evaluation of the two sides of the climate-methane hydrate synergy requires assessing direct and indirect observational data related to gas hydrate dissociation phenomena and numerical models that track the interaction of gas hydrates/methane with the ocean and/or atmosphere. Methane hydrate is likely undergoing dissociation now on global upper continental slopes and on continental shelves that ring the Arctic Ocean. Many factors—the depth of the gas hydrates in sediments, strong sediment and water column sinks, and the inability of bubbles emitted at the seafloor to deliver methane to the sea-air interface in most cases—mitigate the impact of gas hydrate dissociation on atmospheric greenhouse gas concentrations though. There is no conclusive proof that hydrate-derived methane is reaching the atmosphere now, but more observational data and improved numerical models will better characterize the climate-hydrate synergy in the future.

## 1. Introduction

As evidence mounts for sustained global warming during the last half of the 20th century and the start of the 21st century, there is increased awareness of the relative importance of methane ( $\text{CH}_4$ ) to greenhouse warming. In the most recent assessment of the Intergovernmental Panel on Climate Change [*Intergovernmental Panel on Climate Change (IPCC)*, 2013], methane ( $\text{CH}_4$ ) was deemed 84 times more potent than carbon dioxide ( $\text{CO}_2$ ) as a greenhouse gas over a 20-year timeframe and 25 times more potent over a century on a per unit mass basis. Recent years have seen greater scrutiny of global sources of  $\text{CH}_4$  emissions and, in some places, new regulation of anthropogenic activities that enhance these emissions.

The absolute concentration of  $\text{CO}_2$  in the atmosphere (~400 ppm) is ~220 times more than the concentration of  $\text{CH}_4$  (~1.83 ppm), yet the radiative forcing of anthropogenic  $\text{CH}_4$  is ~25% that of anthropogenic  $\text{CO}_2$ .  $\text{CO}_2$  concentrations have increased less than 50% since the preindustrial age, while  $\text{CH}_4$  concentrations have increased by ~150% (Figure 1). Although the rate of change in atmospheric  $\text{CH}_4$  concentrations has been tempered by some periods of slower increases [Dlugokencky *et al.*, 1994, 2003], the rise in absolute concentrations since the middle of the twentieth century and the strong radiative warming associated with this gas justify the prominent role that  $\text{CH}_4$  has been given in discussions of greenhouse warming.

Among the large  $\text{CH}_4$  carbon reservoirs that naturally interact with the ocean-atmosphere system and thus global climate, gas hydrates (Figure 2) have special relevance. Gas hydrate is an ice-like substance formed when water and low-molecular-weight gas ( $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ , and higher-order hydrocarbons) [Sloan and Koh, 2008] combine in a clathrate structure. Methane is by far the predominant gas within natural gas hydrates that have been directly sampled, an observation that may partially reflect the abundance of  $\text{CH}_4$  (as opposed to higher-order thermogenic gases) at the shallow depths typically accessed by coring and drilling. Gas hydrate concentrates  $\text{CH}_4$  within its cage-like molecules, with 1 m<sup>3</sup> of gas hydrate sequestering a maximum of 180 m<sup>3</sup> of methane as measured at standard temperature and pressure (STP).



**Figure 1.** Methane and CO<sub>2</sub> concentrations in the atmosphere since 800 ka from *Environmental Protection Agency* [2015]. Deep time data are from analysis of the European Project for Ice Coring in Antarctica (EPICA) Dome ice core and thus reflect Southern Hemisphere methane. Note the difference in time scales between the panels.

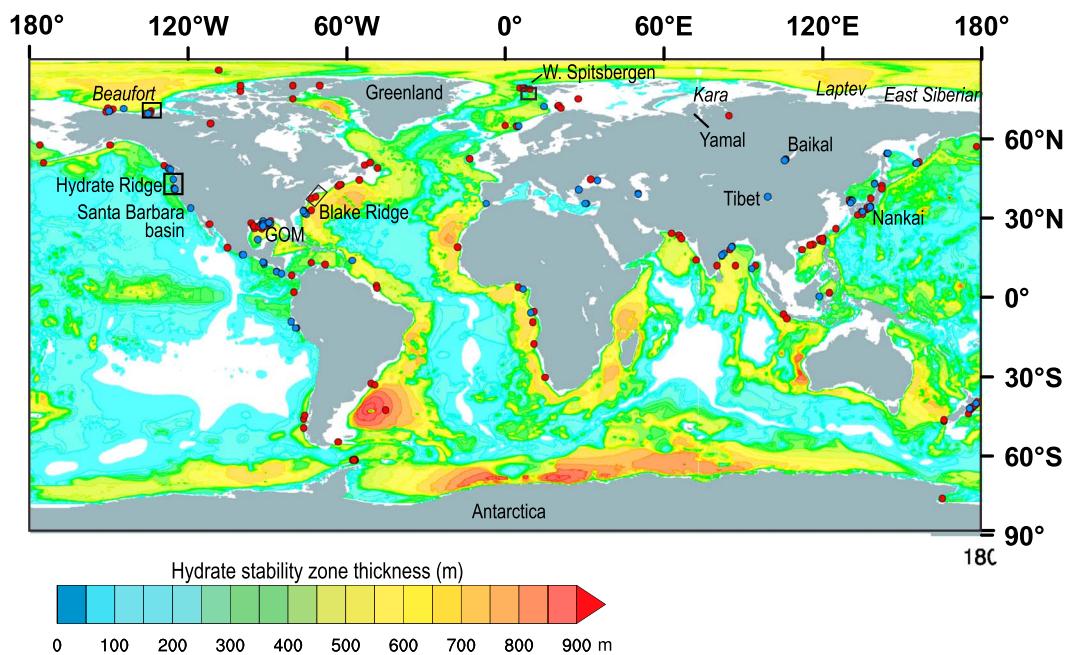
Owing to the predominance of CH<sub>4</sub> as the guest molecule, gas hydrate is often referred to as methane ice, and the terms “gas hydrate” or “methane hydrate” and just “hydrate” will be used interchangeably in this paper.

Methane hydrate is stable over a range of intermediate-pressure and low-temperature conditions found close to the seafloor in the sediments of deepwater (greater than 300–600 m) continental slopes and also within and beneath permafrost at high northern latitudes. These relationships are shown in map form in Figure 3 and on pressure-temperature stability diagrams in Figure 4. These stability conditions and the global distribution of gas hydrate make it susceptible to the key perturbations associated with global warming, namely changes in sea level (pressure) and increases in ocean/air temperatures. Simple calculations demonstrating the impact of changes in pressure and temperature on the gas hydrate reservoir are shown in Figure 5. Gas hydrates sequester large amounts of carbon, with estimates ranging from more than half [Kvenvolden, 1988a] to ~15% [Boswell and Collett, 2011; Milkov, 2004] of Earth’s total mobile carbon, which includes that in soils, land biota, fossil fuels, peat, and other reservoirs. The relative importance of gas hydrates within the global carbon reservoir based on older analyses [Kvenvolden, 1988a] and more modern perspectives [Boswell and Collett, 2011] can be deduced from Figure 6.



**Figure 2.** Gas hydrate (white material) formed beneath mussel-coated carbonate rock on the seafloor of the Gulf of Mexico as photographed by NOAA’s Deep Discoverer remotely operated vehicle in 2014. Image courtesy of the NOAA Ocean Exploration and Research Program. Seafloor gas hydrate is not volumetrically important within the global reservoir, but the existence of such gas hydrates illustrates that methane and other hydrate-forming gases migrate across the sediment-water interface and interact with ocean waters. Methane seeps, authigenic carbonates, and seafloor gas hydrates can be important habitats for chemosynthetic organisms reliant on methane or sulfide for their metabolic processes [e.g., Levin, 2005].

Taken together, the dependence of gas hydrate stability on pressure-temperature (P-T) conditions, the relatively shallow depths of hydrate occurrence beneath the seafloor or in permafrost areas (i.e., relative to conventional natural gas), hydrate’s tendency to concentrate gas, and the large amount of carbon trapped in global gas hydrates contribute to the perception that gas hydrate breakdown, termed “dissociation”, is a potential threat associated with global warming. In addition, large-scale gas hydrate dissociation is sometimes portrayed not only as a consequence of warming but also as a potential synergistic driver for enhanced warming if the CH<sub>4</sub> released from gas hydrates reaches the atmosphere. These dual roles of gas hydrate dissociation—as both an effect and possible contributor to global warming—have led some to adopt a catastrophic perspective on the interaction of the climate system with the global gas

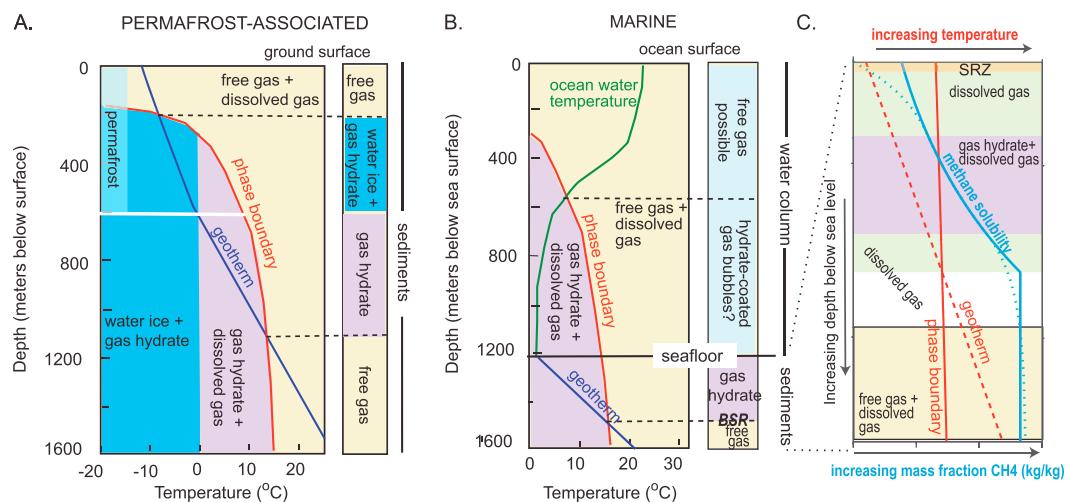


**Figure 3.** Thickness of the theoretical gas hydrate stability zone (GHSZ) as calculated by Kretschmer et al. [2015] as the base map, with locations of known gas hydrate (recovered samples/photographs; blue circles) and inferred gas hydrate (based on well logs or geophysical markers like bottom-simulating seismic reflectors at the base of gas hydrate stability; red circles) superposed. Gas hydrate distribution is typically heterogeneous within the stability zone, and gas hydrate only rarely occurs through the full thickness of the stability zone. The map also shows place names used in the paper. GOM refers to the Gulf of Mexico. Boxes on the Canadian Beaufort margin [Paull et al., 2015], northwest U.S. Pacific margin [Johnson et al., 2015], northern U.S. Atlantic margin [Skarke et al., 2014], and West Spitsbergen margin [Westbrook et al., 2009] show locations where upper continental slope methane seeps may be linked to gas hydrate dissociation processes.

hydrate reservoir [e.g., Bohannon, 2008; Krey et al., 2009; MacDonald, 1990; Mascarelli, 2009; Whiteman et al., 2013].

This paper reviews the current state of knowledge on the interactions between methane hydrates and the global climate system and addresses misconceptions about posited runaway dissociation, the contemporary input of hydrate-derived methane to the atmosphere, the potential for massive methane releases, and the distribution of gas hydrates in high-latitude regions. While there have been numerous studies of marine gas hydrate reservoir changes in response to climate events that occurred millions of years ago (e.g., the Paleocene-Eocene Thermal Maximum at ~55.5 Ma) [Dickens et al., 1997] or during the late Quaternary [Kennett et al., 2000, 2003], less consideration has been given to assessing observational data and other evidence about climate-hydrate interactions over the contemporary period [Archer, 2007; Archer et al., 2009; Nisbet, 1990a, 1990b; Ruppel, 2011a]. O'Connor et al. [2010] considered the fate of methane hydrates under different future climate change scenarios but did not include factors (sinks) that strongly mitigate the impact that hydrate-derived CH<sub>4</sub> has on the ocean-atmosphere system. James et al. [2016] recently explored the interaction between climate change and gas hydrates with full acknowledgement of sinks but with a focus on the Arctic Ocean.

In the following sections, we first review background information on gas hydrates, including their global distribution and the amount of sequestered CH<sub>4</sub>, along with an overview of the impact of climate change processes on gas hydrates. We then assess the Intergovernmental Panel on Climate Change's assumptions about the emission of hydrate-derived CH<sub>4</sub> to the atmosphere, explore the key challenges associated with distinguishing hydrate-derived CH<sub>4</sub> from emissions originating with non-hydrate sources, and review the sinks that prevent most CH<sub>4</sub> released by gas hydrate dissociation from reaching the atmosphere. We briefly consider major pre-Holocene climate episodes for which researchers have inferred large-scale gas hydrate dissociation events and provide an in-depth assessment of each physiographic province that hosts gas hydrates, discussing the impact of climate change processes on those deposits and the existing data on CH<sub>4</sub> emissions. We



**Figure 4.** Gas hydrate stability constraints for nominal (a) permafrost and (b) deepwater marine settings after Ruppel [2007]. Note that gas hydrate stability calculations usually use hydrostatic pressure in shallow subseafloor sediments owing to their high, water-filled porosity. BSR refers to the bottom-simulating reflector that marks the boundary between free gas and overlying hydrate-bearing sediments in some marine reservoirs. The purple zones correspond to gas hydrate with dissolved gas, while yellow regions may have coexisting dissolved gas and free gas (gas bubbles). (c) An expansion of the seafloor part of Figure 4b, demonstrating the relationship among the gas hydrate stability zone (GHSZ) and the zone where gas hydrate actually occurs based on pressure-temperature and methane solubility (activity) constraints. Blue solubility curves are read on the bottom axis and red temperature curves on the top axis. The green areas have dissolved gas as their only methane phase but are within the theoretical GHSZ. The white region has dissolved gas but lies beneath the base of the GHSZ. Figure modified from Xu and Ruppel [1999] after Nimblett and Ruppel [2003]. SRZ refers to the nominal sulfate reduction zone, where methane is consumed via anaerobic oxidation of methane (AOM).

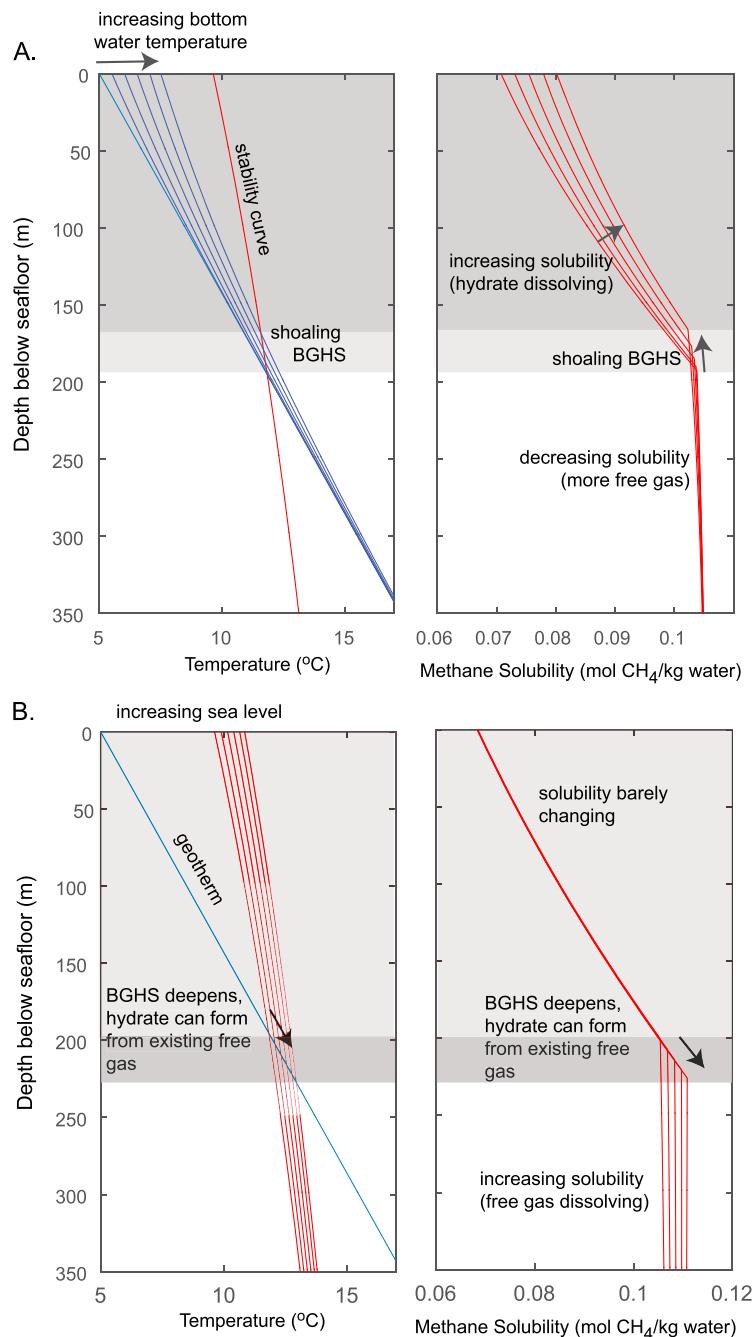
also review modeling efforts that have been used to assess the interaction of gas hydrates and global climate and offer recommendations about the key knowledge gaps to be addressed by researchers in future observational and numerical modeling studies. Finally, we briefly explore the potential climate impact of inadvertent CH<sub>4</sub> leakage during hypothetical production of gas from hydrate deposits.

## 2. Gas Hydrate Background

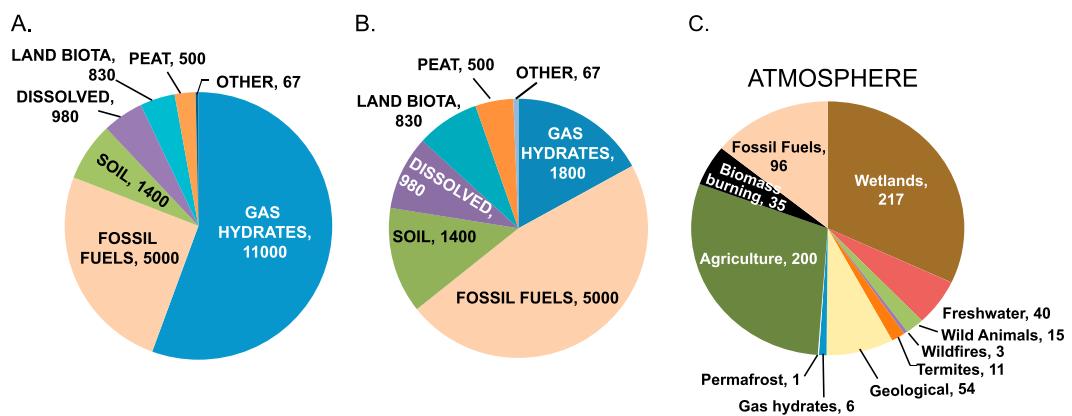
### 2.1. Distribution

Among the most important issues related to assessing climate-hydrates interactions are establishing where gas hydrates occur and estimating the size of the potential CH<sub>4</sub> source associated with them. These elements define the role of methane hydrates within the global carbon cycle. Here we review the general distribution of gas hydrates, leaving specifics for section 6, where we assess the vulnerability of each population of gas hydrate to climate forcing processes. This overview does not include the Antarctic continent, for which only one assessment has been made for subglacial hydrates [Wadham *et al.*, 2012], nor the minor populations of gas hydrate present at inland locations (e.g., Lake Baikal or Tibetan Plateau permafrost) [Scholz *et al.*, 1993; Yang *et al.*, 2010].

About 99% of gas hydrates form in marine sediments [e.g., McIver, 1981] on continental slopes at water depths of greater than ~500 m in temperate latitudes and ~300 m at high latitudes, where bottom waters are colder. These depths mark the shallowest P-T limit for the gas hydrate stability zone (GHSZ) on continental slopes, where the stability zone vanishes. Downslope, the GHSZ in the sedimentary section thickens as pressure increases, and it may eventually encompass the uppermost few hundred meters of sediments in waters deeper than 1000 m. For example, the GHSZ beneath the Blake Ridge sediment drift deposit (>2000 m water depth) reaches ~550 m thickness [Paull *et al.*, 1996]. Owing to the concentration of organic carbon on continental margins, these locations are where most gas hydrates occur (Figure 3), and gas hydrates are largely absent beneath abyssal plains. The organic carbon is delivered to the sediment both by the rain of phytoplankton to the seafloor in highly productive continental margin waters and by export of terrestrial sediment from the continents. Remineralization of sedimentary organic carbon produces CO<sub>2</sub>,



**Figure 5.** The impact of (a) temperature and (b) pressure increases on the marine gas hydrate stability field and methane solubility in pore space assuming initial seafloor depth of 750 m, background geothermal gradient of  $35^{\circ}\text{C km}^{-1}$ , sediment thermal diffusivity of  $3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ , and homogeneous sediments. Large changes were imposed here for the sake of demonstration. In Figure 5a, seafloor temperature increased by  $2.5^{\circ}\text{C}$  over 1000 years, and the BGHS shoals as the geotherm reequilibrates. Solubility decreases slightly beneath the BGHS, squeezing more dissolved gas out of solution into free gas, but increases measurably within the GHSZ, meaning that gas hydrate may dissolve. The original GHSZ encompasses the entire gray zone, with the GHSZ after 1000 yr is reduced to the darker gray zone. In Figure 5b, a pressure change corresponding to a 100 m increase in sea level over 1000 years is imposed. Since these plots are relative to the seafloor, they show the relative change in the position of the stability curve (red) as pressure increases and the BGHS deepens. The geotherm (blue) remains unchanged. Solubility increases below the BGHS, meaning bubbles may dissolve at these depths. Above the BGHS, solubility barely changes. New hydrate will only form near the new BGHS if methane (e.g., from preexisting underlying free gas) is available in excess of the increased solubility curve. The original GHSZ is the light gray zone, while GHSZ after 1000 yr also includes the darker gray zone. Solubility calculations carried out using Matlab code provided by W. Waite (personal communication, 2016).



**Figure 6.** The estimated amount of carbon trapped in global gas hydrate deposits has shrunk over the past few decades, as documented by Boswell and Collett [2011]. With other sources remaining the same, this comparison shows the relative proportion of mobile (exogenic) carbon in gas hydrates from (a) the 11,000 Gt C estimate [Kvenvolden, 1988a] made soon after the first dedicated drilling programs to (b) the 1800 Gt C adopted here, which is a value close to the estimates of Milkov [2004] and Boswell and Collett [2011] and within the range given by Piñero *et al.* [2013]. (c) To place the methane emission rate from dissociating gas hydrates as assumed by several IPCC reports in perspective, the assumed emission of 6 Tg yr<sup>-1</sup> CH<sub>4</sub> is plotted with other estimates of atmospheric methane sources from the bottom-up attribution of Kirschke *et al.* [2013].

and most CH<sub>4</sub> formed in sediments by microbial processes is the result of reducing this CO<sub>2</sub>. Microbial CH<sub>4</sub>, instead of thermogenic CH<sub>4</sub> formed at higher temperatures via the same processes responsible for conventional natural gas, is the type most often found in recovered gas hydrates.

When considering the vertical distribution of gas hydrates in marine sediments, a critical distinction is made between the GHSZ (Figure 4b) and the zone of actual gas hydrate occurrence [e.g., Xu and Ruppel, 1999; Zatsepina and Buffett, 1998], as shown in Figure 4c. For gas hydrate to form from dissolved methane, as much of the gas hydrate in marine sediments likely does, requires not only appropriate P-T conditions but also sufficient water and the presence of methane in excess of its solubility in surrounding pore waters [Klauda and Sandler, 2005; Makogon, 1997; Xu and Ruppel, 1999; Zatsepina and Buffett, 1998]. Thus, based only on thermodynamics and physical chemistry, the zone where gas hydrate can potentially occur will have both a top and a bottom that are controlled by the local solubility of CH<sub>4</sub> in pore space and the availability of CH<sub>4</sub> at each location in the sedimentary section (Figure 4c). Hydrate can form as deep as the base of the gas hydrate stability (BGHS) only when enough gas is available in excess of local solubility, which typically requires elevated flux or long periods of hydrate formation [Nimblett and Ruppel, 2003; Xu and Ruppel, 1999]. In practice, the top of the gas hydrate zone in marine sediments is controlled not only by CH<sub>4</sub> flux but also by a biogeochemical condition, namely the presence of a sulfate reduction zone in which methane is consumed by microbial processes (section 4). Except in certain high-flux cold seep environments or fractured formations, high saturations of gas hydrate are usually not present throughout the GHSZ. Even within homogeneous sediments with sufficient CH<sub>4</sub>, gas hydrate will rarely saturate pore space completely, and subtle heterogeneities (e.g., diatom-rich layers) [Kraemer *et al.*, 2000] cause preferential permeability that affects the final distribution of gas hydrates. In addition, clays, fine-grained sediments, and higher-salinity pore water inhibit gas hydrate formation [Clennell *et al.*, 1999; Ruppel *et al.*, 2005], while high-permeability coarse-grained sediments like sand [Boswell *et al.*, 2009b; Dai *et al.*, 2012] and areas with rapid advection of fluids and gas [Xu and Ruppel, 1999] tend to host higher saturations of hydrate [Ginsburg *et al.*, 2000]. Overall, the amount of CH<sub>4</sub> sequestered in the GHSZ will always be less than the amount of available pore space.

The remaining ~1% or more of global gas hydrates occurs in high northern latitude permafrost areas [McIver, 1981; Ruppel, 2015], both onshore beneath tundra (e.g., Russia, Canada, and the U.S.) and on continental shelves on circum-Arctic Ocean margins whose permafrost has been inundated by sea level rise since ~15 ka [e.g., Kvenvolden, 1993; Lachenbruch *et al.*, 1982; Rachold *et al.*, 2007]. The shallowest permafrost-associated gas hydrates (PAGH) are predicted to lie a few hundred meters deep but still within the permafrost zone (Figure 4a). For permafrost that is several hundreds of meters thick, gas hydrate should also be stable beneath the base of permafrost, depending on the prevailing geothermal gradient. Many PAGH formed by a process that can be described in the vernacular as “freezing in place” of gaseous CH<sub>4</sub> that has presumably

migrated to shallower depths from underlying conventional gas reservoirs containing thermogenic gas [Collett *et al.*, 2011; Judge and Majorowicz, 1992; Ruppel, 2015].

## 2.2. Amount of Methane

Besides the distribution of gas hydrates in sediments, the other important issue related to assessing climate-hydrate interactions is establishing the amount of CH<sub>4</sub> sequestered in climate-sensitive hydrate deposits, which requires a priori constraints on the global CH<sub>4</sub> in place in all gas hydrates. As documented by Boswell and Collett [2011], estimates have ranged over several orders of magnitude in the past four decades (Figure 6), but they have mostly fallen since the 1990s [Klauda and Sandler, 2005; Milkov, 2004]. One reason for the high early estimates is that researchers typically assumed that all potential porosity within the GHSZ was filled with hydrate. After the advent of dedicated drilling programs in the mid-1990s [Boswell and Collett, 2011; Ruppel, 2011b], samples of hydrate-bearing sediments and quantitative borehole logs began to reveal that only a small fraction of formation porosity typically hosts gas hydrate [e.g., Trehu *et al.*, 2006], except in some high-permeability, coarse-grained reservoirs.

The global estimate preferred by Boswell and Collett [2011] based on an exhaustive review of other assessments and considering the lessons of many drilling programs is  $3 \times 10^{15} \text{ m}^3$  of methane gas in place (calculated at STP) in global gas hydrates, corresponding to  $\sim 1500$  gigatons (Gt or  $10^{15}$  g) of carbon or  $\sim 2.0$  million Tg ( $10^{12}$  g) CH<sub>4</sub>. This estimate is similar that of the lower end of the range determined by Milkov [2004], 9–20% higher than that of Archer *et al.* [2009], and more than 30 times smaller than the  $1 \times 10^{17} \text{ m}^3$  gas in place estimated by Klauda and Sandler [2005] at about the same time. A global estimate that apportions gas in place in methane hydrate among different countries yields a value slightly higher ( $\sim 1800$  Gt C) [Johnson, 2011] than the Boswell and Collett [2011] estimate. Another modern estimate made by Dickens [2011] gives an upper bound of 12,400 Gt C,  $\sim 8.3$  times larger than that of Boswell and Collett [2011] and also larger than an independent calculation 500–2300 Gt C for global methane hydrates [Piñero *et al.*, 2013]. This Dickens [2011] value is close to the 11,000 Gt C given by Kvenvolden [1988b] two decades earlier, an estimate that was criticized by Laherrere [1999] as too high. Several independent assessments use various observations, models, and methodology to converge on values that are mostly less than 2000 Gt C sequestered in methane hydrates [e.g., the lower range of Milkov, 2004; Archer *et al.*, 2009; Boswell and Collett, 2011; Piñero *et al.*, 2013]. We here adopt a value of  $\sim 1800$  Gt C ( $\sim 2400$  Gt CH<sub>4</sub>) gas in place in methane hydrates for the global system, excluding Antarctica. To render the discussion more generic, some explanations are also cast in terms of the percentages of the global gas hydrate reservoir, not absolute estimates.

While we primarily focus here on the amount of CH<sub>4</sub> sequestered in gas hydrates, it is critical to note that especially in the marine environment, hydrates are spatially associated with large amounts of CH<sub>4</sub> that occurs as free gas below the BGHS or sometimes within the GHSZ [e.g., Flemings *et al.*, 2003; Gorman *et al.*, 2002]. Hornbach *et al.* [2004] estimated that the amount of free gas that could potentially be released due to perturbations to the GHSZ in gas hydrate provinces could be as large as two-thirds of the estimated gas in place in hydrate.

## 2.3. Climate Change and Methane Hydrates

To set the stage for the rest of this paper, we briefly explore the impact of global climate change processes on gas hydrate deposits, with more in-depth discussion left to section 6. Gas hydrates are destabilized by increasing temperature or decreased pressure (Figure 5), conditions rarely associated with the same climate event. For example, global warming leads to higher average ocean and air temperatures but also increased sea level (pressure). For hydrate conditions close to the phase boundary, the morphology of the gas hydrate stability curve means that the destabilizing impact of slightly higher temperatures usually overwhelms the small stabilizing effect associated with increased sea level (1 m increase in sea level yields  $<0.01$  MPa increase in pressure) but on different time scales. For elastic sediments, the pressure perturbation associated with rising sea level would be relatively instantaneous. In contrast, the impact of temperature changes at the tundra surface (permafrost hydrates) or seafloor (marine hydrates or those associated with subsea permafrost) on hydrates buried at depth may be delayed by hundreds or thousands of years, depending on the thickness and thermal diffusivity of the overlying sediments. This lag means that gas hydrate that remains stable over the scale of centuries in response to climate perturbations [e.g., Kretschmer *et al.*, 2015; Ruppel, 2011a] may liberate significant gas on millennial scales.

While not widespread on present-day Earth, one population of gas hydrates does experience higher temperatures and decreased pressures during the same climate event [e.g., *Nisbet*, 1990b]. Gas hydrates formed beneath continental ice sheets or grounded ice on continental margins may have constituted a significant part of the global gas hydrate inventory during some periods of Earth's history (section 5). The depressurization effect associated with thawing ice sheets that may have reached thicknesses greater than 1 km greatly exceeds that related to the total range in sea level changes (~300 m) [*Miller et al.*, 2005] since 50 Ma. Thawing ice sheets may be a primary driver for gas hydrate dissociation early in deglacial cycles, followed later by dissociation due to warming temperatures.

The fundamental impact of climate-related changes on the gas hydrate reservoir is relatively straightforward, but several points bear mentioning: First, the gas hydrate reservoir tends to be viewed as relatively static during periods of climate stability or in certain settings (e.g., deep oceans). In fact, gas hydrates near the BGHS are nearly always undergoing dissociation due to normal sedimentation, small perturbations in pressure, and propagation of past temperature changes to depth [e.g., *Dickens*, 2001a]. Second, the impact of past climate change events is often used to frame how the gas hydrate reservoir may respond to future climate change. As noted by *Archer and Buffett* [2005], the predicted changes associated with anthropogenically-driven global warming may be far larger than those of many past climate events, affecting even the stability of deep ocean hydrates. Finally, just as snow piles do not instantaneously melt on a hot day, gas hydrate dissociation is also not instantaneous merely because pressure or temperature conditions in the sediments lie outside those required for hydrate stability. The endothermic heat of reaction (~439 J g<sup>-1</sup> of methane hydrate) [*Gupta et al.*, 2008] hinders rapid dissociation and makes the dissociation process self-regulating [*Circone et al.*, 2005]. Without the delivery of additional heat to the hydrate deposits, a scenario of runaway dissociation (dissociation that self-perpetuates once initiated) is unlikely.

### 3. Global Methane Budgets and Gas Hydrate Dissociation

Even before early observational studies attempted to link atmospheric methane records to CH<sub>4</sub> emission processes that might include gas hydrate dissociation [e.g., *Kvenvolden*, 1993], researchers had attempted to include gas hydrate dynamics in their evaluation of global methane budgets [e.g., *Cicerone and Oremland*, 1988; *Revelle*, 1983]. The two approaches applied to evaluating the CH<sub>4</sub> sources in the atmosphere are termed top-down and bottom-up, which are described below and explored in detail by *Nisbet and Weiss* [2010] and *Kirschke et al.* [2013]. Both the fifth *IPCC* [2013] and *Kirschke et al.* [2013] provide up-to-date comparisons of top-down and bottom-up atmospheric CH<sub>4</sub> assessments. Each approach has different implications for the potential role of gas hydrate dissociation in releasing CH<sub>4</sub> to the atmosphere.

A top-down assessment uses as its starting point the total amount of methane in the atmosphere on a global or regional scale. Applying several methods, including sophisticated inversion techniques, the total CH<sub>4</sub> concentration is then attributed to various sources. By its very nature, the top-down assessment accounts for all CH<sub>4</sub> present in the atmosphere at a given spatial scale; however, the attribution to sources is typically not very detailed since several sources are typically lumped together.

A bottom-up assessment scales measurements of CH<sub>4</sub> emissions made at or near the Earth's surface up to a larger area. The contributions of the different emission sources are then summed in order to derive a global estimate of CH<sub>4</sub> flux to the atmosphere. For example, CH<sub>4</sub> emissions measured at a group of terrestrial seeps or at rice paddies in a specific location may be upscaled to estimate the total flux from all such features. Relatively small overestimates in the contributions from different CH<sub>4</sub> sources can become magnified in the upscaling process, leading to a global emissions estimate that cannot be reconciled with the known amount and rate of increase of atmospheric CH<sub>4</sub>. Another challenge is that measurements of CH<sub>4</sub> emissions on the Earth's surface are inherently biased. For example, scientists quantifying geologic methane emissions tend to measure the most active seep sites, and upscaling of the biased sample can lead to attribution of too much methane flux to a particular source.

The annual flux of CH<sub>4</sub> to the atmosphere from all sources is estimated at ~555 Tg yr<sup>-1</sup>. As updated by *Kirschke et al.* [2013] and summarized in the report of the fifth *IPCC* [2013], the total top-down global methane emissions estimate is ~130 Tg yr<sup>-1</sup> smaller than the bottom-up estimate. At present, the top-down estimation methods do not have the capacity to attribute CH<sub>4</sub> to individual geologic sources like gas hydrates. *Kirschke*

**Table 1.** IPCC Attributions of Atmospheric Methane to Gas Hydrate Sources

IPCC Assessment (Year)	Atmospheric Methane Emissions Attributed to Gas Hydrates (Tg CH <sub>4</sub> yr <sup>-1</sup> )	References Cited for Gas Hydrate-Related Atmospheric Methane Emissions
First IPCC [1990]	5 (0–100)	Kvenvolden [1988a] is cited for high end-member, but this reference argues that atmospheric emissions from gas hydrates are less than 160 Tg CH <sub>4</sub> yr <sup>-1</sup> (corresponding to 120 Tg C yr <sup>-1</sup> or 0.12 Gt C yr <sup>-1</sup> )
Second IPCC [1996]	–	Hydrate contributions were not included in the atmospheric methane budget.
Third IPCC [2001]	5, 10	Fung <i>et al.</i> [1991]; Lelieveld <i>et al.</i> [1998] (respectively)
Fourth IPCC [2007]	4, 5	Wang <i>et al.</i> [2004] inverse model; Wuebbles and Hayhoe [2002], citing Judd [2000] (respectively)
Fifth IPCC [2013]	6 (2–9)	Denman <i>et al.</i> [2007]; Dickens [2003b]—a book review; Shakhova <i>et al.</i> [2010a]

*et al.* [2013] note that both the flux of methane to the atmosphere and the global sink for methane are likely overestimated in the bottom-up assessment. The commonly adopted assumption for bottom-up assessment is that ~5 Tg yr<sup>-1</sup> CH<sub>4</sub> is emitted to the atmosphere from gas hydrate dissociation (e.g., IPCC [2001] and subsequent IPCC panels). The only CH<sub>4</sub> source that routinely appears in bottom-up studies and that has a smaller contribution than gas hydrate dissociation is wildfires [e.g., Kirschke *et al.*, 2013].

### 3.1. Attribution of Atmospheric Methane to Gas Hydrate Dissociation

The first published estimates of CH<sub>4</sub> flux to the atmosphere due to gas hydrate dissociation ranged from 0.12 Gt yr<sup>-1</sup> to 8 Gt yr<sup>-1</sup> C [Bell, 1983; Revelle, 1983] as described by Kvenvolden [1988b]. Later, Kvenvolden and Rogers [2005] reported these same numerical values in units of Tg yr<sup>-1</sup> C (1000 times smaller) and cited Kvenvolden [1991] for an estimate of 4 Tg yr<sup>-1</sup> CH<sub>4</sub> (3 Tg yr<sup>-1</sup> C) emitted to the atmosphere by gas hydrate dissociation. From the first IPCC [1990] through the most recent IPCC reports (with the exception of the second IPCC [1996]), CH<sub>4</sub> released by gas hydrate dissociation has appeared on the list of sources contributing to atmospheric CH<sub>4</sub>, usually at the level of ~5 Tg yr<sup>-1</sup> (Table 1). The range in the first IPCC [1990] was 0–100 Tg yr<sup>-1</sup> CH<sub>4</sub> emitted from gas hydrates, while that in the fifth IPCC [2013] is 2–9 Tg yr<sup>-1</sup>. At the rate of 5 Tg yr<sup>-1</sup> CH<sub>4</sub> emissions, 400 ky would hypothetically be required for wholesale transfer of the estimated methane in place in the global gas hydrate reservoir to the atmosphere based on the Boswell and Collett [2011] estimate. Given the depth of burial of some gas hydrate populations and the strong sinks that upward migrating CH<sub>4</sub> would encounter both in the sediments and the overlying ocean on contemporary Earth, it is likely that little of this CH<sub>4</sub> could reach the atmosphere. However, dissociating hydrates could be a major source of atmospheric CH<sub>4</sub> under certain catastrophic, but unlikely, circumstances. Rapid, large-volume CH<sub>4</sub> emissions might bypass strong sediment [e.g., Knittel and Boetius, 2009; Martens and Klump, 1980] or water column [e.g., Elliott *et al.*, 2011] sinks, injecting more methane into the atmosphere. Ruppel [2011a] calculated that instantaneous release of 1.8 Gt C from the gas hydrate reservoir (~0.1% of estimated gas in place) would temporarily increase atmospheric CH<sub>4</sub> concentrations by more than 60% if all of the gas reached the atmosphere.

The values quoted by the various IPCC reports have never been based on observational evidence for CH<sub>4</sub> emissions derived from gas hydrate dissociation since no such measurements exist. A few examples underscore this point: The clearly identified assumption of Cicerone and Oremland [1988] that 5 Tg yr<sup>-1</sup> CH<sub>4</sub> reached the atmosphere from gas hydrate dissociation has set the stage for the subsequent quarter century. The third IPCC [2001] cites the Fung *et al.* [1991] forward modeling study, which merely assigned a value for the contribution to atmospheric CH<sub>4</sub> emissions from gas hydrate dissociation. This was also the case with Lelieveld *et al.* [1998], which assumed 10 Tg yr<sup>-1</sup> CH<sub>4</sub> emissions from gas hydrate for one scenario, a number that was then adopted by the third IPCC [2001]. The Wuebbles and Hayhoe [2002] study cited by the fourth IPCC [2007] is sometimes considered the observationally based source for the now oft-used 5 Tg yr<sup>-1</sup> CH<sub>4</sub> estimate for atmospheric CH<sub>4</sub> flux from gas hydrates. That study in turn cites Judd [2000], which is a geologic methane seepage study that does not provide an independent estimate for emissions derived from gas hydrate dissociation. Cranston [1994], on which Judd [2000] relies for his hydrate-related flux discussion, estimates the sum of global diffusive and ebullitive fluxes from marine sediments to the atmosphere to be ~1.3 Tg yr<sup>-1</sup> to 13 Tg yr<sup>-1</sup> CH<sub>4</sub> considering all sources, including shallow-water seeps and deepwater gas hydrates. The Denman *et al.* [2007] study cited in the fifth IPCC [2013] is the climate coupling chapter from the fourth IPCC [2007] and not an independent source of information. The fifth IPCC [2013] also refers to

Dickens [2003b], which is a book review of Kennett *et al.* [2003] that did not provide an estimate for CH<sub>4</sub> flux to the atmosphere from dissociating gas hydrates, as Dickens [2003a] also did not. Shakhova *et al.* [2010a], also given as a source for the hydrate-derived atmospheric CH<sub>4</sub> flux in the fifth IPCC [2013], did not attribute the 7.98 Tg yr<sup>-1</sup> CH<sub>4</sub> flux that they calculated for the East Siberian Arctic shelf to gas hydrate degradation, rather considering a range of potential sources.

The inclusion of hydrate dissociation as a possible source of atmospheric CH<sub>4</sub> in the IPCC reports is a rightful acknowledgement of the fact that the amount of CH<sub>4</sub> sequestered in this reservoir dwarfs that in some other parts of the Earth system. On the other hand, the IPCC reports cite no direct sources that constrain emissions of CH<sub>4</sub> to the atmosphere as a result of gas hydrate dissociation. Indeed, while gas hydrate deposits are likely dissociating and releasing CH<sub>4</sub> to sedimentary sections and the ocean on contemporary Earth, there remains no evidence that this hydrate-derived CH<sub>4</sub> reaches the atmosphere or that the amounts that could potentially reach the atmosphere are significant enough to affect the overall CH<sub>4</sub> budget. In the following sections, we discuss some of the difficulties in discerning methane released from gas hydrates from other populations of methane in the ocean and atmosphere and also underscore the powerful role of sinks in mitigating the transfer to the atmosphere of methane released by dissociating gas hydrates.

### 3.2. Challenges in Attributing Methane to Gas Hydrate Degradation

Numerous studies have constrained the upward flux of CH<sub>4</sub> through soils and sediments and to seawater and the atmosphere, but fingerprinting CH<sub>4</sub> in the environment as having originated with the dissociation of gas hydrates faces two major challenges. First, a measurable tracer must exist that uniquely identifies CH<sub>4</sub> as once having been encapsulated by hydrates. Second, the true environmental impacts of CH<sub>4</sub> released from dissociating hydrates may not be limited to only the recently encapsulated CH<sub>4</sub> since emissions associated with dissociation of gas hydrate may also release free gas previously stored in the sediments [e.g., Hornbach *et al.*, 2004]. Attempts to fingerprint direct and indirect emissions associated with dissociating CH<sub>4</sub> hydrates have focused on three main approaches: age dating, chemical tracers, and stable isotopic fractionation.

1. *Age dating.* Radioisotopic measurements have been used to determine the age of CH<sub>4</sub> in gas hydrates, which can then be compared with the ages of CH<sub>4</sub> produced locally in sediments (microbial processes), sourced from deeper geologic systems (thermogenic processes), and emitted to overlying waters and/or the atmosphere. Age dating studies have relied on <sup>14</sup>C and <sup>129</sup>I [Fehn *et al.*, 2000, 2003; Grabowski *et al.*, 2004; Kessler and Reeburgh, 2005; Kessler *et al.*, 2005, 2008; Pohlman *et al.*, 2011; Tomaru *et al.*, 2009; Winckler *et al.*, 2002]. While the results are strongly dependent on local CH<sub>4</sub> sources, trends suggest that CH<sub>4</sub> sequestered in gas hydrate is usually older than the surrounding sediments [Fehn *et al.*, 2000, 2003; Kessler *et al.*, 2005; Tomaru *et al.*, 2009], underscoring the role of gas migration in supplying CH<sub>4</sub> for gas hydrates in some settings. Furthermore, both CH<sub>4</sub> in gas hydrate and associated free gas are often too old to be dated by <sup>14</sup>C techniques, rendering this technique useless in discriminating CH<sub>4</sub> recently liberated by dissociation from that of deeper geologic gas that was never bound in hydrate.
  2. *Chemical tracers.* If gas hydrate formation preferentially incorporates specific molecules from the source gas mixture, a unique chemical fingerprint may be retained in these structures. Upon dissociation, this chemical signature would be detectable and enable identification of gas streams originating with gas hydrate dissociation. For example, Dallimore *et al.* [2008] found a mixture of CH<sub>4</sub> and higher-order hydrocarbons in permafrost gas hydrates of the Mackenzie River Delta, and this same mixture was detected seeping from the tundra. This observation could imply that gas hydrate dissociation directly feeds this seep, but an alternate possibility is that a deeper conventional reservoir supplies both the seep and the gas for the hydrate reservoir. More recent investigations of the widespread CH<sub>4</sub> seeps on the West Spitsbergen margin [Westbrook *et al.*, 2009] have discovered a similar chemical composition in the seep gas and the gas supplying the underlying hydrates [Berndt *et al.*, 2014].
- Another promising approach for fingerprinting released gas as possibly derived from recently dissociated CH<sub>4</sub> hydrate exploits noble gas concentrations. In CH<sub>4</sub> hydrates, noble gas molecules enter the lattice in order by molecular weight (MW), meaning that gas hydrate should contain relatively more helium (MW = 4.003 g/mol) than krypton (MW = 83.300 g/mol). Such an ordering of noble gases would not be characteristic of generic gas streams originating with shallowly produced gas, coal beds, and leaking deep reservoirs. Analyses of the noble gas characteristics of natural gas hydrate samples was attempted, but encountered air contamination

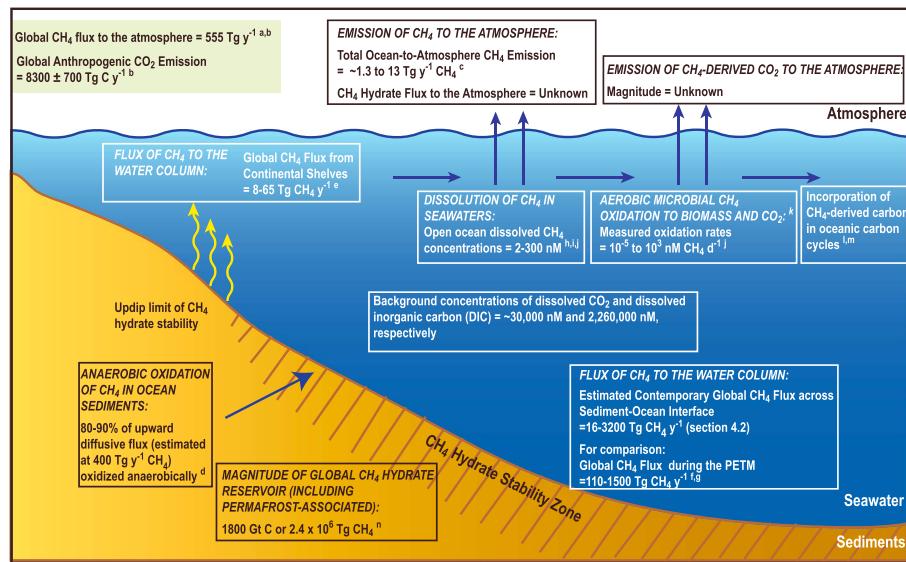
and other problems, for Blake Ridge and Hydrate Ridge [Dickens and Kennedy, 2000; Winckler *et al.*, 2002]. Experiments on synthetic CH<sub>4</sub> hydrates and one set of natural subseafloor gas hydrate samples that were subjected to controlled dissociation proved that that light gases are preferentially released early in the process [Hunt *et al.*, 2013b], probably because their atoms are too small to contribute to stabilizing the gas hydrate lattice [Hunt *et al.*, 2013a]. This approach must now be tested on a greater number of natural gas hydrate samples and on gas streams that may originate with gas hydrate dissociation before it can be rendered a true fingerprinting method for identifying CH<sub>4</sub> gas emissions from degrading natural hydrates. However, even if this fingerprinting technique proves to be a reliable marker of methane that was once encapsulated in hydrate, it still will not identify coexisting free gas that was coreleased to the ocean-atmosphere system during emission events associated with gas hydrate dissociation.

3. *Stable isotopic fractionation.* Physical and chemical processes often modify the naturally-occurring ratio of stable isotopes of various molecules. For example, the dissolution and oxidation of methane [Alperin *et al.*, 1988; Harting *et al.*, 1976; Kessler *et al.*, 2006] systematically change the ratio of <sup>13</sup>CH<sub>4</sub>/<sup>12</sup>CH<sub>4</sub> as well as <sup>12</sup>CDH<sub>3</sub>/<sup>12</sup>CH<sub>4</sub>. Thus, it has been hypothesized that the formation and/or dissolution of gas hydrates may also modify the stable isotopes, producing an isotopic tracer. The formation of hydrates has been shown to fractionate the stable isotopes of water forming the hydrate cages, as noticed in the pore waters of ocean sediment cores [Hesse and Harrison, 1981; Kvenvolden and Kastner, 1990; Matsumoto and Borowski, 2000]. However, if the goal is to trace CH<sub>4</sub> that is emitted from the seafloor to hydrate decomposition in the sediments, any changes in water isotopes in the seep gas stream will be overwhelmed by the overlying aqueous environment.

While it is common practice to measure the stable carbon isotopes of CH<sub>4</sub> ( $\delta^{13}\text{C-CH}_4$ ), these have not been shown to fractionate during formation or dissociation of gas hydrates [Lapham *et al.*, 2012]. Methane is formed by both biological and geological (thermogenic) processes, each displaying a relatively unique value for  $\delta^{13}\text{C-CH}_4$ . Since gas hydrate can incorporate either microbial (light  $\delta^{13}\text{C}$ ) or thermogenic (heavy  $\delta^{13}\text{C}$ ) CH<sub>4</sub>, the gas produced during hydrate dissociation lacks a unique signature with respect to other CH<sub>4</sub> in the environment. In addition, anaerobic and aerobic methane oxidation, which can both affect CH<sub>4</sub> released by gas hydrates (section 4), have been shown to aggressively fractionate  $\delta^{13}\text{C-CH}_4$ . This further complicates source discrimination after CH<sub>4</sub> is released from dissociating hydrates [Alperin *et al.*, 1988; Whiticar, 1999]. Although  $\delta^{13}\text{C-CH}_4$  cannot uniquely fingerprint CH<sub>4</sub> released from dissociating gas hydrates, paleoclimate studies often interpret negative carbon isotopic excursions in carbonates or paleosols as indicating large-scale dissociation of the gas hydrate reservoir. These dissociation events have been assumed to release methane with a  $\delta^{13}\text{C-CH}_4$  isotopic signature of  $-60\text{\textperthousand}$  [e.g., Dickens *et al.*, 1997]. The interpretation of negative carbon isotopic excursions in terms of dissociation events is justified based on the large size and widespread distribution of the gas hydrate reservoir, as well as its relatively unique  $\delta^{13}\text{C}$  signature compared to other global carbon reservoirs. However, while gas hydrate methane is isotopically-light compared to other global carbon reservoirs, no systematic global surveys have been conducted to constrain the global average value for  $\delta^{13}\text{C-CH}_4$  encapsulated by hydrates. It should also be noted that wetlands also produce large amounts of isotopically light  $\delta^{13}\text{C-CH}_4$  ( $<-60\text{\textperthousand}$ ) and are frequently implicated in methane releases investigated in paleoclimate studies that rely on nonmarine records [e.g., Chappellaz *et al.*, 2013; Petrenko *et al.*, 2009; Raynaud *et al.*, 1998; Sowers, 2006]. Measurements of  $\delta\text{D-CH}_4$  have been used in paleoclimate investigations to distinguish marine (e.g., methane hydrate dissociation) from terrestrial methane sources. For example, Sowers [2006] used  $\delta\text{D-CH}_4$  from Greenland ice cores to search for isotopic signals that might indicate that methane from dissociating marine hydrates had reached the atmosphere during late Pleistocene to Holocene warm periods (section 5.4). While  $\delta\text{D-CH}_4$  is useful as a first-order discriminant between marine and terrestrial sources of CH<sub>4</sub>, it cannot distinguish between CH<sub>4</sub> emitted from dissociating gas hydrates and that emitted from other marine sources.

#### 4. Methane Sinks

Even when CH<sub>4</sub> is released from gas hydrate during dissociation, physical, chemical, and biological sinks in the sediments and ocean waters mitigate the amount that reaches the atmosphere (Figure 7). These sinks are so strong that there are likely very few locations on present-day Earth where gas hydrate dissociation could release CH<sub>4</sub> that reaches the atmosphere in any significant quantities.



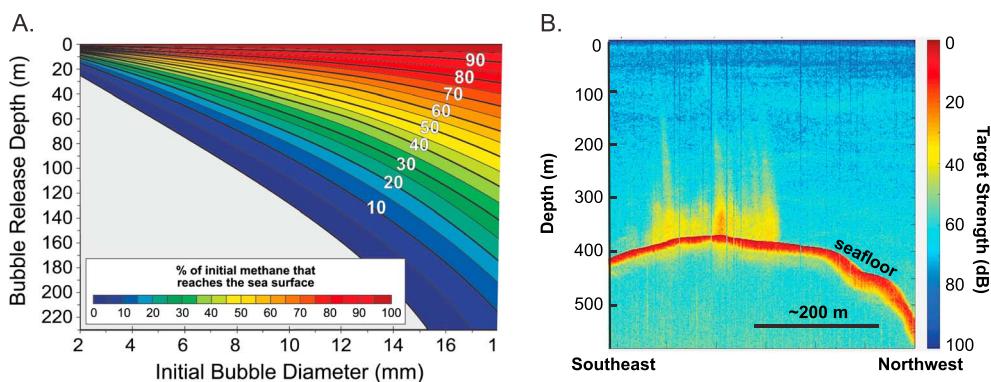
**Figure 7.** Schematic of the sources and sinks associated with methane release from gas hydrates. Tg =  $10^{12}$  g. Gt =  $10^{15}$  g. Modified from Kessler [2014]. (a) Kirschke et al. [2013]. (b) Fifth IPCC [2013]. (c) Cranston [1994]. (d) Reeburgh [2007]. (e) Hovland et al. [1993]. (f) Dickens et al. [1995]. (g) Zeebe et al. [2016] (h) Heintz et al. [2012]. (i) Rona et al. [2015]. (j) Mau et al. [2013]. (k) Boudreau et al. [2015]. (l) Pohlman et al. [2011]. (m) Wang et al. [2001]. (n) Boswell and Collett [2011]. Note that the annual anthropogenic emission of carbon as CO<sub>2</sub> far exceeds the estimated emission of carbon in CH<sub>4</sub> during even an extreme climate event like the PETM.

#### 4.1. Marine Sediments

In the shallow marine sedimentary section, the strongest biochemical sink is the anaerobic oxidation of methane (AOM) [Barnes and Goldberg, 1976; Martens and Berner, 1977; Reeburgh, 1976], which is carried out by a consortium of microbes [Knittel and Boetius, 2009] and is strongly coupled to sulfate reduction [e.g., Malinverno and Pohlman, 2011], particularly in diffusion-dominated provinces lacking additional hydrocarbon sources [Joye et al., 2004]. The sulfate reduction zone (SRZ) occupies the centimeters to meters just below the seafloor, with a thicker SRZ corresponding to areas of lower upward methane flux [Borowski et al., 1997]. The microbial consortium that carries out AOM [Boetius et al., 2000] has been termed a biofilter that prevents upwardly-migrating CH<sub>4</sub> from reaching the seafloor, where it could be emitted to the ocean. A summary by Reeburgh [2007] concluded that up to 80% to 90% of the estimated 400 Tg yr<sup>-1</sup> CH<sub>4</sub> that reaches the SRZ via upward migration through the sediments is consumed by AOM [Hinrichs and Boetius, 2003]. At sites with vigorous seepage, AOM has sometimes been found to be highly efficient [Joye et al., 2004], while only about 20% of the CH<sub>4</sub> is consumed by AOM at other locations [Boetius and Wenzhofer, 2013]. The reduced efficiency of AOM in some higher flux settings leads to the possibility that rapidly ascending gas in the form of bubbles may bypass the sediment biofilter [e.g., Martens and Klump, 1980] and be injected into the overlying ocean without major alteration by the AOM sediment sink.

AOM is also closely coupled to carbonate precipitation at shallow depths beneath the seafloor since AOM produces bicarbonate, which increases alkalinity. The resulting authigenic carbonates, which are often exhumed at the seafloor at methane seeps, effectively remove carbon from the mobile carbon cycle. The carbonates also carry a record of CH<sub>4</sub> emissions in both their absolute age [e.g., Bayon et al., 2009; Crémère et al., 2016; Liebetrau et al., 2010; Teichert et al., 2003; Watanabe et al., 2008] and in their changing carbon isotopic characteristics [e.g., Aloisi et al., 2000]. In some places, the isotopic characteristics of these carbonates have been interpreted as reflecting local destabilization of gas hydrate [Bohrmann et al., 1998].

The physical characteristics of marine sediments also constitute a type of sink for CH<sub>4</sub> released from dissociating gas hydrates. These physical sinks do not transform CH<sub>4</sub> in the way that AOM does, but they can prevent it from interacting with the ocean-atmosphere system for thousands of years. The most important physical factors are those that impede the migration of methane through the sedimentary section. Examples include low-permeability sediments, structural traps, and hydrate- and/or gas-saturated sediments that impede fluid



**Figure 8.** (a) From McGinnis *et al.* [2006]. The original caption is “Contour plot of the percentage of the initial methane mass reaching the atmosphere as a function of initial bubble diameter and release depth (methane reaching the surface is read at the point where the bubble diameter and release depth intersect on the plot). Environmental conditions were those from the Black Sea; however, these results are also valid as a first approximation for “normal” open ocean (e.g., Monterey Bay) or lake/reservoir conditions.” (b) Hydroacoustic image of seeping methane gas collected with a 38 kHz split-beam sensor on the Baltimore Canyon seep field of the U.S. Atlantic margin in 2015, after Prouty *et al.* [2016].

advection [e.g., Bhatnagar *et al.*, 2007; Chatterjee *et al.*, 2014; Davies and Clarke, 2010; Davies *et al.*, 2014; Garg *et al.*, 2008; Liu and Flemings, 2007; Nimblett and Ruppel, 2003].

#### 4.2. Water Column Methane Sinks

Once  $\text{CH}_4$  is emitted at the seafloor, two major factors may prevent its reaching the atmosphere. First, despite methane’s low solubility in seawater [Wiesenburg and Guinasso, 1979], the concentrations of  $\text{CH}_4$  in most ocean waters are still so low that the gas diffuses rapidly from rising  $\text{CH}_4$ -filled bubbles following emission at the seafloor. During this bubble-stripping process,  $\text{CH}_4$  is replaced by oxygen and nitrogen [McGinnis *et al.*, 2006; Vielstädte *et al.*, 2015]. Bubbles emitted deeper than the shallowest extent of gas hydrate stability in the water column may develop an armor of gas hydrate [Chen *et al.*, 2014, 2016; Graves *et al.*, 2015; Rehder *et al.*, 2002, 2009; Sauter *et al.*, 2006; Topham, 1984; Wang *et al.*, 2016; Warzinski *et al.*, 2014; Zhang, 2003], but such armoring may or may not reduce the rate at which  $\text{CH}_4$  leaves the rising bubbles [Rehder *et al.*, 2002; Wang *et al.*, 2016]. Overall, most  $\text{CH}_4$  emitted from the seafloor either above or below the top of the GHSZ and whether originating with gas hydrate dissociation or other processes will be dissolved relatively deep in the water column.

As an example, for 50% of the  $\text{CH}_4$  contained in the bubble at the seafloor to reach the atmosphere requires 14 and 20 mm diameter bubbles to be emitted at 50 and 100 m water depths, respectively, and even larger bubbles at greater water depths. (Figure 8a). While quantification of bubble sizes at marine seeps is in its infancy, the bubble sizes measured to date are far smaller than would be necessary to ensure that  $\text{CH}_4$  reaches the atmosphere [e.g., Römer *et al.*, 2012; Skarke *et al.*, 2014; Wang *et al.*, 2016]. Once dissolved in ocean waters,  $\text{CH}_4$  can eventually be emitted to the atmosphere by gas exchange, which can be enhanced by certain conditions (e.g., high winds and storminess [Shakhova *et al.*, 2014; Wanninkhof, 1992]). In deeper waters,  $\text{CH}_4$  could remain in the oceans for centuries, depending on the nature of ocean circulation and the depth below the surface mixed layer at which the  $\text{CH}_4$  is dissolved.

Once dissolved in seawater, aerobic microbial oxidation (MOx) is a strong sink that can limit the flux of dissolved methane to the atmosphere [e.g., Mau *et al.*, 2007; Ward *et al.*, 1987]. MOx was traditionally thought to be a relatively slow process [e.g., Valentine *et al.*, 2001], but more recent studies show that oxidation rates can increase when seawater is perturbed with elevated concentrations of  $\text{CH}_4$  [e.g., Crespo-Medina *et al.*, 2014; de Angelis and Scranton, 1993; Du and Kessler, 2012; Heintz *et al.*, 2012; Kessler *et al.*, 2011; Mau *et al.*, 2013; Pack *et al.*, 2015]. Most of these studies inoculate seawater samples with radioisotope tracers to measure MOx rates in discrete parcels of water at the specific locations and times of sampling. The true strength of this sink can only be assessed by measuring the total integrated amount of MOx in the water column, either regionally [e.g., Du and Kessler, 2012; Leonte *et al.*, 2017] or globally. For example, assuming that the open ocean is in steady state with a dissolved methane concentration of 2 nM, this would equate to an open-ocean methane

burden of 43.2 Tg CH<sub>4</sub> [Reeburgh, 2007]. If methane emissions to the water column are balanced by aerobic methane oxidation with first-order MOx rate constants ranging from 0.001 to 0.2 d<sup>-1</sup> [de Angelis and Scranton, 1993; Mau *et al.*, 2013; Pack *et al.*, 2011; Valentine *et al.*, 2001], then both the rates of MOx and seafloor CH<sub>4</sub> emission to the water column probably lie in the range of 16 to 3200 Tg yr<sup>-1</sup>. While we make no attempt to constrain the most likely value within this large range, combining even the low end-member with the global sink associated with CH<sub>4</sub> oxidation in marine sediments (80–90% of 400 Tg yr<sup>-1</sup>) [Reeburgh, 2007] suggests that oceanic sinks of methane are at least equal to, and potentially greater than, all atmospheric sinks of CH<sub>4</sub> (~540 Tg yr<sup>-1</sup> from top-down calculations in Kirschke *et al.* [2013]).

Several aspects of the aerobic MOx sink remain poorly understood. For example, the chemical stoichiometry of this reaction, especially how it changes as the microbial population is aggressively growing in response to a seafloor injection of CH<sub>4</sub>, is unknown [Chan *et al.*, 2016]. In addition, several investigations have documented depletions in dissolved oxygen, trace metals, and nutrients following the aerobic oxidation of CH<sub>4</sub> and oil in the deep waters of the Gulf of Mexico after the Deepwater Horizon incident [Du and Kessler, 2012; Joung and Shiller, 2013; Schiller and Joung, 2012], leading to questions about whether these chemical species may be limiting factors for oxidation of seafloor CH<sub>4</sub> emissions. Also unknown is whether currents can disperse elevated concentrations of CH<sub>4</sub> to levels below the threshold to initiate MOx before microbial populations can increase in response to CH<sub>4</sub> injection or whether transport of dissolved CH<sub>4</sub> to the surface mixed layer and hence to the sea-air interface can outcompete oxidation. Measurements of the natural radiocarbon content of CH<sub>4</sub> at a few locations have suggested that CH<sub>4</sub> in the surface mixed layer is not originating with seafloor emissions [Kessler *et al.*, 2008] but rather with unique methane generation processes active in the near-surface ocean [Damm *et al.*, 2008; Karl *et al.*, 2008; Metcalf *et al.*, 2012; Repeta *et al.*, 2016].

Bubble stripping and the water column oxidation sink may prevent much of the CH<sub>4</sub> emitted at the seafloor from reaching the sea-air interface, but these processes could still potentially have an important impact on ocean chemistry and habitats. As noted above, aggressive oxidation following massive CH<sub>4</sub> releases can deoxygenate waters and deplete certain chemical species while also increasing dissolved CO<sub>2</sub> that could enhance acidification [e.g., Archer *et al.*, 2009; Biastoch *et al.*, 2011; Dickens, 2001a; Elliott *et al.*, 2011; Kessler *et al.*, 2011]. Outside of semienclosed anoxic basins, typical CH<sub>4</sub> concentrations range from 2 to 300 nM [Heintz *et al.*, 2012; Mau *et al.*, 2013; Rona *et al.*, 2015], while the background concentrations of dissolved CO<sub>2</sub> and dissolved inorganic carbon (DIC) are approximately 30 μM and 2260 μM, respectively. The 4 to 6 orders of magnitude difference between dissolved methane concentration and DIC concentration suggests that even complete oxidation of CH<sub>4</sub> emitted at the seafloor from natural seeps will have an insignificant influence on inorganic carbon chemistry and, by extension, seawater pH, unless CH<sub>4</sub> and CH<sub>4</sub>-derived DIC can substantially accumulate in seawater.

#### 4.3. Terrestrial Methane Sinks

A discussion of cold region terrestrial CH<sub>4</sub> sinks [Jorgensen *et al.*, 2015; Walter Anthony *et al.*, 2014] is largely beyond the scope of this paper and is most relevant where CH<sub>4</sub> from dissociating deeply buried permafrost-associated gas hydrates (estimated ~1% or more of the global inventory) [Ruppel, 2015] migrates upward and encounters microbial soil sinks. Aerobic and anaerobic CH<sub>4</sub> oxidation in permafrost settings depends on a variety of factors [Lee *et al.*, 2012; Preuss *et al.*, 2013]. The paucity of sulfate in terrestrial sediments means that oxidation pathways and rates are substantially different in tundra settings relative to deep marine sediments. Still, if CH<sub>4</sub> from dissociating gas hydrates were to pass through sediments in dissolved (bioavailable) form, some oxidation processes might be expected to mitigate the fraction of this CH<sub>4</sub> that reaches the surface [Lau *et al.*, 2015]. Like marine sediments, tundra may also have low-permeability traps that act as a kind of physical sink, retarding upward migration of CH<sub>4</sub>. A unique physical barrier in high-latitude settings is pore-filling ice, which could trap CH<sub>4</sub> released during subpermafrost gas hydrate dissociation.

#### 4.4. Atmospheric Methane Sinks

If CH<sub>4</sub> from dissociating gas hydrate reaches the atmosphere, it encounters a strong photolytic sink in the troposphere. An estimated 90% of CH<sub>4</sub> emitted to the atmosphere by all sources is removed by oxidation with the hydroxyl (OH) radical within about a decade [e.g., Cicerone and Oremland, 1988]. Numerous intermediate species, each with its own global warming potential, are generated during the process of tropospheric

oxidation. However, the ultimate result of this CH<sub>4</sub> oxidation is CO<sub>2</sub>. A small proportion of CH<sub>4</sub> that reaches the atmosphere is transported to the stratosphere. Oxidation there results in the production of water vapor, itself a strong greenhouse species and a significant participant in the catalytic reaction for stratospheric ozone destruction. Forster *et al.* [2007] estimate that the combined products of CH<sub>4</sub> oxidation in the troposphere and stratosphere have about the same radiative forcing as the CH<sub>4</sub> itself, further underscoring the importance of CH<sub>4</sub> in the climate system. This rough equivalence between the radiative forcing associated with CH<sub>4</sub> and its oxidative products means that precisely determining the lifetime of atmospheric methane in the range of 8.9 ± 0.6 years [Prinn *et al.*, 1995] to 12.4 yr [IPCC, 2013] may not be critical for models that track the impact of CH<sub>4</sub> release at time scales of centuries to millennia.

## 5. Past Hyperthermals and Gas Hydrate Dissociation

Hypotheses suggesting positive feedback between modern climate change and the release of methane from dissociating gas hydrates are based on the susceptibility of gas hydrates to pressure and temperature changes, the large amount of CH<sub>4</sub> sequestered in gas hydrates, and paleoclimate studies that have implicated such a feedback during certain periods of Earth's history. In this section, we explore some of the key paleoclimate evidence for the interaction of gas hydrates and the global climate system during past climate events. Throughout the discussion, it should be recognized that (1) paleoclimate interpretations that connect warming events and hydrate destabilization remain controversial; (2) the inferred release rate of CH<sub>4</sub> from hydrates in some paleoclimate interpretations is a small fraction of the current anthropogenic CO<sub>2</sub> release rate [Archer and Buffett, 2005; Zeebe *et al.*, 2016]; and (3) globally significant releases of methane from hydrates, either in the past or future, generally require millennia or at least centuries.

### 5.1. Neoproterozoic (1000 Ma to 541 Ma)

The Neoproterozoic was a period of at least two extreme glaciations (snowball Earth) [Hoffman *et al.*, 1998] that brought ice to low latitudes [Sohl *et al.*, 1999]. Overlying the siliciclastic glacial sediments deposited in conjunction with these global cooling events are authigenic cap carbonates that occur in thin (up to 5 m thick) layers. The cap carbonates have textures and features similar to those produced by contemporary CH<sub>4</sub> cold seep processes and a strongly negative (up to 5‰)  $\delta^{13}\text{C}$  excursion and related  $\delta^{34}\text{S}$  anomaly, as would be expected if a large reservoir of light  $\delta^{13}\text{C}$  methane had been released and oxidized during the formation of the carbonates [e.g., Jiang *et al.*, 2003; Kennedy *et al.*, 2001]. The major hypothesis for these observations is widespread degassing of terrestrial permafrost-associated gas hydrates [Kennedy *et al.*, 2001], subsea permafrost hydrates [Kennedy *et al.*, 2008], and/or most of the marine gas hydrate reservoir [Jiang *et al.*, 2003] during ice sheet retreat and other deglacial events. Kennedy *et al.* [2008] estimate that ~3000 Gt C may have been released from nonmarine gas hydrates during warming following the Marinoan (~635 Ma) deglaciation and postulate that the deglaciation event set the stage for biogeochemical changes that were necessary for the explosion of life in the Cambrian. Bjerrum and Canfield [2011] focus on a younger climate event (~551 Ma) in the Neoproterozoic and conclude that large-scale dissociation of marine gas hydrates beneath an anoxic ocean led to CH<sub>4</sub> being injected into an oxygen-poor atmosphere during a short-lived warming episode.

### 5.2. Early Jurassic (Toarcian; ~183 Ma)

At the end of the Early Jurassic, three distinct negative carbon isotopic shifts during the Toarcian (~183 Ma) collectively produced an excursion of ~5–7‰ in  $\delta^{13}\text{C}$  [Kemp *et al.*, 2005]. This carbon isotope signature is larger than that associated with the end of the snowball Earth episodes in the Neoproterozoic and also with the one that characterizes the well-studied Paleocene-Eocene Thermal Maximum (section 5.3). Astronomical changes (Milankovitch cycles) superposed on a longer-term warming event are postulated to have repeatedly triggered the release of isotopically-light carbon [Kemp *et al.*, 2005] during the Toarcian, and large-scale methane hydrate dissociation [Hesselbo *et al.*, 2000] is the primary hypothesis for injection of ~5000 Gt C to the ocean-atmosphere system [Beerling *et al.*, 2002]. Several major ocean geochemical changes coincided with this inferred dissociation event [e.g., Jenkyns *et al.*, 2001; Schouten *et al.*, 2000], including ocean anoxia that would have affected the strength of the water column methane sink. Whereas dissociation events in the Neoproterozoic were precursors to expanding biodiversity, at least two of the events in the Toarcian were associated with widespread extinctions [e.g., Harries and Little, 1999; Kemp *et al.*, 2005].

### 5.3. Paleocene-Eocene Thermal Maximum (~55.5 Ma)

The most widely studied hyperthermal event was first recognized by *Kennett and Stott* [1991] and is termed the Paleocene-Eocene Thermal Maximum (PETM) or the Late Paleocene Thermal Maximum (LPTM) in older literature. This abrupt, multiphase extreme warming event [e.g., *Bowen et al.*, 2015] produced ~5°C increase in global temperature [*Zachos et al.*, 2007] and even more heating in deep ocean basins [*Tripathi and Elderfield*, 2005] and also coincided with a 3.5 to 5‰ negative excursion in marine  $\delta^{13}\text{C}$  [*McCarren et al.*, 2008]. The carbon isotopic data are supplemented by oxygen isotopic analyses of benthic forams, which provide a temperature proxy for the deep ocean [*Zachos et al.*, 2001, 2010]. *Dickens et al.* [1995, 1997] hypothesized that large-scale dissociation of marine gas hydrates released 1100 to 2100 Gt C of isotopically-light carbon to the ocean-atmosphere system during the PETM.

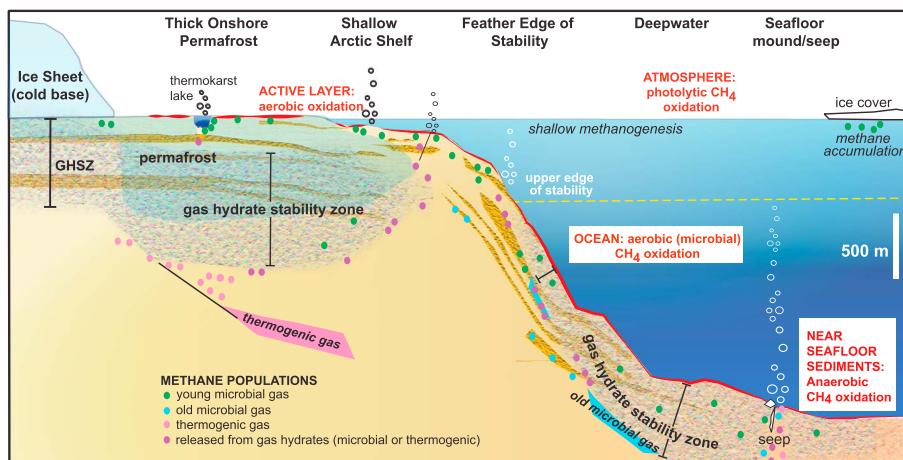
To explain observations during the PETM, researchers must rely on some form of an isotope mass balance in order to infer the source of carbon causing the isotopic excursion. Hypotheses as disparate as comet impact [*Kent et al.*, 2003], permafrost thaw [*DeConto et al.*, 2012], biomass burning [*Kurtz et al.*, 2003], and volcanic heating that causes contact metamorphism of organic carbon [*Svensen et al.*, 2004] have been advanced to explain the PETM. A few recent studies give credence to some of these mechanisms and increase the estimate of the amount of carbon released, as is necessary to satisfy the isotope mass balance [e.g., *Wright and Schaller*, 2013]. The methane hydrate dissociation hypothesis continues to garner the most attention, although the triggering mechanism for the dissociation remains uncertain. In addition, the amount of  $\text{CH}_4$  release required to produce the observed carbon isotopic anomaly is unlikely to have caused sustained warming of the atmosphere [*Higgins and Schrag*, 2006; *Zachos et al.*, 2003]. Another quandary is that terrestrial records reveal a consistently larger isotopic excursion [*Bowen et al.*, 2001] than deep ocean sediment cores, which may have poorer preservation of the event [*McCarren et al.*, 2008]. If the global carbon isotopic anomaly is related to a marine source, then the marked change in terrestrial carbon isotopes during the PETM implies that the water column oxidation sink did not prevent emissions of methane carbon to the atmosphere [e.g., *Zhang*, 2003]. Interestingly, a recent study constrained the release rate of carbon during the PETM to  $<1.1 \text{ Pg yr}^{-1}$  [*Zeebe et al.*, 2016]. Since the current rate of  $\text{CH}_4$  release from the seafloor ranges from 0.016 to  $3.2 \text{ Pg yr}^{-1}$  (section 4.2; 1 Pg = 1000 Tg), the modern seafloor  $\text{CH}_4$  emission regime is potentially comparable to that during the PETM. Recent modeling has also shown that multiple carbon ( $\text{CH}_4$  and/or  $\text{CO}_2$ ) emission events and possibly multiple sources may be required to explain observational data [*Carozza et al.*, 2011] for the PETM.

### 5.4. Quaternary Warming Periods: The Clathrate Gun

Paleoceanographic records [e.g., *Kennett and Ingram*, 1995] and biomarker evidence [*Hinrichs et al.*, 2003] have also been used to infer repeated dissociation of marine gas hydrates during late Quaternary climate events, including during late Pleistocene glaciations [*de Garidel-Thoron et al.*, 2004]. On the basis of a high-resolution carbon isotopic record obtained in Santa Barbara Basin, *Kennett et al.* [2000, 2003] advanced the clathrate gun hypothesis for the late Quaternary. This idea postulates that interstadials, which are temporary warming episodes within glacial periods (often called Dansgaard-Oeschger or D/O events), are associated with warming of intermediate ocean waters and dissociation of continental slope gas hydrates that released  $\text{CH}_4$  to the overlying waters and atmosphere. More recent studies use  $\delta\text{D-CH}_4$  (section 3.2) to show that changing atmospheric  $\text{CH}_4$  concentrations at and between some D/O events cannot be linked to dissociation of the marine gas hydrate reservoir and more likely represent the influence of wetlands methane [*Bock et al.*, 2010].

A secondary aspect of the clathrate gun hypothesis is the conjecture that warming ocean waters above sediments hosting gas hydrates leads to an increased incidence of submarine slope failures. Some researchers posit that large-scale submarine slope failures or erosional episodes are an efficient means to rapidly dissociate gas hydrate and release large amounts of gas that can reach the atmosphere without being lost to sediment or water column sinks [*Bangs et al.*, 2010; *Nixon and Grozic*, 2006; *Paull et al.*, 2002]. Through the careful analysis of large-scale submarine slides in the late Quaternary, *Maslin et al.* [2004] showed that these slope failures most often originated during Heinrich events, not D/O events. Heinrich events are associated with massive rafting of icebergs from glacial ice sheets, leading to the addition of cool, dense waters to the oceans, not warming of intermediate waters.

An evaluation of the clathrate gun hypothesis, although during a more recent time period, can be made using terrestrial ice core records. *Sowers* [2006] used Greenland ice cores to search for isotopic signals that might



**Figure 9.** Schematic of methane hydrate dynamics and methane distributions in different physiographic provinces. This diagram is updated from Ruppel [2011a] with the addition of subglacial hydrates and methane accumulation under ice. The most climate-susceptible hydrates are associated with (1) thawing subsea permafrost beneath Arctic Ocean shelves that were unglaciated at the Last Glacial Maximum (LGM) and (2) dissociating gas hydrates on upper continental slopes, respectively corresponding to Sectors 2 and 3 of Ruppel [2011a].

indicate that CH<sub>4</sub> from dissociating gas hydrates had reached the atmosphere during key late Pleistocene to Holocene warm periods. Given that microbial CH<sub>4</sub> released from wetlands and from dissociating gas hydrates cannot be distinguished on the basis of carbon isotopes alone (section 3), Sowers [2006] instead relied on hydrogen isotopic signatures ( $\delta D$ ) that should provide a clear marker for deep ocean CH<sub>4</sub> hydrate dissociation (heavy deuterium) versus CH<sub>4</sub> expulsion from wetlands (light deuterium). The correlation between warmer climates and increases in atmospheric methane is well-established, but the hydrogen isotope analyses by Sowers [2006] and some associated numerical modeling demonstrated that the atmospheric CH<sub>4</sub> did not originate with deep marine gas hydrate dissociation. A later ice core analysis by Petrenko *et al.* [2009] focused on the rise in atmospheric methane at  $\sim 11.6$  ka warming event (Younger Dryas termination), explaining the increased methane in terms of wetland processes. Melton *et al.* [2012] used carbon isotopic evidence from a Greenland ice core to confirm the low likelihood that methane hydrate dissociation was a key source for atmospheric methane emissions at this time. More recently, Chappellaz *et al.* [2013] have used analytical methods with subdecadal resolution to study CH<sub>4</sub> in a Greenland ice core, revealing atmospheric CH<sub>4</sub> signals that correlate with local temperature. This implies that a marine gas hydrate dissociation source is not necessary to explain this high-resolution ice core CH<sub>4</sub> record.

## 6. Climate Susceptibility of Gas Hydrates by Physiographic Province

Ruppel [2011a] briefly explored the potential for dissociation of contemporary gas hydrate deposits over the next several centuries by considering the distinct physiographic settings where gas hydrate occurs and the susceptibility of each hydrate population to global warming processes. Figure 9 is an updated version of the hypothetical cross section from Ruppel [2011a], showing CH<sub>4</sub> sources, gas hydrate distributions, and possible leakage points. The following sections examine climate-hydrates interactions in each setting, as summarized in Table 2.

### 6.1. Gas Hydrates Associated With Terrestrial Permafrost

For high-latitude regions, discussions of climate-hydrate interactions often focus on hydrates associated with terrestrial permafrost, not marine settings. As for the global assessment of methane trapped in gas hydrate (section 2), we here consider only permafrost at high northern latitudes given the paucity of data on Antarctic gas hydrates [Wadham *et al.*, 2012] and the relatively minor amount of permafrost in settings like the Tibetan Plateau [Yang *et al.*, 2010]. Warming climate, which is more pronounced at polar latitudes than at more temperate locations (Arctic amplification), is already causing significant thawing of terrestrial permafrost [e.g., Oberman, 2008; Romanovsky *et al.*, 2010] that sometimes cap gas hydrate deposits. Such thawing in turn leads to the liberation of carbon long bound in ice-bearing strata [Schuur *et al.*, 2009] and the consequent

**Table 2.** Assessment of Climate-Hydrate Synergies in Characteristic Locations for Gas Hydrates

Geographic Setting	Estimated Methane in Place in Hydrates (%) <sup>a</sup>	Predominant Type of Methane	Nominal Shallowest Depth Beneath Land Surface/Seafloor <sup>b</sup>	Susceptibility to Climate Change	Pre-atmospheric Sinks for Liberated Methane
Onshore permafrost-associated gas hydrates	20 Gt C <sup>c</sup> (1.11%)	Thermogenic	~200 m (for pure methane); as shallow as 100 m for mixed gases	Intermediate: substantial climate warming and permafrost thaw expected at high latitudes, but hydrates are deeply buried	Sediment permeability, ice-blocked migration pathways, anaerobic/aerobic processes in sediments
Subsea permafrost-associated gas hydrates (PAGH) on arctic continental shelves		Thermogenic	~200 m	Intermediate: hydrates are deeply buried but will continue to dissociate as warming from inundation propagates to depth on Arctic Ocean shelves	Sediment permeability and some ice-blocked migration paths, AOM in near-seafloor sediments, aerobic oxidation/dissolution of methane in the water column
Subglacial	Unknown at LGM; contemporary Antarctica: ~80–400 Gt C <sup>d,e</sup>	Microbial and thermogenic in Antarctica; could have been primarily shallow microbial at LGM in other areas	Very shallow	High at LGM due to widespread thawing of ice sheets on land and grounded ice sheets on shelves; low in Antarctica over next centuries	For onshore settings, few sinks except anaerobic/aerobic processes in sediments; for inundated settings, see subsea PAGH
Upper continental slopes	63 Gt C <sup>f</sup> (~3.5%)	Microbial except in thermogenic basins (e.g., Gulf of Mexico)	Base of sulfate reduction zone (centimeters to tens of meters, depending on methane flux rate)	High, owing to warming of intermediate ocean waters and very small magnitude of offsetting stabilization effect associated with rising sea level	AOM in sediments, sediment permeability, aerobic oxidation/dissolution of methane in water column
Deep marine	~1717 Gt C (95.3%)	Microbial except in thermogenic basins	Base of sulfate reduction zone (centimeters to tens of meters, depending on methane flux rate)	Low due to long-term stability of deep ocean temperatures and the fact that the hydrates are generally far inside the stability zone	AOM in sediments, sediment permeability, aerobic oxidation/dissolution of methane in water column

<sup>a</sup>Based on a base inventory of 1800 Gt C [Johnson, 2011] methane gas in place in hydrates, not including Antarctica. One gigaton of C corresponds to 1.33 Gt CH<sub>4</sub>, which can also be expressed as 133 Tg or 0.133 Pg CH<sub>4</sub>.

<sup>b</sup>For pure methane hydrate.

<sup>c</sup>Ruppel et al. [2015].

<sup>d</sup>Wadham et al. [2012].

<sup>e</sup>No percentage calculated because not included in estimated inventory.

<sup>f</sup>Ruppel [2011a].

release of CO<sub>2</sub> and CH<sub>4</sub> from the shallow sediments as a result of microbial processes. In some areas arctic tundra is net sink for CH<sub>4</sub> [e.g., Jorgensen et al., 2015], and thermokarst lakes may also have become a net sink for carbon during the Holocene [Walter Anthony et al., 2014]. Where emissions dominate, CO<sub>2</sub> [Schadel et al., 2016] and CH<sub>4</sub> [McCalley et al., 2014] have alternately been identified as the major greenhouse gas released from thawing permafrost. Local geology plays a critical role in CH<sub>4</sub> emissions, which are enhanced near the boundaries of continuous permafrost and where faults intersect thawing permafrost [Walter Anthony et al., 2012].

The primary factors mitigating the potential impact of climate change on PAGH are their depth of occurrence and their limited extent relative to better studied marine gas hydrates [e.g., Ruppel, 2015]. In unglaciated areas, the shallowest PAGH should be found at depths of 200 m or more for pure CH<sub>4</sub> as the guest gas and possibly as shallow as 100 m for some mixtures of CH<sub>4</sub> and higher-order thermogenic gases. The GHSZ can extend hundreds of meters beneath the base of permafrost (Figures 4 and 9). With sustained climate warming, permafrost thaws and CH<sub>4</sub> hydrate dissociates at both the top and bottom of its stability fields [e.g., Ruppel, 2011a]. As in marine sediments, CH<sub>4</sub> released from gas hydrate dissociation at depth has to overcome numerous physical and chemical sinks to reach the tundra surface, and ice-bearing permafrost can be an effective permeability cap for upward migration of CH<sub>4</sub> liberated during dissociation.

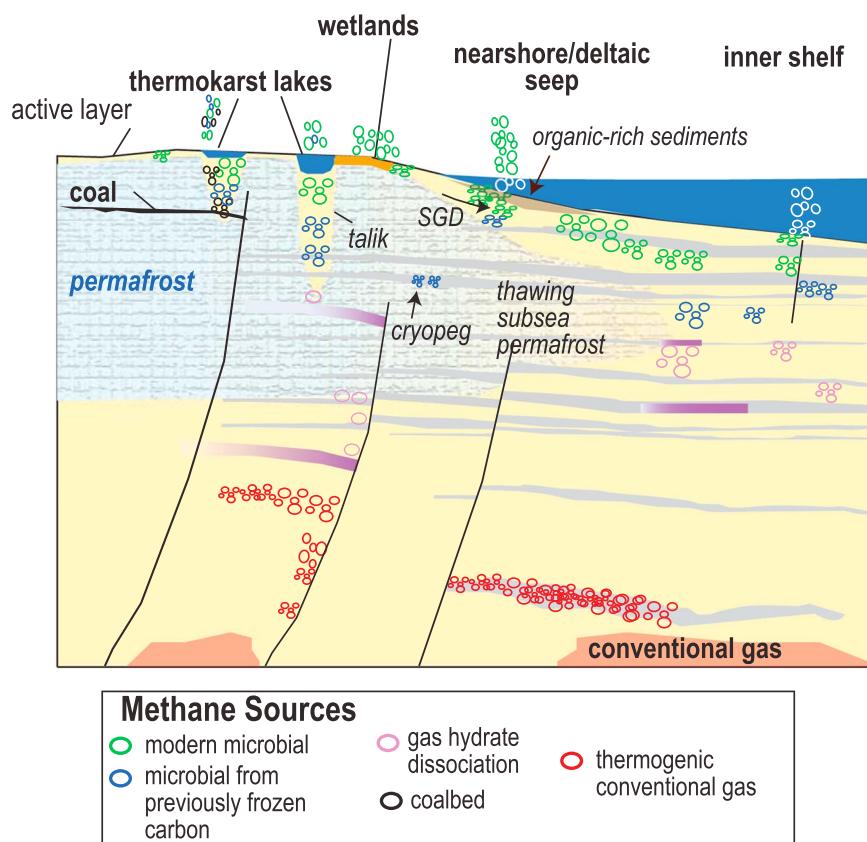
While conditions are suitable for gas hydrate stability in areas with thick permafrost, whether hydrates actually occur there is a more complicated issue that directly bears on the amount of methane that could be released from these deposits. As outlined by Ruppel [2015], gas hydrates are not as ubiquitous in permafrost areas as deepwater marine gas hydrates are in continental margin sediments. PAGH at high northern latitudes probably formed as gas bubbles froze in place during profound cooling of the land surface in unglaciated areas [Majorowicz *et al.*, 2008], with the most recent episode being during the late Pleistocene [Collett *et al.*, 2011]. The emphasis on unglaciated regions is related to their having experienced very low sustained temperatures at the land surface (e.g.,  $-10$  to  $-30^{\circ}\text{C}$ ), which can lead to the development of thick, continuous permafrost and thus a thick GHSZ. The origin of PAGH deposits as bubbles implies that migration pathways may link conventional gas reservoirs to the loci for hydrate formation. Thus, spatial coincidence with and/or geologic links to conventional reservoirs and the existence of a structural or permeability trap for the gas may be a requirement for the formation of PAGH [Ruppel, 2015]. In addition, contemporary PAGH settings are characterized by variegated clastic sedimentary sequences (e.g., intercalated silts, sands, and clays), and the high-permeability, coarse-grained layers critical to formation of high-saturation gas hydrates [e.g., Boswell *et al.*, 2009a; Winters *et al.*, 2011] may be limited in thickness and regional distribution or occur in a part of the section that was inaccessible to a source of gas [Ruppel, 2015].

To date, numerous direct measurements have been made to quantify bulk  $\text{CH}_4$  emissions from tundra, high-latitude wetlands, and thermokarst lakes [e.g., Christensen, 1993; Walter *et al.*, 2006; Whalen and Reeburgh, 1988; Wille *et al.*, 2008; Zona *et al.*, 2016], but attributing a fraction of this  $\text{CH}_4$  stream to gas hydrate dissociation is not currently possible. Furthermore, the observed increase in atmospheric  $\text{CH}_4$  concentrations since about 2007 [Dlugokencky *et al.*, 2009] cannot be attributed to arctic emissions, which are expected to continue rising as global warming leads to enhanced methane production and/or release from several sources [World Meteorological Organization, 2013]. Even under a possible future scenario of rising arctic  $\text{CH}_4$  emissions, which are expected to lag warming, discerning the component related to gas hydrate dissociation may always remain more challenging at high northern latitudes due to the number of methane sources in these settings and their overlapping depths of origin (Figure 10).

Except for the observation described earlier, in which Dallimore *et al.* [2008] detected tundra gas emissions having the same composition as the gas mixture in underlying gas hydrates, there has so far been no evidence to link tundra  $\text{CH}_4$  emissions to dissociation of gas hydrates at depth. Heterogeneous thawing of permafrost may deliver substantially more heat to great depths in one location than another, implying that there may be locations where intrapermafrost or subpermafrost gas hydrate could be affected as climate warming continues. For example, thick thaw bulbs (taliks) beneath thermokarst lakes may thermodynamically perturb or even intersect the gas hydrate stability zone [e.g., Nicolsky *et al.*, 2012; Frederick and Buffett, 2014], and a Mackenzie Delta seismic study by Bellefleur *et al.* [2009] images one such candidate talik. In recent years the discovery of deep, rapidly developed Yamal Peninsula craters that emit  $\text{CH}_4$  has been attributed by some to thawing gas hydrates, although recent analyses of high-resolution satellite imagery implies pingo collapse as a more likely cause [Kizyakov *et al.*, 2015]. Although PAGH dissociation likely played an outsized role in  $\text{CH}_4$  emissions from the deglaciating snowball Earth episodes during the late Neoproterozoic [Kennedy *et al.*, 2008], even unanticipated, centuries-scale outgassing of a portion of the 20 Gt C (26,600 Tg  $\text{CH}_4$ ) estimated to be sequestered in PAGH deposits onshore and offshore [Ruppel, 2015] would have little impact on atmospheric  $\text{CH}_4$  given current annual emissions of  $\sim 555$  Tg  $\text{CH}_4$ .

## 6.2. Shallow Water: Gas Hydrates Associated With Subsea Permafrost

A special class of PAGH are those associated with subsea permafrost (Figures 9 and 10). Warming after the Last Glacial Maximum (LGM;  $\sim 20$  ka) thawed large continental ice sheets (e.g., Laurentide and Fennoscandian) and raised global sea level up to  $\sim 125$  m [e.g., Fairbanks, 1989], resulting in the inundation of permafrost tundra at the edges of the Arctic Ocean. The inundation replaced frigid average annual air temperatures with ocean water that was warmer by as much as  $10\text{--}15^{\circ}\text{C}$  [Kvenvolden, 1988b; Shakhova *et al.*, 2010a]. On Arctic Ocean continental shelves, the inundation-associated warming led to thawing of some of the continuous permafrost, with the remainder comprising contemporary subsea permafrost. Early maps [Brown *et al.*, 1997] placed the edge of subsea permafrost at the shelf break ( $\sim 100$  m water depth) in the Arctic Ocean, but geophysical studies reveal that contemporary ice-bearing subsea permafrost does not extend much beyond the 20 or 30 m isobath in the U.S. Beaufort and Kara Seas [Brothers *et al.*, 2012, 2016; Portnov *et al.*, 2013; Ruppel *et al.*, 2016], may remain in



**Figure 10.** Terrestrial and continental shelf stores of methane and potential emissions to the ocean and atmosphere at high northern latitudes. The primary onshore and offshore methane sources to the atmosphere include wetlands, in situ methane generation in organic-rich sediments (e.g., thermokarst lakes, and deltaic sediments), methane generation from carbon newly thawed from former permafrost zones, coalbeds, leakage from deep thermogenic reservoirs, and possible gas hydrate dissociation. Gas hydrate is shown concentrated in purple layers in the sediments, with the sparsity of gas hydrate portrayed here thought to be representative of these hydrates in nature [Ruppel, 2015]. SGD refers to relatively freshwater submarine groundwater discharge from thawing permafrost [Lecher et al., 2016]. A cryopeg is a layer of thawed sediment set within permafrost, and these features could contain methane bubbles. Not shown is riverine transport of methane, which delivers methane to coastal waters in some areas [e.g., Bussmann, 2013]. As described in the text, thermokarst lakes have been interpreted as a net sink of carbon in the Holocene [Walter Anthony et al., 2014], despite their well-characterized CH<sub>4</sub> emissions [Walter et al., 2006]. There is conflicting information about the predominance of CO<sub>2</sub> versus CH<sub>4</sub> emissions from tundra due to microbial processes in shallow sediments. Not shown is methanogenesis in near-surface ocean waters [e.g., Damm et al., 2008].

patches farther offshore in the Laptev Sea [Rekant et al., 2005, 2015], and could reach the 100 m isobath in parts of the Canadian Beaufort Sea [Hu et al., 2013; Hunter and Hobson, 1974]. Relative to the Brown et al. [1997] map, the more restricted distribution of relict permafrost beneath Arctic Ocean continental shelves likely means that some PAGH have already dissociated since the onset of post-LGM inundation.

Gas hydrates associated with subsea permafrost lie in water-covered areas, but they have some characteristics that distinguish them from both marine gas hydrates and their terrestrial PAGH counterparts. As noted above, marine gas hydrates cannot form in the contemporary ocean beneath waters shallower than ~300 to 600 m. However, PAGH that now lie offshore on high-latitude continental shelves are in sediments covered by a maximum of 100 to 120 m of water. This adds up to ~1 MPa of additional hydrostatic pressure, may cause formation of new gas hydrate near the top of the stability zone, and serves as a slightly stabilizing influence offsetting the profound destabilization caused by warming of the sedimentary section during and after inundation. Dissociating gas hydrates associated with subsea permafrost liberate CH<sub>4</sub> that is subject to the full suite of marine sedimentary and water column sinks that affect marine gas hydrates [Overduin et al., 2015; Thornton and Crill, 2015]. However, sulfate, which is necessary for marine sedimentary AOM sink processes, may not fully

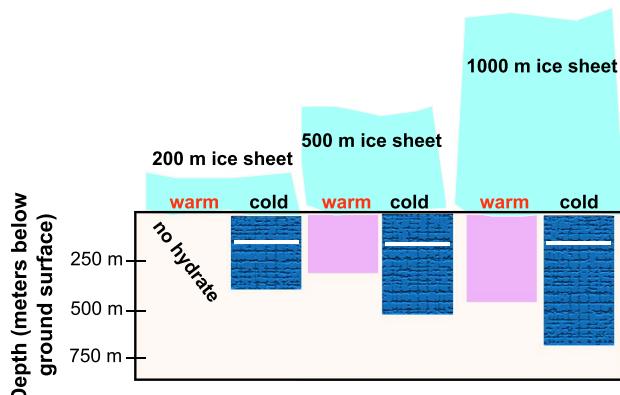
intrude sediments inundated only since ~15 ka, and the shallow water depths mean that gas emitted at the seafloor is more likely to reach the sea surface before bubble stripping [McGinnis *et al.*, 2006], CH<sub>4</sub> dissolution, and/or microbial oxidation can have a large mitigating impact. As in other settings, CH<sub>4</sub> liberated from dissociating gas hydrates at depth must also navigate overlying sediments to reach the seafloor. In addition, ice-related processes have contributed to the widespread development of indurated (low-permeability) sediments that could be particularly effective at trapping CH<sub>4</sub> beneath some Arctic Ocean shelves.

Like other PAGH, those that ended up within submerged shelves are unlikely to be widely distributed or sequester large amounts of CH<sub>4</sub> [Ruppel, 2015]. Some researchers do infer large amounts of PAGH beneath arctic continental shelves (e.g., 35 Gt C in hydrate beneath the Laptev Sea shelf) [Shakhova *et al.*, 2010a], but several assumptions used in making this estimate may not fully account for the complexity of PAGH systems. Shakhova *et al.* [2010a] also invoked anomalous shallow gas hydrates beneath the East Siberian Arctic shelf as a potential CH<sub>4</sub> source and to explain elevated estimates of CH<sub>4</sub> sequestered in gas hydrates. This area was not glaciated at the LGM, as is usually required for shallow gas hydrates to occur, and the origin and existence of possible anomalous gas hydrate deposits remain controversial and require further examination.

Intact arctic continental shelf gas hydrate certainly remains today within or beneath subsea permafrost, but distinguishing hydrate- from ice-bearing sediments based on geophysical data is nearly impossible without direct sampling. During the top-down warming associated with Holocene inundation, gas hydrate deposits require longer to leave their stability field and to degrade than the associated permafrost takes to thaw (Figure 4a). Even without anomalous preservation processes such as submarine groundwater discharge [e.g., Frederick and Buffett, 2016], hydrate can remain where ice-bearing permafrost is no longer detectable [e.g., Pokrovsky, 2003]. Where ice-bearing subsea permafrost has now thawed on the U.S. Beaufort margin, Collett *et al.* [2011] identify possible gas hydrate at 530 m below the seafloor, and drilling of an outer shelf well yielded gas hydrate from the formation at a maximum depth of 754 m below seafloor [Ruppel *et al.*, 2016]. The fact that hydrate can remain in the section even where the subsea permafrost has completely thawed means that (a) methane may be released by hydrate dissociation over a region that extends beyond the seaward edge of subsea permafrost [Paull *et al.*, 2007; Portnov *et al.*, 2013; Serov *et al.*, 2015; Shakhova *et al.*, 2010a, 2010b], sometimes at pingo-like features; and (b) methane emissions from these dissociating hydrates could lag permafrost thaw by hundreds or thousands of years.

Circum-Arctic Ocean continental shelves have long been presumed as a source of atmospheric CH<sub>4</sub> emissions [e.g., Kvenvolden *et al.*, 1993], and attention in recent years has focused on the Siberian shelves, where [Shakhova *et al.*, 2014] estimate annual atmospheric CH<sub>4</sub> emissions of up to 17 Tg CH<sub>4</sub> when ebullitive and diffusive fluxes are combined. Thornton *et al.* [2016] described a continuous shipboard survey of CH<sub>4</sub> concentrations in the atmosphere and near-surface waters in much of this same area. They conclude that ebullition does not substantially contribute to the sea-air CH<sub>4</sub> flux, which they calculate to be less than 2.9 Tg yr<sup>-1</sup> CH<sub>4</sub>. They also note that some of the previously reported atmospheric CH<sub>4</sub> concentrations on the East Siberian Arctic shelf may be unrealistic. Like Kvenvolden *et al.* [1993] and Kort *et al.* [2012], Thornton *et al.* [2016] underscored the critical role of sea ice in trapping CH<sub>4</sub> until leads or ice-out conditions render possible the diffusive release across the sea-air interface. Continuous sea-air CH<sub>4</sub> flux surveys like that of Thornton *et al.* [2016] have also been conducted on the U.S. and Canadian Beaufort shelf [Pohlman *et al.*, 2012]. Measurements there reveal high nearshore CH<sub>4</sub> concentrations inferred to be produced in organic-rich sediments, but regional annual flux is several orders of magnitude lower than the Thornton *et al.* [2016] estimate for the Siberian shelves and comparable to that recorded for the North Sea [Bange *et al.*, 1994].

Several key lessons emerge from these studies: (1) Accurate constraints on CH<sub>4</sub> emissions to the atmosphere are particularly critical in settings where gas hydrates may be the most susceptible to global warming processes, such as Arctic Ocean continental shelves. Refining sea-air CH<sub>4</sub> fluxes in these settings may address concerns raised about catastrophic methane releases accompanying continued climate warming [Whiteman *et al.*, 2013] and help to reconcile bottom-up CH<sub>4</sub> measurements with top-down time series of atmospheric CH<sub>4</sub> observations, which show no recent increase in arctic atmospheric CH<sub>4</sub> emissions [Bruhwiler *et al.*, 2015; World Meteorological Organization, 2013]. (2) Methane fluxes to the atmosphere vary significantly on high-latitude continental shelves, and measurements made in one area cannot be upscaled for application to the entire Circum-Arctic Ocean. (3) Numerous sources—most of them shallower and more



**Figure 11.** The theoretical distribution of permafrost (ground with temperature less than 0°C whose base is delineated by the thick white line) and the pure methane hydrate GHSZ (calculated with 0% pore water salinity from *Sloan and Koh* [2008]) for warm-base (0.5°C; purple represents GHSZ) and cold-base ( $-5^{\circ}\text{C}$ ; blue denotes GHSZ) ice sheets that are 200 m, 500 m, and 1000 m thick. The thick white line marks the base of permafrost. The assumed conductive geothermal gradient is  $30^{\circ}\text{ km}^{-1}$ , with constant thermal properties assumed for both the permafrost and subpermafrost zones, a substantial simplification. Ice density for pressure calculations is  $910 \text{ kg m}^{-3}$ ; using a higher density will result in a thinner GHSZ. Subglacial gas hydrates are likely widespread in Antarctica [*Wadham et al.*, 2012], and thawing ice sheets and rising sea levels could have destabilized significant subglacial deposits at the end of the LGM [*Nisbet*, 1990b; *Portnov et al.*, 2016] or during other time periods [*Maslin et al.*, 2010]. In practice, *Hunter and Hobson* [1974] found that ice-bearing permafrost in the Beaufort Sea corresponds to temperatures less than  $-1.8^{\circ}\text{C}$ , so the extent of permafrost is likely overestimated in this calculation.

tions. They postulate that degassing of these gas hydrates during post-LGM ice sheet thaw may have occurred in shallow waters at the ice sheet's terminus as shelfal inundation got underway. *Portnov et al.* [2016] also propose that these degassing processes could have preconditioned upper continental slope sediments to be the loci of contemporary ebullitive  $\text{CH}_4$  flux [e.g., *Westbrook et al.*, 2009], although their extrapolation to the northern U.S. Atlantic margin seeps described by *Skarke et al.* [2014] does not appropriately consider well-established LGM ice distributions on that margin.

Figure 11 shows nominal conditions for permafrost evolution and gas hydrate stability beneath cold and warm-base ice sheets. Even where permafrost is lacking beneath warm-base ice, gas hydrate is stable at shallow depths in the sedimentary section for ice sheets a mere 500 m thick. Such shallow hydrates could form from microbial gas instead of the thermogenic gas thought to be sourcing many contemporary PAGH [*Ruppel*, 2015]. Anomalously shallow gas hydrates have been postulated for the Yamal Peninsula [*Chuvilin et al.*, 2002] and invoked to explain some observations on the East Siberian Arctic Shelf [*Shakhova et al.*, 2010a], as discussed above. Neither area was glaciated at the LGM, and the shallow gas releases on which the anomalous hydrate interpretation is based [*Chuvilin et al.*, 2002] are common in permafrost areas during drilling and thought to be unrelated to gas hydrate dynamics. Even if proof for anomalous gas hydrates is eventually found, it remains uncertain how the pressure and temperature conditions at shallow depths (e.g., less than 100 m) could have been within the gas hydrate stability field absent recent glacial loading or a highly unusual mixture of hydrocarbons.

While the possible existence of relict subglacial gas hydrates at high northern latitudes is not likely to greatly expand the estimate of global gas in place, a recent review of Pleistocene glacial extents [*Jakobsson et al.*, 2014] could provide guidance for locating other margins where these unusual hydrates may have existed at the LGM and may have degassed during the Holocene. This category of gas hydrates should probably also be included in millennial scale models of global warming impacts on the Greenland and Antarctic ice sheets [*Maslin et al.*, 2010].

directly connected to the seafloor than dissociating gas hydrates—contribute to  $\text{CH}_4$  concentrations in the seawater of Arctic Ocean continental shelves and  $\text{CH}_4$  emissions to the atmosphere (Figure 10). Only by systematically eliminating the contributions of most of these sources will it be possible to identify emissions that could be related to gas hydrates.

### 6.3. Gas Hydrates in Glaciated Areas

*Ruppel* [2011a] identified only five geographic sectors for gas hydrates in assessing their interaction with the climate system, and a missing category was gas hydrates that formed beneath ice sheets during the late Pleistocene [e.g., *Nisbet*, 1990b] or that currently occur beneath ice sheets (Figures 9 and 11). Subglacial hydrates in Antarctica could presently sequester enough methane to increase global estimates of gas in place [*Wadham et al.*, 2012], and *Portnov et al.* [2016] recently described PAGH that could have been stable under the West Spitsbergen ice sheet at the LGM for either warm-base or cold-base conditions.

#### 6.4. Upper Continental Slopes

As described by *Kvenvolden* [1988b] and considered in numerous observational and modeling studies [e.g., *Berndt et al.*, 2014; *Brothers et al.*, 2014; *Davies et al.*, 2015; *Gorman and Senger*, 2010; *Johnson et al.*, 2015; *Kennett et al.*, 2003; *Marín-Moreno et al.*, 2015; *Marín-Moreno et al.*, 2013; *Mienert et al.*, 2005; *Pecher et al.*, 2005; *Phrampus and Hornbach*, 2012; *Phrampus et al.*, 2014; *Reagan and Moridis*, 2009; *Reagan et al.*, 2011; *Ruppel*, 2011a; *Skarke et al.*, 2014; *Stranne et al.*, 2016a; *Stranne et al.*, 2016b; *Weinstein et al.*, 2016; *Westbrook et al.*, 2009] gas hydrates within upper continental slope sediments constitute the key marine hydrate population that is susceptible to degradation during ocean warming (Figure 9). The GHSZ vanishes on upper slopes (i.e., the “feather edge” of hydrate stability in *Ruppel* [2011a]). Small perturbations in the temperatures of impinging intermediate ocean waters or even small pressure perturbations associated with tides or other oceanographic phenomena can affect the stability of these deposits. Dissociation driven by these processes may also condition submarine slopes to failure, particularly at the shallower water depths (300–800 m) close to the landward limit of gas hydrate stability [*Nixon and Grozic*, 2006].

Based on potential distributions of upper slope gas hydrates on marine continental margins and conservative assumptions about gas hydrate saturations, but ignoring any biogeochemical sinks in the sediments, *Ruppel* [2011a] estimated that ~3.5% of the global gas hydrate inventory (~63 Gt C or ~83,790 Tg CH<sub>4</sub> based on an assumed inventory of 1800 Gt C) might be susceptible to climate change on a time scale of centuries. While upper continental slope gas hydrates are generally viewed as being in a net dissociation regime in light of contemporary climate warming, the details are certainly more complicated, with gas hydrate dissociating and re-forming at the shallowly buried BGHS in response to oscillating temperatures and pressures on the slopes. Key questions include the degree to which gas hydrates remain out of equilibrium with local P-T conditions, the rate at which upper slope gas hydrates respond to climate forcing, and whether upper slope hydrate dissociation processes that do not produce seafloor seepage can be detected by geophysical surveys.

Despite the expectation that upper continental slopes host the most climate-susceptible gas hydrate populations, widespread upper slope seepage has so far only been recognized on the West Spitsbergen margin [*Westbrook et al.*, 2009], the U.S. Atlantic margin [*Skarke et al.*, 2014], and the northwestern U.S. Pacific margin [*Johnson et al.*, 2015]. Given the role of salt tectonism (section 6.5) and the lack of a systematic catalog for northern Gulf of Mexico seeps associated with hydrates, these are not considered here, although upper slope dissociation processes are clearly active [e.g., *MacDonald et al.*, 1994; *Weber et al.*, 2014]. Upper continental slope seepage on the other margins has been interpreted in terms of warming of intermediate waters on time scales of years to centuries [*Berndt et al.*, 2014; *Biastoch et al.*, 2011; *Brothers et al.*, 2014; *Ruppel*, 2011a; *Stranne et al.*, 2016b], but so far only the West Spitsbergen margin seepage has been firmly linked to dissociating gas hydrate [*Berndt et al.*, 2014]. On the northwestern U.S. Pacific margin, many of the seeps are close to the feather edge of hydrate stability on the upper continental slope, providing circumstantial evidence for their origin in methane hydrate destabilization [*Johnson et al.*, 2015]. In the Arctic Ocean, some researchers have used thermal infrared (TIR) data from satellites to infer methane emissions linked to seasonal ocean warming that may drive hydrate dissociation on continental slopes and nearby shelves [*Leifer et al.*, 2014]. However, the TIR technology has low sensitivity in the lower troposphere, rendering the data poor at distinguishing local and regional methane sources [*Jacob et al.*, 2016]. Furthermore, the strength of water column sinks makes it unlikely that upper continental slope methane is reaching the ocean-atmosphere interface in any case, leading to questions about the origin of the signal being detected in the satellite data.

A full discussion of the approaches for estimating methane fluxes from deepwater marine gas hydrate settings is included in section 6.5, and here we focus only on the results related specifically to upper continental slopes and choose the West Spitsbergen margin [e.g., *Westbrook et al.*, 2009] as the focus. *Sahling et al.* [2014] estimated flux of 9 to  $118 \times 10^6$  mol yr<sup>-1</sup> CH<sub>4</sub> from seeps in a depth range mostly updip of the landward edge of gas hydrate stability and note that several methane sources likely contribute to this flux. *Graves et al.* [2015] recorded near-bottom methane concentrations as high as 825 nM over the upper slope seeps but show that most of this methane remains near the bottom and that the methane at shallower depths in the water column does not originate with in situ seafloor emissions. *Steinle et al.* [2015] documented the strength of the MOx sink in these cold waters, demonstrating that changing ocean currents have a profound effect on the efficiency of the sink. *Myhre et al.* [2016] and *Graves et al.* [2015] used direct measurements and indirect arguments to demonstrate that sea-air flux over the upper continental slopes is not elevated, while *Fisher et al.*

[2011] concluded that the atmospheric methane in this area lacks a signal related to gas hydrate dissociation. Nonetheless, at least for the CH<sub>4</sub> detected near the seafloor, there is strong evidence that it is being sourced in gas hydrate dissociation [Berndt *et al.*, 2014].

Establishing the link between upper slope seepage and gas hydrate dissociation on the U.S. Atlantic margin will be more difficult since the gas appears to have no thermogenic component like that which assisted with fingerprinting on the West Spitsbergen margin. Furthermore, as noted by Skarke *et al.* [2014], the U.S. Atlantic margin seepage occurs mostly at water depths upslope from the contemporary updip limit of methane hydrate stability, except in Hudson Canyon [Weinstein *et al.*, 2016]. The large percentage of excess heat absorbed by the Atlantic Ocean over the past few decades [Lee *et al.*, 2011; Levitus *et al.*, 2012] may imply greater dynamism for the GHSZ on upper slopes here than in other ocean basins and may also lead to more rapid downdip migration of the gas hydrate stability field [e.g., Brothers *et al.*, 2014]. Still, in situ gas hydrate dissociation has been ruled out as a gas source for one prominent seep cluster [Prouty *et al.*, 2016] that may have been active starting after the LGM, and seepage at other upper slope locations would require updip migration of gas through permeable strata [Brothers *et al.*, 2014; Skarke *et al.*, 2014]. In addition to seepage, certain erosional and other features have been described at the upper feather edge of gas hydrate stability on global margins [Davies *et al.*, 2015; Pecher *et al.*, 2005]. These merit further attention as potential markers for gas hydrate dissociation.

The types of exhaustive studies of seafloor CH<sub>4</sub> flux rates that are available for the West Spitsbergen margin have not yet been completed for the U.S. Atlantic or northwestern U.S. Pacific margin seeps. Based on limited bubble observations, Skarke *et al.* [2014] gave a conservative estimate of 15–90 Mg yr<sup>-1</sup> CH<sub>4</sub> for seafloor flux for the ~570 seeps they describe along 950 km of the Atlantic margin, while Weinstein *et al.* [2016] used indirect methods to infer 70–280 Mg yr<sup>-1</sup> CH<sub>4</sub> in Hudson Canyon alone. How much, if any, of these emissions originate in dissociating gas hydrate remains unknown. Preliminary continuous sea-air flux measurements indicate that the Atlantic margin seeps are unlikely to be contributing CH<sub>4</sub> to the atmosphere [Ruppel *et al.*, 2015].

### 6.5. Deepwater Marine Hydrates

Deepwater gas hydrates occur in marine sediments at water depths so profound (i.e., nominally greater than 1000 m; Figures 3 and 9) that ocean temperatures do not typically undergo dramatic change on time scales of centuries or more [Brothers *et al.*, 2013; Plaza-Faverola *et al.*, 2015; Ruppel, 2011a; Skarke *et al.*, 2014]. Even if deep ocean temperatures were to increase by several degrees, which is larger than anticipated in any global warming scenario over the multicentury scale and comparable to the difference between the LGM and the present [Adkins *et al.*, 2002], the ambient hydrostatic pressure regime means that gas hydrates in the shallow part of the sedimentary section at these locations would generally remain stable [Reagan and Moridis, 2008; Ruppel, 2011a]. During intervals of slight bottom-water warming, gas hydrates near the BGHS would eventually dissociate as the sediment's geotherm reequilibrates. Depending on the rheology and characteristics of the sediments, slight decreases in pressure could also drive dissociation.

As the locus of most of Earth's methane hydrates, deepwater marine settings might be expected to liberate the most substantial amount of CH<sub>4</sub> during warming episodes if the deep oceans experience notable temperature increases. In recent years, evidence is emerging that some of the highest saturation, regionally extensive gas hydrate deposits occur deep in sedimentary sections [e.g., Boswell *et al.*, 2009b], sometimes because their gas is supplied by a large, underlying conventional (thermogenic) gas reservoir. Whereas many studies of climate-driven gas hydrate release from marine reservoirs in the distant past [e.g., Dickens *et al.*, 1997; Dickens *et al.*, 1995; Kennett *et al.*, 2000] have focused on a strongly microbial source of methane (light δ<sup>13</sup>C), it is possible that degassing of the highest-saturation contemporary deepwater hydrate reservoirs could release substantial quantities of thermogenic CH<sub>4</sub>.

Despite the expected short- and longer-term stability of gas hydrate in deepwater settings, seafloor methane seeps do occur in these environments on both passive and active margins and in inland seas [e.g., Aloisi *et al.*, 2000; Brothers *et al.*, 2013; Feng *et al.*, 2010; Paull *et al.*, 2015; Roberts and Carney, 1997; Römer *et al.*, 2012; Sauter *et al.*, 2006; Skarke *et al.*, 2014]. Methane emissions at deepwater seeps are sometimes driven from below, meaning that climate-related perturbations are not the causal process. For example, the high thermal conductivity of salt diapirs perturbs the stability of mantling hydrate-bearing sediments, and faults that accommodate the diapirs act as conduits for gas migration to the seafloor on some parts of the conjugate

Atlantic margins and in the Gulf of Mexico [Hornbach *et al.*, 2005; Ruppel *et al.*, 2005]. Deep marine mud volcanoes often store CH<sub>4</sub> in the form of gas hydrate [e.g., Milkov, 2000], and some fluid mobilization processes associated with these features could lead to seafloor methane emissions from dissociating deposits. Another bottom-up driver for deepwater CH<sub>4</sub> emission in gas hydrate provinces may be gas trapped in overpressured sediments [e.g., Dugan and Sheahan, 2012]. In these settings, gas migration may drive fracturing of the sediment [Züldorff and Spieß, 2004] or exploit existing fractures to traverse the GHSZ without re-forming hydrate [e.g., Flemings *et al.*, 2003] before the gas emerges at a seafloor seep. A rare bottom-up mechanism driving deepwater CH<sub>4</sub> seepage has been described on part of the Vestnesa Ridge, where heat from the nearby mid-ocean ridge system perturbs the gas hydrate stability field [Bünz *et al.*, 2012].

In areas lacking diapirs or other known bottom-up driving mechanisms for gas hydrate dissociation, deep-water methane seeps emerging from hydrate-bearing sedimentary sections seem anomalous. Not surprisingly, observations have for decades shown that fractures and faults play a key role in feeding such seeps [e.g., Crutchley *et al.*, 2015; Roberts and Carney, 1997], and sustained seepage may require a water-limited environment in the sediments [e.g., Flemings *et al.*, 2003] lest the fracture be clogged by gas hydrate [Daigle and Dugan, 2010; Nimblett and Ruppel, 2003]. For the Vestnesa Ridge, Plaza-Faverola *et al.* [2015] argue that the tectonic stress field controls faulting and the slight pressure perturbations that drive dissociation events. Skarke *et al.* [2014] infer that deepwater seeps discovered on the Atlantic margin may in some places tap into faulted Eocene rock that contains older gas unrelated to contemporary methane hydrates, although gas hydrates are certainly present in the shallow sedimentary section, which the migrating gas passes through before being emitted at the seafloor [Ruppel *et al.*, 2015]. On Hydrate Ridge, researchers describe a novel pumping mechanism that involves gas and fluid recharge of the seafloor accompanied by potential dissolution of gas hydrate [Tryon *et al.*, 1999]. These events are followed by gas migration, possible propagation of new fractures, and then periodic gas release [Tryon *et al.*, 2002]. Even at water depths of several hundred meters, tidal processes may be a key driver for such hydrologic pumping [Römer *et al.*, 2016; Torres *et al.*, 2002]. In any consideration at the intersection of gas hydrate destabilization and formation, free gas migration, and fracture dynamics, a central issue is the relative importance of preexisting fractures and active hydraulic fracturing associated with free gas/gas hydrate processes (e.g., dissociation) [Sultan, 2007; Xu and Germanovich, 2006] or external drivers. As shown by Daigle and Dugan [2010], pore pressure accumulation is an important mechanism for driving fractures in some settings, while preexisting fractures dominate flow dynamics in others.

Several physical and chemical markers have been used to identify climate-related changes in marine gas hydrate reservoirs. The BGHS in marine sediments is sometimes marked by a seismic reflector that mimics a subdued version of seafloor relief and cuts across regional stratigraphy in low-frequency seismic data. This bottom-simulating reflector (BSR) is characterized by a negative impedance contrast consistent with free gas beneath and possibly hydrate-charged sediments above. On the Nankai margin, Hydrate Ridge, the Storegga slide, and at a few other locations, researchers have recognized two distinct BSRs [e.g., Bangs *et al.*, 2005; Foucher *et al.*, 2002; Posewang and Mienert, 1999; Trehu *et al.*, 1999]. These are typically interpreted as indicating stranding of the deeper BSR during shoaling of the GHSZ that accompanied warming after the LGM. BSRs are not ubiquitous in hydrate-bearing sediments [Paull *et al.*, 1996; Xu and Ruppel, 1999] and are difficult to recognize on upper continental slopes [Davies *et al.*, 2015; Phrampus *et al.*, 2014], limiting their usefulness for tracking of climate-related changes in gas hydrate reservoirs.

Other proxies are also used to infer climate-related changes in the gas hydrate reservoir. Researchers have noted dramatic reductions in greigite and pyrrhotite, iron sulfides produced within the marine gas hydrate zone, beneath the shallower BSR on Hydrate Ridge, possibly owing to conversion of greigite to pyrite in underlying free gas zone [Musgrave *et al.*, 2006]. Barite is another mineral phase that has been used to track the dynamics of the GHSZ, in this case the depth to the top of the methane-bearing zone. If upward CH<sub>4</sub> flux through the sediments decreases, as might be expected during periods of reduced dissociation, paleobarite fronts can be preserved in the sediments [Dickens, 2001b; Torres *et al.*, 1996]. Biomarkers like diploterol, which is produced when methanotrophs aerobically oxidize methane in the water column, are also detectable in the sedimentary record and constrain past changes in seafloor CH<sub>4</sub> emissions [Hinrichs *et al.*, 2003]. Lipid biomarkers for archaeal methanotrophy are also increasingly being used to constrain past gas hydrate dynamics, particularly dissociation events [Zhang *et al.*, 2011]. The new clumped isotopic methods may be the next horizon for discerning CH<sub>4</sub> populations that could have originated with dissociation of gas hydrate [Douglas *et al.*, 2016].

Two methane emission components are relevant to considering the dissociation of deepwater hydrates in response to climate warming: seafloor emissions and sea-air methane fluxes. Directly determining seafloor methane emissions requires intercepting methane streams with fluxmeters as gas leaves the seafloor [Solomon *et al.*, 2008; Tryon and Brown, 2004; Tryon *et al.*, 2002, 1999] or observing bubble sizes and the rate at which bubbles emerge from the seafloor, parameters that have been measured only in a few deepwater locations [Leifer and MacDonald, 2003; Naudts *et al.*, 2010; Römer *et al.*, 2012; Sauter *et al.*, 2006; Skarke *et al.*, 2014; Torres *et al.*, 2002]. Even with such measurements, spatial and temporal heterogeneity in seep characteristics often frustrates attempts at upscaling these fluxes to larger areas. Hydroacoustic methods (Figure 8b) are gaining favor for imaging gas plumes in the water column and locating deepwater seeps [Artemov *et al.*, 2007; Brothers *et al.*, 2013; Greinert *et al.*, 2006; Kannberg *et al.*, 2013; Naudts *et al.*, 2010; Sahling *et al.*, 2014; Skarke *et al.*, 2014], but estimating CH<sub>4</sub> flux with these techniques remains challenging and has been attempted in only a few studies [Greinert and Nutzel, 2004; Jerram *et al.*, 2015; Ostrovsky, 2003; Scandella *et al.*, 2016; Veloso *et al.*, 2015; Wang *et al.*, 2016; Weber *et al.*, 2014]. Seafloor emissions can also be indirectly determined through analysis of pore water sulfate profiles in shallow subseafloor sediments [e.g., Borowski *et al.*, 1996; Dickens, 2001b] or from CH<sub>4</sub> concentration measurements in near-bottom waters [Graves *et al.*, 2015; Weinstein *et al.*, 2016].

Constraining sea-air methane fluxes is the second component necessary for evaluating the interplay between climate warming and release of methane by marine gas hydrate dissociation. Scientists measure dissolved CH<sub>4</sub> concentration in surface waters using discrete [Reeburgh *et al.*, 1991] or continuous [Du *et al.*, 2014; Hu *et al.*, 2012] sampling techniques and then apply the method of Wanninkhof [1992] to estimate the flux of CH<sub>4</sub> to the atmosphere at the sea-air interface. A major challenge in drawing conclusions about hydrate dissociation from these studies is the difficulty of tracing CH<sub>4</sub> in near-surface waters to a hydrate source. Indeed, in some situations CH<sub>4</sub> is produced in near-surface waters [e.g., Damm *et al.*, 2008], and many places have shallow ocean waters that are supersaturated with respect to CH<sub>4</sub>, even when no discrete seafloor CH<sub>4</sub> seepage or gas hydrate dissociation is implicated.

Here we use the Gulf of Mexico (GOM) as an example of an area in which myriad techniques have been used to infer CH<sub>4</sub> dynamics, even if little of the CH<sub>4</sub> flux may eventually be attributed to hydrate dissociation in this leaky, world-class hydrocarbon basin. Seafloor fluxmeter data at the well-known Bush Hill seep site yield  $\sim 5 \times 10^6 \text{ mol yr}^{-1}$  CH<sub>4</sub> emitted at the seafloor [Solomon *et al.*, 2008], while bubble measurements in other parts of the northern Gulf constrain the fluxes associated with individual methane bursts to 0.01 to 0.23 L/min at their in situ pressure (corresponding to 0.0175 to  $0.55 \times 10^6 \text{ mol yr}^{-1}$  CH<sub>4</sub> or 0.3 to  $9 \times 10^{-6} \text{ Tg yr}^{-1}$  CH<sub>4</sub>) [Wang *et al.*, 2016]. Lapham *et al.* [2008] used pore water characteristics in sediments to estimate methane flux of  $2\text{--}58 \text{ mol m}^{-2} \text{ yr}^{-1}$  from a GOM brine pool, while Winkel *et al.* [2010] obtained flux of  $1.1 \text{ mol m}^{-2} \text{ yr}^{-1}$  CH<sub>4</sub> through direct mass spectrometer measurements at another brine pool. Each of these rates is reasonable, but the challenge lies in upscaling the data to estimate emissions in the entire basin and attributing some of the emissions to dissociating gas hydrate. Using hydroacoustic methods, Weber *et al.* [2014] surveyed 6000 km<sup>2</sup> of the GOM and estimated seafloor emissions of all gases (not just CH<sub>4</sub>) of 0.0004 to 0.005 Tg yr<sup>-1</sup>. The GOM has a layered water column structure that impedes wholesale transport of dissolved methane from deeper to shallower waters and a strong water column aerobic oxidation sink [Kessler *et al.*, 2011] that ramps up as CH<sub>4</sub> concentrations increase. Continuous sea-air flux measurements over natural seeps [Hu *et al.*, 2012] and over the methane plume associated with the Deepwater Horizon incident [Yvon-Lewis *et al.*, 2011] revealed low sea-air methane flux. A study using discrete near-surface seawater CH<sub>4</sub> concentrations [Solomon *et al.*, 2009] over the same set of natural seeps surveyed by Hu *et al.* [2012] determined a much higher sea-air methane flux, underscoring the need to reconcile the outcomes from disparate techniques for making these measurements.

## 7. Models of Climate Interactions With Gas Hydrate

The equivocal evidence for gas hydrate dissociation having injected CH<sub>4</sub> into the atmosphere during past and ongoing warming events and the paucity of contemporary data to constrain this process have led researchers to rely on numerical models to assess gas hydrate-climate interactions. The models split roughly between those that examine the impact of climate change on gas hydrate deposits and those that study climate changes that may result after CH<sub>4</sub> is emitted to the ocean and/or atmosphere from dissociating gas

hydrate deposits. In the section below, we review challenges with existing models for climate-hydrate interactions, focusing on the problems with the assumed source size, incomplete consideration of methane sinks, and oversimplification of oceanographic conditions. Many numerical models dramatically overestimate the amount of CH<sub>4</sub> liberated during gas hydrate dissociation events, an outcome that can feed into unrealistic catastrophic scenarios.

### 7.1. Size of the Methane Hydrate Source

Overprediction of gas release from dissociating hydrates can often be traced to ascribing too large a methane source to hydrate deposits. If the a priori gas hydrate distributions are based primarily on P-T stability constraints, with no consideration of more complex factors (e.g., lithology, methane solubility, permeability, availability of methane or its organic carbon precursor), then the amount of sequestered CH<sub>4</sub> is likely to be overestimated. This is particularly true when researchers assume high hydrate saturation (amount of pore space filled by hydrate) within the GHSZ. For example, *Harvey and Huang* [1995] adopted >10% saturation in their early model of the impact of marine gas hydrate dissociation and CH<sub>4</sub> release in exacerbating global warming, purposely seeking to generate a worst case scenario. *Gornitz and Fung* [1994] first determined the geographic regions in which marine gas hydrates might occur based on a phytoplankton proxy for sediment organic carbon distributions (instead of actual sediment measurements) [*Klauda and Sandler*, 2005] and then adopted relatively high saturations (i.e., 5–10% of bulk porosity) for their in situ CH<sub>4</sub> generation model and as high as 50% at the BGHS for their fluid migration model. Among the numerical models that have conservatively estimated the potential marine hydrate source by using low bulk saturations are those by *MacDonald* [1990], *Reagan et al.* [2011], and *Biajstoch et al.* [2011]. A different approach to source estimation abandons a priori assumptions about gas hydrate saturations and allows the reservoir to evolve to steady state based on the global distribution of organic carbon in sediments [*Buffett and Archer*, 2004] and other variables (e.g., temperature, oxygen availability, rates of sedimentation and methanogenesis, and clay content).

A final note related to the size of the CH<sub>4</sub> source is the treatment of thermodynamics in many numerical models. For simplicity, researchers often ignore the endothermic heat of dissociation in modeling the impact of temperature changes on the gas hydrate reservoir. The degree to which this effect offsets the impact of top-down temperature changes on the gas hydrate reservoir is proportional to hydrate saturation, and including the heat of dissociation often requires a more challenging iterative approach for tracking the BGHS. However, failure to include this thermodynamics can lead to predictions of too much gas liberated and too rapid a disappearance of the GHSZ during warming events.

### 7.2. Methane Sinks

Even when the assumptions about the size of the CH<sub>4</sub> hydrate source are reasonable, numerical models can overestimate CH<sub>4</sub> emitted to the atmosphere if sinks are not appropriately incorporated along each part of the transport path: sediment, ocean, and atmosphere. For example, few numerical models assessing climate-hydrate interactions address the gas dynamics affecting CH<sub>4</sub> as it migrates from the dissociation site at the BGHS through the overlying GHSZ. Within the GHSZ, gas hydrate may re-form, gas may dissolve in methane-undersaturated pore waters, or free gas bubbles may be trapped. *Xu et al.* [2001] did consider these processes in detail, and *Stranne et al.* [2016b] have recently reiterated the critical role of multiphase flow dynamics for appropriate modeling of reservoir changes in response to climate forcing. The role of sediment properties in impeding the migration of methane released by gas hydrate dissociation is another factor that is rarely taken into account in climate-hydrate models, even though low-permeability sediments in some cases may shut down much of the methane migration to the sediment-water interface [*Reagan and Moridis*, 2009; *Stranne et al.*, 2016b] or retard dissociation [*Reagan and Moridis*, 2008]. The models that best incorporate these processes capture multiphase flow and transport processes in porous media through use of tools like the TOUGH code [e.g., *Reagan and Moridis*, 2008, 2009; *Reagan et al.*, 2011; *Stranne et al.*, 2016a].

The strong AOM sink for CH<sub>4</sub> in marine sediments is rarely given full consideration in numerical models [e.g., *Gornitz and Fung*, 1994; *Harvey and Huang*, 1995; *Isaksen et al.*, 2011; *O'Connor et al.*, 2010; *Reagan and Moridis*, 2007; *Reagan and Moridis*, 2008; *Stranne et al.*, 2016b]. Some models approach geochemical sinks by assuming that sediment-based processes (particularly AOM) prevent a certain percentage of methane released by dissociation of gas hydrate from reaching the overlying ocean [e.g., *Biajstoch et al.*, 2011]. Others selectively incorporate non-AOM geochemical sinks (e.g., methane dissolution in pore space by *Xu et al.* [2001] and

*Buffett and Archer* [2004]). *Archer et al.* [2009] assume that most migration of methane liberated from hydrate within the sedimentary section occurs as rising bubbles, which could open sediment pathways that bypass AOM or dissolution in pore waters and allow a larger proportion to reach the seafloor [*Knittel and Boetius*, 2009; *Thornton and Crill*, 2015].

Water column methane sinks are increasingly being incorporated into numerical models of climate-hydrate interactions as knowledge of methane stripping from rising bubbles [e.g., *Kowee et al.*, 2016; *Leifer and Patro*, 2002; *McGinnis et al.*, 2006] and aerobic methane oxidation in the water column [e.g., *Mau et al.*, 2013; *Valentine et al.*, 2001] becomes better established. Models are beginning to acknowledge that most CH<sub>4</sub> bubbles emitted at the seafloor at water depths deeper than a few tens of meters will retain little or no methane by the time they reach the near-surface mixed layer (Figure 8a), meaning that the primary repository of methane liberated by gas hydrate dissociation within any deepwater marine reservoir will be the ocean, not the atmosphere [e.g., *Biastoch et al.*, 2011]. The only hydrate-related methane source used by *Isaksen et al.* [2011] in their atmospheric chemistry models is associated with subsea permafrost thaw beneath circum-Arctic Ocean continental shelves, a source of CH<sub>4</sub> that has also been proposed by *Shakhova et al.* [2015] for these settings. In an acknowledgement of the importance of CH<sub>4</sub> stripping from rising bubbles, *Isaksen et al.* [2011] ignored the atmospheric impact of possible deepwater releases of CH<sub>4</sub> from dissociating gas hydrate during climate events but assumed a high end-member—no loss of methane between the seafloor and sea-air interface—on the shallow-water Arctic shelves for myriad CH<sub>4</sub> sources. While focusing mostly on the seafloor emission component of the climate-hydrates problem, *Stranne et al.* [2016b] also acknowledged that this population of CH<sub>4</sub> is unlikely to reach the sea-air interface due to methane loss from rising bubbles.

As described in section 4.2, once CH<sub>4</sub> has dissolved in the ocean, it becomes available for microbially driven oxidation (MOx) processes [*Valentine et al.*, 2001], which are a strong sink (Figure 7) for methane in intermediate ocean layers [e.g., *Mau et al.*, 2013]. Because MOx rates rely on a complex set of parameters, including a priori microbial populations, water depth, temperature, ocean chemistry, ocean currents [*Steinle et al.*, 2015], and the concentrations of oxygen and the CH<sub>4</sub> itself, relatively few climate-hydrate models have attempted to explicitly incorporate the MOx sink. This sink has been considered in models evaluating the potential impact of non-hydrate seafloor CH<sub>4</sub> emissions [*Kessler et al.*, 2011] on the ocean and atmosphere, but in these cases substantial data were available to constrain the role of MOx [*Du and Kessler*, 2012]. *Biastoch et al.* [2011] incorporated MOx in their Arctic Ocean climate-hydrate models by assuming that 50% of the methane released at the seafloor is consumed in the water column, resulting in lowering of pH (acidification) and depletion of oxygen, while *Archer et al.* [2009] completed one scenario in which all seafloor CH<sub>4</sub> emissions are oxidized in the water column, eventually releasing about 25% of the product CO<sub>2</sub> to the atmosphere. However, no model has directly investigated the incorporation of CH<sub>4</sub>-derived CO<sub>2</sub> into other oceanic carbon cycles (Figure 7), such as the biological pump [*Kessler*, 2014], a factor that may limit the interaction of this CO<sub>2</sub> with the atmospheric. A global hydrate-climate model that specifically focuses on MOx variations by region was formulated by *Elliott et al.* [2011]. They explored the possibility that MOx may be so vigorous in some locations following a climate-driven release of CH<sub>4</sub> from gas hydrates that some deep ocean basins may become oxygen-depleted. This would allow CH<sub>4</sub> to accumulate and increase the likelihood of diffusive sea-air methane transfer. Unfortunately, the assumed seafloor methane emissions from dissociating gas hydrate in *Elliott et al.* [2011] did not also account for the strong sediment methane sinks that are likely to substantially reduce the methane entering the water column in the first place.

The final CH<sub>4</sub> sink sometimes missing from more geologically focused climate-hydrates models is the atmospheric one. Failure to include this sink can lead to overestimation of the radiative warming of the atmosphere owing to the stronger greenhouse potential of CH<sub>4</sub> relative to CO<sub>2</sub>. The early model by *Harvey and Huang* [1995] focused on methane emissions from the sediments and considered neither sediment, water column, nor atmospheric sinks. This is one reason why their models predict climate warming elevated by up to several degrees above baseline cases when hydrate-related CH<sub>4</sub> emissions were included. Other models from the same era [e.g., *Fung et al.*, 1991] included atmospheric sinks, although separating the impact of CH<sub>4</sub> released from gas hydrate from that of other methane sources is not possible. *Archer et al.* [2009], who did include the atmospheric CH<sub>4</sub> sink, showed that either of their fossil fuel-driven warming scenarios (hydrate-derived methane directly crossing the sea-air interface or being oxidized in the water column, with

a fraction of the resulting CO<sub>2</sub> entering the atmosphere) resulted in enhanced warming (0.4–0.5°C) of the atmosphere. There is also a need for less simplification in accounting for the atmospheric methane sinks. For example, *Isaksen et al.* [2011] explicitly incorporated water vapor, CO<sub>2</sub>, and intermediate products of atmospheric methane oxidation in their model to constrain greenhouse forcing, an approach that could enhance other models focused on climate-hydrates interactions. Coupled with the emergence of better data on CH<sub>4</sub> emissions to the atmosphere, a fuller treatment of atmospheric chemistry processes in models could provide more reliable insights into the direct, as well as indirect, effects of CH<sub>4</sub> on climate over the full range of the timescales of interest for unraveling climate-hydrate interactions.

### 7.3. Oceanographic Conditions

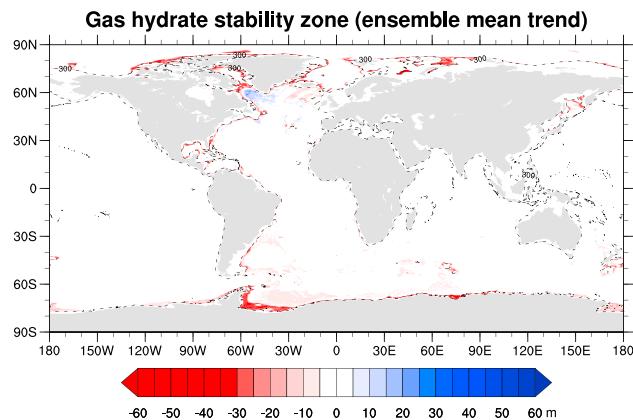
Another challenge for the credibility of some models for climate-hydrate interactions is the widespread practice of adopting geographically uniform oceanographic conditions, particularly for increased bottom-water temperatures that drive gas hydrate dissociation over large areas. About two-thirds of the increased heat content of the oceans since the midtwentieth century resides in the upper 700 m of the water column [Levitus *et al.*, 2012], meaning that upper continental slopes are most affected (section 6.4). In addition, the Atlantic basin has absorbed an outsized portion of the excess heat [Lee *et al.*, 2011]. These observations underscore the need to appropriately account for regional variations and to move away from deterministic approaches that apply instantaneous step function bottom-water temperature changes. *Lamarque* [2008] used the predictions made by IPCC [2007] climate models for ocean bottom-water temperature changes under the global warming scenario corresponding to an increase of 1% yr<sup>-1</sup> in CO<sub>2</sub>. He determines that 5–21 Tg yr<sup>-1</sup> CH<sub>4</sub> (4–15.75 Tg yr<sup>-1</sup> C) might be released by dissociation of gas hydrates due to warming bottom waters, although the estimate does not explicitly include some of the other sinks and caveats explored above. *Marín-Moreno et al.* [2015] extended this approach a step further for the West Spitsbergen margin, using bottom-water changes based on historical records and those predicted by nine climate models and climate scenarios to predict 97–1050 Tg C emitted from upper slope gas hydrate dissociation by 2100. *Hunter et al.* [2013] used fewer scenarios over the same time period and estimated that atmospheric methane release that originates in dissociating hydrates may range from 0.75 to 1.4 Tg yr<sup>-1</sup> CH<sub>4</sub> once the water column oxidation sink is taken into account.

A recent generation of studies [e.g., *Biastoch et al.*, 2011; *Elliott et al.*, 2011; *Kretschmer et al.*, 2015] has used sophisticated ocean/ice models to explicitly account for contemporary ocean circulation patterns. Such modeling efforts are the first steps in capturing the heterogeneity of processes driving gas hydrate dissociation and circulation of seafloor CH<sub>4</sub> emissions. Importantly, both the *Biastoch et al.* [2011] and *Elliott et al.* [2011] models revealed that much of the CH<sub>4</sub> released at the seafloor remains deep in the water column instead of ascending toward the sea-air interface.

### 7.4. Model Outcomes

The predictions of climate models are increasingly used to drive hydrate dissociation in response to changes in ocean circulation and temperature [e.g., *Kretschmer et al.*, 2015], but atmospheric chemistry models in turn only rarely account for the consequences of hydrate dissociation. For present-day Earth and marine hydrates, this approach makes sense given that the most complete model among the current generation predicts an upper bound of ~4.73 Mt yr<sup>-1</sup> CH<sub>4</sub> (~3.75 Mt yr<sup>-1</sup> C) emissions to the ocean from dissociating gas hydrate over a 100 year warming scenario with no sediment or water column sinks [Kretschmer *et al.*, 2015]. Even if all of this methane were to reach the atmosphere, the impact would be negligible compared to the 555 Gt yr<sup>-1</sup> CH<sub>4</sub> of combined natural and anthropogenic emissions [Kirschke *et al.*, 2013]. In the *Kretschmer et al.* [2015] model, as argued as far back as *Kvenvolden* [1988b], most of the CH<sub>4</sub> is emitted as upper continental slope gas hydrates dissociate, particularly at high latitudes (Figure 12). In the future, models of ocean transport and ocean chemistry should be refined to determine how the combination of top-down acidification due to atmospheric CO<sub>2</sub> drawdown and bottom-up acidification due to oxidation of seafloor CH<sub>4</sub> emissions will affect parcels of water frequently in contact with continental slopes (Figure 7).

The situation for PAGH could be slightly different than that for marine hydrates since CH<sub>4</sub> emitted from the shallow continental shelf seafloor or the tundra has a more direct path into the atmosphere. To date, the modeling of PAGH hydrate dissociation has sometimes assumed large reservoir sizes or high efficiencies for the migration of methane to the seafloor or tundra surface [e.g., *Isaksen et al.*, 2011]. With the most current



**Figure 12.** Results from the modeling of Kretschmer *et al.* [2015] show the changes predicted to the GHSZ. The original caption is: “Global map of the predicted thickness of the gas hydrate stability zone ( $L_{GHSZ}$ ) in m, calculated under steady state conditions for the ensemble mean trend, where the colored shadings indicate either a reduction (red) or an increase (blue) in the  $L_{GHSZ}$ .... The dashed contour line marks the 300 m isobath.”

in destabilizing gas hydrate deposits and the effect of released methane on the ocean-atmosphere system. A related issue is the impact on the environment of CH<sub>4</sub> that might be released inadvertently during production of methane from gas hydrates, particularly at the large scale envisioned for a commercial operation. Currently, CH<sub>4</sub> is not commercially produced from gas hydrates anywhere. There has been only one formal assessment of methane that may be technically recoverable from gas hydrates ( $\sim 2.4 \times 10^{12} \text{ m}^3$  or 1.3 Gt C from the Alaskan North Slope) [U.S. Geological Survey Alaska Gas Hydrate Assessment Team, 2013], in addition to the postulated value of  $3 \times 10^{14} \text{ m}^3$  (150 Gt C) for technically recoverable gas hydrate resources on a global basis [Boswell and Collett, 2011]. A long-term production test required to prove the technology and the viability of routine production of CH<sub>4</sub> from gas hydrate has yet to be completed. The most promising production techniques are a combination of depressurization of the formation and occasional thermal stimulation [Collett, 2002; Collett *et al.*, 2009], both of which would be used to dissociate the gas hydrate in the formation in order to release the gas. The gas would then flow up the well for extraction. The endothermic nature of gas hydrate dissociation renders this production scenario a self-regulating process [Circone *et al.*, 2005] that cannot persist without additional energy being expended to drive further dissociation.

As interest has increased in quantifying possible gas leakage from conventional and unconventional onshore production wells [Brandt *et al.*, 2014; Howarth *et al.*, 2011], questions have also been raised about leakage from future gas hydrate wells. The lessons of the natural system can be extended to evaluate the potential impact of an inadvertent gas leak associated with such a well. In onshore permafrost settings, a leak from a gas hydrate production well would have the same impact as that from a conventional well, with the methane directly reaching the atmosphere. In marine settings, the earlier discussion of water column sinks and the outcomes of the Deepwater Horizon event [e.g., Du and Kessler, 2012; Kessler *et al.*, 2011] are relevant. Except in some special high-latitude (subsea permafrost) cases, gas hydrates do not occur beneath continental shelves, where methane releases at the seafloor have the greatest potential to directly affect the atmosphere [McGinnis *et al.*, 2006]. Hydrates there are not likely to be widespread [Ruppel, 2015; Ruppel *et al.*, 2016] nor likely to be exploited for production. Deepwater sites have the advantage that inadvertently released CH<sub>4</sub> is most likely to remain in the water column and be oxidized by microbes, whose populations might increase dramatically in response to the availability of CH<sub>4</sub> [e.g., Kessler *et al.*, 2011]. While the impact of such a seafloor CH<sub>4</sub> leak is not innocuous in terms of ocean chemistry, the situation is largely analogous to that of naturally-occurring deep marine seeps, of which thousands are believed to remain undiscovered [Boetius and Wenzhofer, 2013; Skarke *et al.*, 2014].

Since the first long-term production test on gas hydrates is still in the planning stages, the actual impact of eventual production is impossible to assess. Particularly in the deepwater environment, an inadvertent leak

estimate of only 20 Gt CH<sub>4</sub> trapped in PAGH [Ruppel, 2015], the amount of CH<sub>4</sub> available for eventual release to the ocean-atmosphere system is dwarfed by annual emissions [Kirschke *et al.*, 2013]. Certainly, CH<sub>4</sub> releases from non-hydrate sources are significant on circum-Arctic Ocean continental shelves [e.g., Shakhova *et al.*, 2010a; Thornton *et al.*, 2016], but liberation of CH<sub>4</sub> by gas hydrate since the onset of post-LGM warming has likely comprised only a small component of emissions during this period.

## 8. Environmental Impact of Methane Production From Gas Hydrates

This paper has primarily focused on the role of global climate change processes

is unlikely to increase global atmospheric CH<sub>4</sub> concentrations at a detectable level owing to strong microbial sinks and the tendency of methane to remain deeper in the water column. Regardless, gas detection technology can monitor for methane leaks at the wellhead of a gas hydrate production site on permafrost or in marine environments. Acquiring such scientific data could even provide information useful for assessing the impact on the ocean-atmosphere system of gas hydrates that are liberating CH<sub>4</sub> due to climate forcing.

## 9. Suggested Directions for Future Work

The amount of CH<sub>4</sub> sequestered in and spatially associated with gas hydrates remains uncertain, and better constraints on these values and on the distribution of hydrates and associated free gas in different physiographic settings will advance understanding of the exogenic carbon cycle and long-term synergies between the hydrate reservoir and the climate system. Special attention should be focused on mapping the contemporary distribution and inferring the saturation of methane hydrates in settings that are most susceptible to climate-driven dissociation. For example, data that can delineate the baseline state of upper continental slope gas hydrates will prove useful in future decades as warming intermediate waters continue to drive dissociation. On Arctic Ocean margins, field expeditions that constrain the current distribution of subsea permafrost can identify where PAGH may remain in association with intact permafrost and in thawed zones beyond the edge of that permafrost. With rapid thawing of subsea permafrost expected to continue throughout the 21st century [Rachold *et al.*, 2007], baseline data sets on Arctic Ocean shelves will have particular significance for tracking the impact of climate change.

For the shorter term, the central challenge remains determining how much CH<sub>4</sub> is being released to the ocean and atmosphere on regional to global scales due directly or indirectly (e.g., removal of a low-permeability cap on other gas deposits) to hydrate dissociation. Given the substantial differences between top-down and bottom-up estimates of atmospheric CH<sub>4</sub> emissions [Kirschke *et al.*, 2013], delineating the small component that might be attributable to gas hydrates will be challenging for decades to come. In fact, little progress has been made on this score since the same point was made by Kvenvolden [1988b] nearly three decades ago. In the deep marine environment, advances in technology have led to the discovery of hundreds of CH<sub>4</sub> seeps in the past decade, underscoring that current estimates of global seafloor methane emissions are incomplete. Until this regional and global CH<sub>4</sub> flux to the ocean is better constrained, teasing out the component of emissions that is related to gas hydrate dissociation will be as challenging in marine environments as it is for the atmosphere.

Ultimately, the CH<sub>4</sub> flux attributable to gas hydrate dissociation can only be constrained by identifying, testing, and standardizing a method to fingerprint the hydrate-derived component of bulk CH<sub>4</sub>. Still, an advance in fingerprinting techniques will only yield information about gas streams as they emerge at the seafloor or tundra surface, the point at which they can start to have an impact on and interact with the ocean or atmosphere. Studying gas emissions will not elucidate the full impact of climate change on the gas hydrate reservoir since a substantial fraction of gas released by dissociation often remains in the formation. Seismic surveys repeated at an interval of several years or more [e.g., Bangs *et al.*, 2011; Riedel, 2007] at locations where hydrate is vulnerable to climate forcing may detect gas migration or changes in gas distribution/concentration that can provide a fuller picture of the impact of climate processes on hydrate stability.

As highlighted throughout this paper, strong sinks dramatically affect the amount of CH<sub>4</sub> emitted from the seafloor, transferred across the sea-air interface, or persisting as CH<sub>4</sub> in the atmosphere. Sinks probably also mitigate some methane emissions from tundra settings. Among these sinks, the atmospheric ones, while imperfectly described, are better known than many associated with the ocean environment. Continued research should quantify the strength of marine sediment (AOM) and water column sinks (MOx) and to identify the microbes responsible for these processes in a wide range of environmental settings. In addition, investigations of water column CH<sub>4</sub> oxidation will continue so as to better elucidate its impact on ocean chemistry (e.g., pH, nutrients) and determine whether CH<sub>4</sub> oxidation is limited by nutrients or trace metals under certain circumstances. Research might also focus on CO<sub>2</sub> produced by water column oxidation to track its fate in the ocean and near the sea-air interface. Careful observational studies will also be needed to test theoretical models for such physical sinks as methane stripping from bubbles. More focused effort could be expended to determine the prevalence and details of processes that may armor deep ocean CH<sub>4</sub> bubbles with hydrate

shells and whether these phenomena allow methane to travel to shallower depths in the water column [Rehder *et al.*, 2002].

Numerical models can be a powerful tool to place bounds on likely CH<sub>4</sub> emissions to the ocean and atmosphere as a result of gas hydrate dissociation but only if based on appropriate assumptions and reliable data about (a) gas hydrate distributions, (b) CH<sub>4</sub> migration dynamics through sediments, (c) biogeochemical CH<sub>4</sub> sinks, and (d) climate forcing. New modeling studies should resist selectively choosing which sinks to include since this approach tends to bias results toward more catastrophic emissions and global warming scenarios. As a first step, careful modeling that isolates the CH<sub>4</sub> contribution related to gas hydrate dissociation based on regional knowledge of the source (hydrate distribution) and sink strengths will have the best prospect for providing reliable, quantitative information about emissions. In light of the heterogeneity of gas hydrate deposits, though, caution is necessary when upscaling of results obtained based on regional scenarios to the global system. Recent numerical models that couple the ocean and atmosphere and that account for ocean circulation represent a major advance in tracking global climate-hydrate interactions, although researchers must often adopt knowledge of contemporary ocean currents and temperature distributions to study processes in the past.

## 10. Conclusions

On the contemporary Earth, gas hydrate is dissociating in specific terrains in response to post-LGM climate change and probably also due to warming since the onset of the Industrial Age. Nevertheless, there is no conclusive proof that the released methane is entering the atmosphere at a level that is detectable against the background of ~555 Tg yr<sup>-1</sup> CH<sub>4</sub> emissions. The IPCC estimates are not based on direct measurements of methane fluxes from dissociating gas hydrates, and many numerical models adopt simplifications that do not fully account for sinks, the actual distribution of gas hydrates, or other factors, resulting in probable overestimation of emissions to the ocean-atmosphere system. The new generation of models based on ocean circulation dynamics holds the greatest promise for robustly predicting the fate of gas hydrates under climate change scenarios [Kretschmer *et al.*, 2015] and could be improved further with better incorporation of sinks.

At high latitudes, the key factors contributing to overestimation of the contribution of gas hydrate dissociation to atmospheric CH<sub>4</sub> concentrations are the assumption that permafrost-associated gas hydrates are more abundant and widely distributed than is probably the case [Ruppel, 2015] and the extrapolation to the entire Arctic Ocean of CH<sub>4</sub> emissions measured in one area. Appealing to gas hydrates as the source for CH<sub>4</sub> emissions on high-latitude continental shelves lends a certain exoticism to the results but also feeds catastrophic scenarios. Since there is no proof that gas hydrate dissociation plays a role in shelfal CH<sub>4</sub> emissions and several widespread and shallower sources of CH<sub>4</sub> could drive most releases, greater caution is necessary.

For marine settings, the emerging research underscores the vulnerability of upper continental slope hydrates to ongoing and future dissociation in response to warming intermediate waters. In light of predictions that thousands of methane seeps remain to be discovered [Boetius and Wenzhofer, 2013; Skarke *et al.*, 2014] on the world's continental margins, surveys should focus on identifying sites of possible upper continental slope gas hydrate breakdown and degassing. Such research should better constrain hydrate reservoir dynamics, CH<sub>4</sub> release, and carbon cycling in response to climate forcing. As on the circum-Arctic Ocean shelves, it is important to continue investigating the source of CH<sub>4</sub> emissions on upper continental slopes to prevent attributing too much to hydrate dissociation, and establishing clear linkages between CH<sub>4</sub> emissions and known gas hydrates is critical for proving the climate-hydrates interaction. At the same time, focused paleoceanographic studies should also constrain bottom-water temperature changes on upper slopes since 20 ka, the critical period for placing present-day emissions in the context of post-LGM climate and oceanographic changes.

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## Erratum

In the originally published version of this article, in the caption for Figure 3, the red and blue circles were designated incorrectly. This has since been corrected and this version may be considered the authoritative version of record.