

# Methane hydrate stability and anthropogenic climate change

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**Abstract.** Methane frozen into hydrate makes up a large reservoir of potentially volatile carbon below the sea floor and associated with permafrost soils. This reservoir intuitively seems precarious, because hydrate ice floats in water, and melts at Earth surface conditions. The hydrate reservoir is so large that if 10% of the methane were released to the atmosphere within a few years, it would have an impact on the Earth's radiation budget equivalent to a factor of 10 increase in atmospheric CO<sub>2</sub>.

Hydrates are releasing methane to the atmosphere today in response to anthropogenic warming, for example along the Arctic coastline of Siberia. However most of the hydrates are located at depths in soils and ocean sediments where anthropogenic warming and any possible methane release will take place over time scales of millennia. Individual catastrophic releases like landslides and pockmark explosions are too small to reach a sizable fraction of the hydrates. The carbon isotopic excursion at the end of the Paleocene has been interpreted as the release of thousands of Gton C, possibly from hydrates, but the time scale of the release appears to have been thousands of years, chronic rather than catastrophic.

The potential climate impact in the coming century from hydrate methane release is speculative but could be comparable to climate feedbacks from the terrestrial biosphere and from peat, significant but not catastrophic. On geologic timescales, it is conceivable that hydrates could release as much carbon to the atmosphere/ocean system as we do by fossil fuel combustion.

## 1 Methane in the carbon cycle

### 1.1 Sources of methane

#### 1.1.1 Juvenile methane

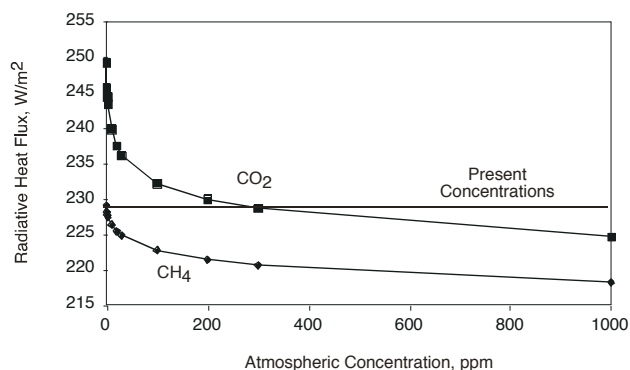
Methane, CH<sub>4</sub>, is the most chemically reduced form of carbon. In the atmosphere and in parts of the biosphere controlled by the atmosphere, oxidized forms of carbon, such as CO<sub>2</sub>, the carbonate ions in seawater, and CaCO<sub>3</sub>, are most stable. Methane is therefore a transient species in our atmosphere; its concentration must be maintained by ongoing release. One source of methane to the atmosphere is the reduced interior of the Earth, via volcanic gases and hydrothermal vents. Reducing power can leak from the interior of the Earth in other forms, such as molecular hydrogen, which creates methane from CO<sub>2</sub>. The other source of reduced carbon is from photosynthesis, harvesting energy from sunlight. By far the greatest portion of the methane on Earth today was generated originally from photosynthesis, rather than juvenile release from the Earth.

Photosynthesis does not produce methane directly, because methane as a gas has little use in the biochemical machinery. Most biomolecules utilize carbon in an intermediate oxidation state, such as carbohydrates made up of multiples of the unit CH<sub>2</sub>O with zero oxidation state, or on the reduced end of the spectrum lipids with an oxidation state near –2. Once produced, biomolecules can be post-processed into methane by one of two general pathways. One is biological, mediated by bacteria at low temperatures, and the other is abiological, occurring spontaneously at elevated temperatures.

#### 1.1.2 Biogenic methane

Biogenic methane is a product of organic matter degradation. Microbial respiration tends to utilize the partner electron acceptor that will maximize the energy yield from the organic

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**Fig. 1.** Radiative impacts of atmospheric methane and CO<sub>2</sub> concentrations: the outgoing longwave radiation flux over midlatitude winter conditions, from the Modtran model (Rothman, 1992), with a web interface at <http://geosci.uchicago.edu/~archer/cgimodels/radiation.html>. The sensitivities to methane and CO<sub>2</sub> are fundamentally similar, but because methane is present at lower concentration, the atmosphere is at a steeper part of the curve where a single molecule of methane would have approximately twenty times the radiative impact of a single molecule of CO<sub>2</sub>. The leveling off of this curve is due to saturation of absorption bands.

matter. In the presence of molecular oxygen, O<sub>2</sub>, oxic respiration is the most energetically lucrative, and this is the pathway that is followed. With the depletion of O<sub>2</sub>, respiration proceeds using electron acceptors in the order NO<sub>3</sub><sup>-</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, then SO<sub>4</sub><sup>2-</sup>. Of these, SO<sub>4</sub><sup>2-</sup> has potentially the highest availability, because seawater contains high concentrations of SO<sub>4</sub><sup>2-</sup>. Once the SO<sub>4</sub><sup>2-</sup> is depleted, methanogenesis can begin. Fresh water has less SO<sub>4</sub><sup>2-</sup> than seawater, so methanogenesis begins diagenetically earlier in fresh water systems. Fresh versus saltwater pathways can be distinguished by their isotopic signatures of  $\delta^{13}\text{C}$  and  $\delta\text{D}$  in the methane (Whiticar and Faber, 1986; Sowers, 2006). In sulfate-depleted salt water, the dominant pathway is the reduction of CO<sub>2</sub> by molecular hydrogen, H<sub>2</sub>. H<sub>2</sub> is produced bacterially by fermentation of organic matter, and is ubiquitous in marine sediments, implicated in many other diagenetic reactions such as iron, manganese, and nitrate reduction (Hoehler et al., 1999). Carbon isotopic values range from  $-60$  to  $-100\text{‰}$ , while  $\delta\text{D}$  is typically  $-175$  to  $-225\text{‰}$ . In fresh waters, the dominant pathway appears to be by the splitting of acetate into CO<sub>2</sub>+CH<sub>4</sub>. Acetate, CH<sub>3</sub>COO<sup>-</sup>, can be produced from molecular hydrogen, H<sub>2</sub>, and CO<sub>2</sub> (Hoehler et al., 1999). The H<sub>2</sub> is produced by fermentation of organic matter (Hoehler et al., 1998). The isotopic signature is  $-40$  to  $-50$  in  $\delta^{13}\text{C}$ , and  $-300$  to  $-350\text{‰}$  in  $\delta\text{D}$ . Ultimately, by conservation of oxidation state, if the source of reducing power is organic matter, then a maximum of 50% of the organic carbon can be converted to methane (Martens et al., 1998), by the reaction



In most sediments, for example at the Blake Ridge, biogenic methane production is inferred to take place hundreds of meters below the depth where SO<sub>4</sub><sup>2-</sup> is depleted, as indicated by linear gradients in SO<sub>4</sub><sup>2-</sup> and CH<sub>4</sub> as they diffuse toward their mutual annihilation at the methane-sulfate boundary (Egeberg and Barth, 1998). At other locations methanogenesis is inferred to be occurring throughout the sulfate-rich zone, but methane only accumulates to high concentrations when sulfate is gone (D'Hondt et al., 2002, 2004). Biological activity has been inferred to take place as deep as 800 m below the sea floor (D'Hondt et al., 2002, 2004; Wellsbury et al., 2002; Wellsbury et al., 2002; D'Hondt et al., 2004).

### 1.1.3 Thermogenic methane

As temperatures increase to about 110°C degrees (Milkov, 2005), methane is produced, abiologically, from photosynthetically-produced organic matter. This thermogenic methane is distinguished by carbon isotopic values of about  $-30\text{‰}$  (Whiticar and Faber, 1986), in contrast with the much lighter values,  $-60$  to  $-110\text{‰}$  of biogenic methane. Thermogenic methane is often associated with petroleum, coal, and other forms of fossil carbon. Petroleum is converted to methane if the deposits have ever been buried deeper than the “oil window” of 7–15 km depth (Deffeyes, 2001). Most of the hydrates in the ocean derive from biogenic methane, but the Gulf of Mexico (Milkov, 2005) and the Siberian gas fields (Grace and Hart, 1986) are examples of hydrate systems dominated by thermogenic methane.

Thermogenic methane is also accompanied by other low-molecular weight organic compounds such as ethane (Milkov, 2005). In addition to serving as a tracer for the origin of the methane, these compounds affect the thermodynamics of hydrate formation. Pure methane forms Type I structural hydrates, while the inclusion of a few percent of ethane or H<sub>2</sub>S favors Type II structure. Type II hydrates are stable to 5–10°C warmer, or perhaps 100 m deeper in the geothermal gradient in warmer temperatures (Sloan, 1998).

## 1.2 Radiative impacts of methane release

### 1.2.1 Atmospheric release

CO<sub>2</sub> is the dominant anthropogenic greenhouse gas in the atmosphere, because the anthropogenic perturbation to the CO<sub>2</sub> concentration is much larger than the anthropogenic change in CH<sub>4</sub>. However, the higher concentration of CO<sub>2</sub> means that on a per-molecule basis, CO<sub>2</sub> is a less potent greenhouse gas than CH<sub>4</sub>. Figure 1 shows the direct radiative impact of changes in CO<sub>2</sub> and CH<sub>4</sub> concentrations. The most significant practical distinction between the gases is that CO<sub>2</sub> is more concentrated in the atmosphere than is methane. For this reason, in the strongest absorption bands of CO<sub>2</sub>, most of the outgoing longwave light from the ground as already

absorbed. An increase in CO<sub>2</sub> concentration tends to make the absorption bands a bit wider, but they cannot get any more intense. Methane is less concentrated than CO<sub>2</sub>, and its absorption bands less saturated, so a single molecule of additional methane has a larger impact on the radiation balance than a molecule of CO<sub>2</sub>, by about a factor of about 40 (based on the total anthropogenic concentration changes of each gas and their radiative forcings from IPCC (2007)). Methane has an indirect radiative effect, as its oxidation in the stratosphere produces water vapor (Hansen et al., 2005). The radiative impact of CH<sub>4</sub> follows the concentration to roughly the 1/3 power, while the CO<sub>2</sub> impact follows the log of the concentration. To get an idea of the scale, we note that a doubling of methane from present-day concentration would be equivalent to 60 ppm increase in CO<sub>2</sub> from present-day, and 10 times present methane would be equivalent to about a doubling of CO<sub>2</sub>. A release of 500 Gton C as methane (about 10% of the hydrate reservoir) to the atmosphere would have an equivalent radiative impact to a factor of 10 increase in atmospheric CO<sub>2</sub>.

Once methane is released to the oxic, sunlit atmosphere, it oxidizes to CO<sub>2</sub> on a time scale of about a decade. Ultimately, the oxidizing power comes from O<sub>2</sub>, but the reactive compound OH is a necessary intermediate, following the reaction



where CH<sub>3</sub> produced is a reactive radical compound, quickly reacting with water vapor and other gases to form ultimately CO<sub>2</sub>. OH is produced by photolysis, the absorption of light energy by the severing of a chemical bond. Ozone photolyzes in the troposphere and combines with water to yield OH, as do H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub>. In the absence of sunlight, such as in ice cores, no OH is produced, and CH<sub>4</sub> and O<sub>2</sub> are able to coexist with negligible reaction for hundreds of thousands of years.

The implication of the short lifetime of methane in the atmosphere is that the concentration of methane at any given time is determined by the rate of methane emission over the past few decades. If emission is steady with time, then the steady-state atmospheric concentration can be expressed as

$$\begin{aligned} \text{Inventory [mol]} = \\ \text{Emission flux [mol/year]} \times \text{Atmospheric lifetime [years]} \end{aligned} \quad (3)$$

One uncertainty in this equation is how strongly the methane lifetime may depend on the methane source flux. If the methane oxidation rate is limited by the supply rate of OH, then an increase in the methane source flux could increase the methane lifetime in the atmosphere. In atmospheric photochemical models, a doubling of the source flux results in more than a doubling of the concentration (Pavlov et al., 2000).

The concentration of OH, and hence the lifetime and steady-state concentration of methane, could be affected by anthropogenic emissions of combustion products such as the nitrogen oxides NO<sub>x</sub>, hydrocarbons, and carbon monoxide. In another atmospheric chemistry model (Wang and Jacob, 1998), the concentrations of several gases have undergone order-one changes, but the effects of these changes on the OH concentration appear to largely cancel each other out.

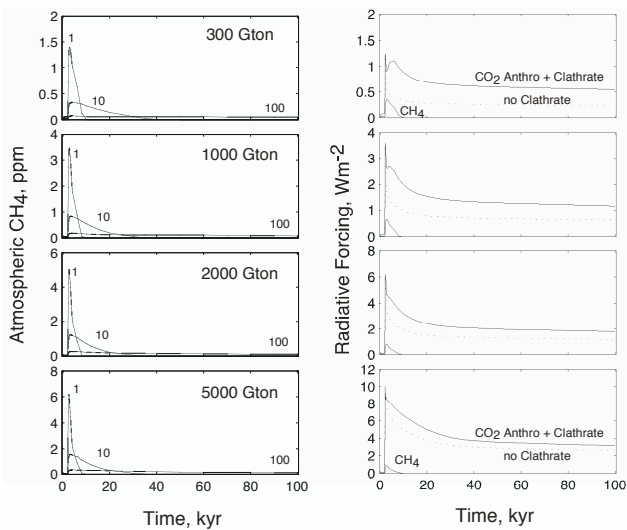
If the methane is released quickly, on a time scale that is short compared to the atmospheric lifetime, the methane concentration spikes upward, decaying back toward the steady-state concentration. We will refer to a fast release as a “catastrophic” methane release, as opposed to a long-term ongoing or “chronic” release. If the record of methane concentration recorded in an ice core is undersampled or smoothed by diffusion within the fern or heterogeneous bubble closure depth, then the maximum concentration of the event may not be recorded in ice cores (Thorpe et al., 1996). The current inventory of methane in the atmosphere is about 3 Gton C. Therefore, the release of 10 Gton C would triple atmospheric methane.

### 1.2.2 Radiative impact of methane oxidized in the ocean

Once the methane is oxidized to CO<sub>2</sub>, it still acts as a greenhouse gas, albeit with less intensity. CO<sub>2</sub> equilibrates between the atmosphere and the ocean on a time scale of hundreds of years (Archer, 2005). Depending on the magnitude of the CO<sub>2</sub> release, i.e. the pH perturbation of the ocean, the equilibrium between the atmosphere and the ocean leaves 15–30% of the CO<sub>2</sub> release remaining in the atmosphere. This partitioning will apply whether the methane is oxidized in the atmosphere or in the oxic ocean. If the methane is oxidized in the atmosphere, the initial condition has more CO<sub>2</sub> in the atmosphere than at equilibrium, and the excess CO<sub>2</sub> will invade the ocean. Methane oxidized in the ocean will increase the inventory of CO<sub>2</sub> in the ocean, leading to gradual degassing of 15–30% over the coming centuries. After atmosphere-ocean equilibration, the distribution of the CO<sub>2</sub> between the atmosphere and ocean will be the same regardless of whether the source of the CO<sub>2</sub> was in the atmosphere or the ocean.

Excess CO<sub>2</sub> in the atmosphere is gradually neutralized by dissolution of carbonate and silicate rocks, on time scales that range as long as 400 kyr (Archer, 2005). So, while methane is a transient species in the atmosphere, CO<sub>2</sub> accumulates. For this reason, the impact of a slow, ongoing methane release might be to have greater radiative forcing from the accumulated CO<sub>2</sub> than from the increased methane concentration, even while the methane release is ongoing (Fig. 2 from Archer and Buffett (2005), see also Harvey and Huang (1995), Schmidt and Shindell (2003)).

There exists an alternate pathway for methane oxidation that does not produce CO<sub>2</sub>, but rather bicarbonate ion HCO<sub>3</sub><sup>-</sup>.



**Fig. 2.** Model projection of the radiative impact of a fossil fuel CO<sub>2</sub> release over the coming 100 kyr, from Archer and Buffett (2005). The model curves labeled 1, 10, and 100 assume methane release time constants from hydrates of 1, 10, and 100 kyr. **(a)** The warming from the CO<sub>2</sub> (300, 1000, 2000, and 5000 Gton releases) provokes methane to degas from the ocean hydrate reservoir, increasing the methane concentration during the time interval that the methane is released. The methane is oxidized and accumulates in the atmosphere. **(b)** Radiative impacts of the CO<sub>2</sub> and methane releases. The methane direct effect is smaller than the original CO<sub>2</sub> radiative forcing, and it is also smaller and much shorter-lived than the radiative effect of the oxidized methane as CO<sub>2</sub>, gauged by the difference between the anthropogenic CO<sub>2</sub> radiative forcing with and without clathrate feedback. The point of the figure is to show that the greatest impact from a slow, ongoing methane release may be from the accumulation of its oxidation product, CO<sub>2</sub>.

This is anaerobic oxidation of methane (AOM) (Boetius et al., 2000),



The fate of the released alkalinity is often to precipitate as CaCO<sub>3</sub>. Authigenic CaCO<sub>3</sub> has been used as a tracer for the locations of CH<sub>4</sub> emissions at Hydrate Ridge (Teichert et al., 2003, 2005), and invoked as an active player in the life cycle of an emission field (Luff et al., 2005). A young vent site should have an irregular, patchy distribution of carbonates, while an old site has become paved over with large flat CaCO<sub>3</sub> slabs, which tend to seal off the methane emission (Sager et al., 1999).

## 2 The geology of methane hydrate

### 2.1 Methane production

The majority of the hydrate deposits on Earth are composed of biogenic methane, as indicated by its isotopic composi-

tion and the lack of other short hydrocarbons such as ethane. Most of the organic matter raining to the sea floor decomposes in the top few centimeters of the sediment, called the zone of early diagenesis. However, the production of methane from this decaying organic matter is usually inhibited by the presence of dissolved sulfate, providing a more energetically favorable respiration pathway.

Sulfate is removed from pore waters deeper in the sediment by reaction with methane (anaerobic oxidation of methane, AOM, described above). This reaction prevents sulfate and methane from coexisting at high concentrations in sediment porewaters. Typically both species diffuse toward their mutual annihilation at a well-defined methane/sulfate boundary (Borowski et al., 1996, 1999; D'Hondt et al., 2004). After the depletion of sulfate, methane can be produced from solid organic carbon, or by reaction of dissolved organic carbon, notably acetate, carried into the methanogenesis zone by diffusion or pore water advection. Wellsbury et al. (1997) found that heating sediment in the lab, up to 60°C, stimulates the bacterial production of acetate. At Blake Ridge, the concentration of acetate reaches very high concentrations, supplying 10% of the reduced carbon necessary for methane production (Egeberg and Barth, 1998).

Bacterial abundances and metabolic rates of methanogenesis, acetate formation, and AOM are extremely high at the base of the hydrate and gas zone, rivaling metabolic rates at the sediment surface (Parkes et al., 2000). Bacterial activity is detected within the hydrate zone as well (Orcutt et al., 2004).

### 2.2 Methane transport

#### 2.2.1 Diffusion

Once formed, methane moves within the sediment column by diffusion, porewater flow, or migration of bubbles. The time scale for diffusion depends on the length scale as

$$T[s] = \Delta x^2 [m^2] / D [m^2/s] \quad (5)$$

where  $D$  is a diffusion coefficient, of order 10<sup>-9</sup>, 10<sup>-6</sup>, and 10<sup>-4</sup> m<sup>2</sup>/s for a solute, for heat, and for pressure, respectively. Heat can diffuse approximately 100 m in about 300 years (Fig. 3). Solutes such as dissolved methane diffuse more slowly, while a pressure perturbation, such as would result from decomposition of hydrate to yield methane bubbles, diffuses away more quickly.

Diffusion is slow enough to insulate most of the hydrate reservoir from anthropogenic warming in the coming century. Hydrate melting to yield dissolved methane in porewaters, such as proposed by Sultan et al. (2004), is unlikely to have much impact on climate for this reason also.

#### 2.2.2 Aqueous flow

Pore-water flow has the potential to determine the distribution of hydrates within the sediment column. One source of

fluid flow is the compaction of sediment as it is buried and subjected to increasing lithostatic pressure. The degree of compaction of sediment grains is a conserved diagnostic of the maximum lithostatic pressure they have endured (Flemings et al., 2003). Subducting sediments on active margins expel water more quickly than on passive margins. Formation of hydrates at the surface and dissolution at depth apparently also acts as a source of upward-flowing pore fluid at Hydrate Ridge (Suess et al., 1999).

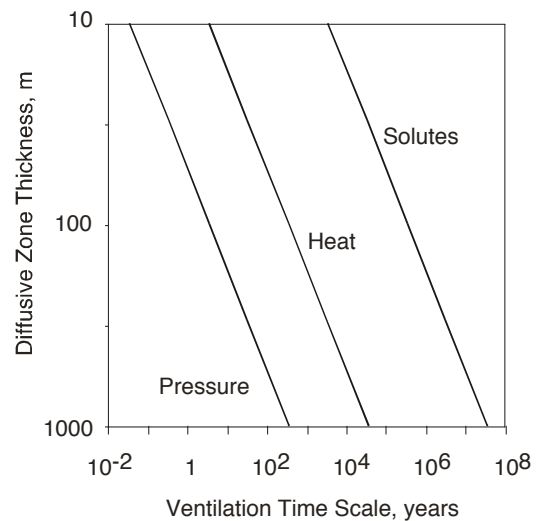
Pore water flow can be focused by layers of high permeability in sediments (Hovland et al., 1997; Aoki et al., 2000; Flemings et al., 2002). Lateral flow steered by sediment permeability predicts expulsion of fluid near the base of the continental slope off New Jersey, consistent with the observed patterns of porewater seeps, and leading to nucleation of landslides from the base of the slope, consistent with the observation of submarine canyons on continental margins (Dugan and Flemings, 2000). Fluid flow of methane-bearing porewater might be regulated by the formation of authigenic carbonate, blocking and steering the channels of flow (Luff et al., 2005).

Focused ongoing fluid effluent from the sediment into the ocean generates a structure known as a mud volcano. Approximately 1800 mud volcanoes have been discovered around the world, above and below sea level, mostly in a belt beginning in the Mediterranean Sea and winding across Asia to Indonesia (Dimitrov, 2002). Submarine mud volcanoes are often associated with methane hydrates (see below).

### 2.2.3 Gas migration

In addition to pore water flow, methane is able to migrate through the sediment column as a gas. In cohesive sediments, bubbles expand by fracturing the sediment matrix, resulting in elongated shapes (Boudreau et al., 2005). Bubbles tend to rise because they are less dense than the water they are surrounded by, even at the 200+ atmosphere pressures in sediments of the deep sea. If the pressure in the gas phase exceeds the lithostatic pressure in the sediment, fracture and gas escape can occur (Flemings et al., 2003). Modeled and measured (Dickens et al., 1997) pressures in the sediment column at Blake Ridge indicate that this may be going on.

There is a differential-pressure mechanism which begins to operate when the bubbles occupy more than about 10% of the volume of the pore spaces (Hornbach et al., 2004). If a connected bubble spans a large enough depth range, the pressure of the pore water will be higher at the bottom of the bubble than it is at the top, because of the weight of the pore water over that depth span. The pressure inside the bubble will be more nearly constant over the depth span, because the compressed gas is not as dense as the pore water is. This will result in a pressure gradient at the top and the bottom of the bubble, tending to push the bubble upward. Hornbach et al. (2004) postulated that this mechanism might be responsible for allowing methane to escape from the sediment col-

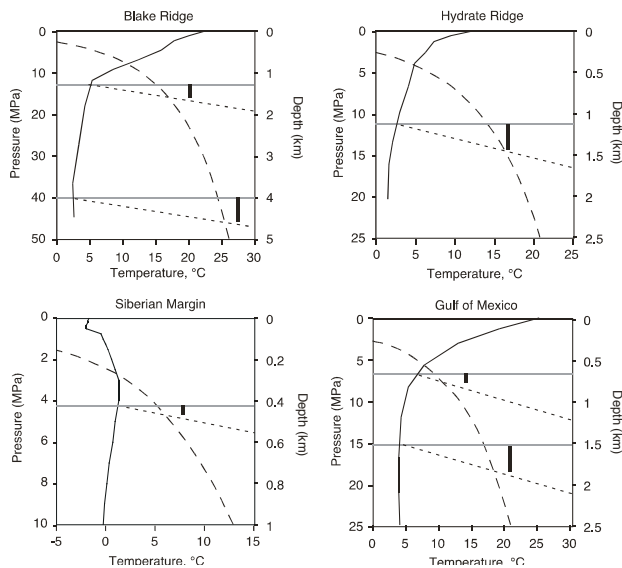


**Fig. 3.** The diffusive time scale, given by  $(Dt)^{1/2}$ , where  $D$  is a diffusion coefficient and  $t$  is time, plotted as a function of distance, for heat, pressure, and solutes.

umn, and calculated the maximum thickness of an interconnected bubble zone, before the bubbles would break through the overlying sediment column. In their calculations, and in stratigraphic deposits (they refer to them as “basin settings”) the thickness of the bubble column increases as the stability zone gets thicker. It takes more pressure force to break through a thicker stability zone, so a taller column of gas is required. In compressional settings, where the dominant force is directed sideways by tectonics, rather than downward by gravity, the bubble layer is never as thick, reflecting an easier path to methane escape.

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





**Fig. 4.** The methane hydrate stability zone in surface sediments. Hydrate solubility temperature is given by the long-dashed line. Offshore water column temperatures are from Levitus et al. (1993), given by the solid black lines. Nearshore, the sea floor impinges on the water column, so that temperature follows the geotherm (short dashes). The thickness of the stability zone (heavy solid lines) increases with ocean depth.

(Taylor et al., 2000; Wood et al., 2002).

The potential for gas migration through the stability zone is one of the more significant uncertainties in forecasting the ocean hydrate response to anthropogenic warming (Harvey and Huang, 1995).

## 2.3 Physical chemistry of methane hydrate

### 2.3.1 Thermodynamics

If the dissolved methane concentration reaches the saturation value for hydrate formation at the local temperature and pressure conditions, methane and water will freeze together into methane hydrate or clathrate deposits. Thermodynamically, the stability of hydrate is determined by the temperature and by the availability of methane. The phase boundary is usually drawn assuming the presence of bubbles of pure methane, so that the partial pressure of methane is determined by the total fluid pressure. The partial pressure of methane dissolved in oxic seawater is vanishingly small, but if hydrate would be stable given the presence of methane bubbles, we call that the phase boundary of hydrate stability in Fig. 4. At atmospheric pressure, hydrate is never stable at Earth surface temperatures. At water depths of 100 m, hydrate would form at about  $-20^{\circ}\text{C}$ , while at 500 m depth, the melting temperature approaches in-situ temperatures. This minimum stability depth is somewhat shallower in the high-latitude oceans, about 200 m in the Arctic Ocean, because the upper water

column is colder (Fig. 4). In some locations, such as under the sealed-off ice complex in Siberia, or in rapidly depositing or low permeability sediments, the fluid pressure can be influenced by the weight of solids, and the fluid pressure will approach the lithostatic pressure rather than the hydrostatic pressure. The stability depth for hydrate in permafrost in the lithostatic case is about 200 m (Buffett, 2000), but hydrate has been inferred to exist shallower than that, sealed into “ice-bonded” permafrost (Dallimore and Collett, 1995).

### 2.3.2 Kinetics

Hydrate can persist metastably, several degrees above its thermodynamic melting temperature, because of the energy barrier of nucleating small bubbles of methane gas (Buffett and Zatsepina, 1999). Rapid depressurization such as occurs during core retrieval does lead to melting of hydrate (Circione et al., 2000). The dissolution of hydrates appears to be diffusion-controlled (Rehder et al., 2004). In general, kinetic effects are probably of secondary importance for predicting the hydrate response to anthropogenic climate change, because the thermal forcing takes place on such long time scales.

Lab experiments show that hydrate can nucleate from the pure aqueous phase, with no bubbles required, helping the creation of hydrate from advective or biogenic methane (Buffett and Zatsepina, 2000). Several studies (Clennell et al., 1999, 2000; Lorenson, 2000) predict inhibition of hydrate formation in fine-grained sediment caused by the high activation energy of forming small crystals in the hydrophobic small cavities of the pore water. This would explain the characteristic textures of hydrate: as pore-filling cement in coarse-grained sediment, but as irregularly shaped masses of pure hydrate in fine-grained sediment, and predicts that hydrates should form first or predominantly in sandy sediments (Lorenson, 2000; Winters et al., 2004).

## 2.4 Mechanisms of methane release

### 2.4.1 Deep ocean temperature change

The time-dependence of changes in the inventory of methane in the hydrate reservoir depends on the time scales of temperature and chemical processes acting. Figure 5 shows the approximate time scales for altering the temperatures of the ocean, as a function of depth. There is evidence from paleotracers (Martin et al., 2005) and from modeling (Archer et al., 2004) that the temperature of the deep sea is sensitive to the climate of the Earth’s surface. Some warming has already been detected in intermediate depths of the ocean in response to anthropogenic greenhouse gas warming (Levitus et al., 2003). In general, the time scale for changing the temperature of the ocean increases with depth. There are significant regional variations in the ventilation time of the ocean, and in the amount of warming that might be expected

in the future. As has already been mentioned, the Arctic is expected to warm particularly strongly, because of the albedo feedback from melting the Arctic ice cap. Temperatures in the North Atlantic appear to be sensitive to changes in ocean circulation such as during Dansgaard Oeschger climate events (Dansgaard et al., 1989).

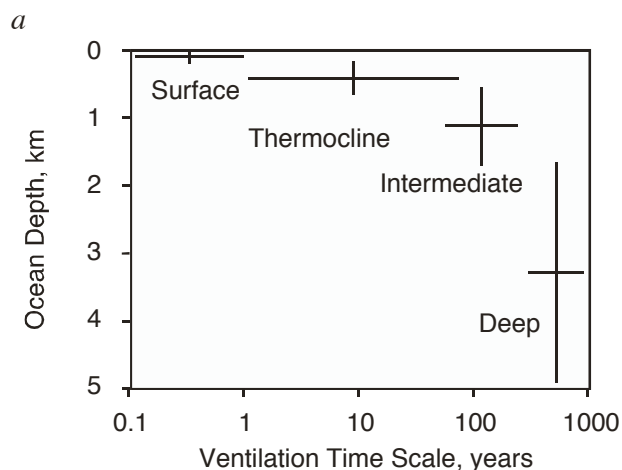
As described above, the top of the hydrate stability zone is at 200–600 m water depth, depending on the temperature of the water column and the solubility of the hydrate under the local chemical conditions (sulfide, hydrocarbons). Within the sediment column, the temperature increases with depth along the geothermal temperature gradient, 30–50°C/km (Harvey and Huang, 1995). The shallowest sediments that could contain hydrate only have a thin hydrate stability zone, and the stability zone thickness increases with water depth.

A change in the temperature of the deep ocean will act as a change in the upper boundary condition of the sediment temperature profile. Warming of the overlying ocean does not put surface sediments into undersaturation, but the warmer overlying temperature propagates downward until a new profile with the same geothermal temperature gradient can be established. How long this takes is a strong (second order) function of the thickness of the stability zone, but the time scales are in general long. In 1000 years the temperature signal should have propagated about 180 m in the sediment (Fig. 3). In the steady state, an increase in ocean temperature will decrease the thickness of the stability zone. Dickens et al. (2001) calculated that the volume of the stability zone ought to decrease by about a factor of 2 with a temperature increase of 5°C.

After an increase in temperature of the overlying water causes hydrate to melt at the base of the stability zone, the fate of the released methane is difficult to predict. The increase in pore volume and pressure could provoke gas migration through the stability zone (see Section 2.2.3) or a landslide, or the bubbles could remain enmeshed in the sediment matrix. Hydrate is carried to the base of the stability zone by the accumulation of sediment at the sea floor, so melting of hydrate at the stability zone takes place continuously, not just associated with ocean warming.

#### 2.4.2 Pockmarks

The sediment surface of the world's ocean has holes in it called pockmarks (Hovland and Judd, 1988; Hill et al., 2004), interpreted to be the result of catastrophic or continuous escape of gas to the ocean. Pockmarks off Norway are accompanied by authigenic carbonate deposits associated with anaerobic oxidation of methane (Hovland et al., 2005). Pockmarks range in size from meters to kilometers (Hovland et al., 2005), with one 700 km<sup>2</sup> example on the Blake Ridge (Kvenvolden, 1999). If the Blake Ridge pockmark is the result of a catastrophic explosion, it could not have released more than a Gton C as methane (assuming a 500 m thick layer of 4% methane yields 1 Gton). Pockmark methane



**Fig. 5.** A rough estimate of the ventilation time of the ocean as a function of ocean depth. Shallow waters warm in response to climate change more quickly than deep waters. Ventilation times of the real ocean vary laterally, as well; the North Atlantic, for example, ventilates more quickly than the ocean average because of the pathway of subsurface flow in the ocean.

emission is most significant as an ongoing “chronic” source rather than single “catastrophic” releases.

#### 2.4.3 Landslides

Another mechanism for releasing methane from the sediment column is by submarine landslides. These are a normal, integral part of the ocean sedimentary system (Hampton et al., 1996; Nisbet and Piper, 1998). Submarine landslides are especially prevalent in river deltas, because of the high rate of sediment delivery, and the presence of submarine canyons. The tendency for slope failure can be amplified if the sediment accumulates so quickly that the excess high porosity of surface sediments cannot be squeezed out. This can lead to instability of the sediment column, causing periodic Storegga-type landslides off the coast of Norway (see below), in the Mediterranean Sea (Rothwell et al., 2000) and potentially off the East coast of the United States (Dugan and Flemings, 2000). Maslin et al. (2004) find that 70% of the landslides in the North Atlantic over the last 45 kyr occurred within the time windows of the two meltwater peaks 15–13 and 11–8 kyr ago. These could have been driven by deglacial sediment loading or warming of the water column triggering hydrate melting.

Warming or sea level fall may trigger the melting of hydrate deposits, provoking landslides (Kvenvolden, 1999; Driscoll et al., 2000; Vogt and Jung, 2002). Paul (1978) calculates that landslides can release up to about 5 Gton C as methane, enough to alter the radiative forcing by about 0.2 W/m<sup>2</sup>. The origin of these estimates is discussed in the section on the Storegga Slide, below.

#### 2.4.4 Fate of methane released as bubbles

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

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

#### 2.4.5 Fate of methane hydrate in the water column

Pure methane hydrate is buoyant in seawater, so floating hydrate is another potential way to deliver methane from the sediment to the atmosphere (Brewer et al., 2002). In sandy sediment, the hydrate tends to fill the existing pore structure of the sediment, potentially entraining sufficient sediment to prevent the hydrate/sediment mixture from floating, while in fine-grained sediments, bubble and hydrate grow by fracturing the cohesion of the sediment, resulting in irregular blobs of bubbles (Gardiner et al., 2003; Boudreau et al., 2005) or pure hydrate. Brewer et al. (2002) and Paull et al. (2003) tried the experiment of stirring surface sediments from Hydrate Ridge using the mechanical arm of a submersible remotely operated vehicle, and found that hydrate did manage to shed its sediment load enough to float. Hydrate pieces of 0.1 m

survived a 750 m ascent through the water column. Paull et al. (2003) described a scenario for a submarine landslide, in which the hydrates would gradually make their way free of the turbidity current comprised of the sediment / seawater slurry.

#### 2.4.6 Oxidation of dissolved methane in the ocean

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

An oxidation lifetime of 50 years leaves plenty of time for methane gas to evaporate into the atmosphere. Typical gas-exchange timescales for gas evasion from the surface ocean would be about 3–5 m per day. A surface mixed layer 100 m deep would approach equilibrium (degas) in about a month. Even a 1000-m thick winter mixed layer would degas about 30% during a three-month winter window. The ventilation time of subsurface waters depends on the depth and the fluid trajectories in the water (Luyten et al., 1983), but 50 years is enough time that a significant fraction of the methane dissolving from bubbles might reach the atmosphere before it is oxidized.

#### 2.5 Stratigraphic-type sedimentary hydrate deposits

The most common hydrate deposits on Earth are in the ocean, and are the product of largely one-dimensional processes of organic carbon burial, bacterial methanogenesis, and methane transport in slow fluid flow. Following the terminology of Milkov and Sassen (2002), we will refer to these as stratigraphic-type hydrate deposits.

In the steady state, the maximum concentration of hydrate is found at the base of the stability zone, with bubbles found below (Davie and Buffett, 2001). Typical concentrations of hydrate are a few percent of pore volume, and the amount of bubbles below the stability zone is also a few percent by volume. The layer of bubbles is clearly apparent in seismic sections of the subsurface sediment. Temperature contours within the sediment column tend to parallel the sea floor, and so the layer of bubbles tends to parallel the sea floor as well. For this reason, the bubble layer below the base of the stability zone is referred to as a “bottom simulating reflector” or BSR. Because it is remotely detectable, the distribution of



the BSR is one of the best indications of the distribution of hydrates in sediments.

Most of the hydrate deposits on Earth correspond to the stratigraphic type, and hence the estimates of the global inventory of hydrates are based on the physics or on the observed distribution of these types of deposits. Estimates range from 500 to 10 000 Gton C as methane in hydrate globally. The estimates can be compared according to two metrics. One is the area of the sea floor where hydrates can be found, and the other is the inventory of methane, as hydrate and in some tabulations as bubbles, per square meter. Milkov (2004) does a detailed and very thorough comparison of these characteristics of estimates, leaving no need for more than a summary of his results here.

The first piece of the estimate is the area of the sea floor, between 500 and 3000 m depth, that has high concentration of hydrates. MacDonald (1990) assumed a high-hydrate slope-area fraction of 10%. Borowski et al. (1999) estimate that 30% of this area could contain hydrates, based on the proportion of cores where porewater sulfate reaches zero within 50 m of the sea floor. Milkov (2004) views Borowski's 30% as an upper limit, and takes 10% as his best estimate of the high-hydrate slope area fraction. The Buffett and Archer (2004) model predicts nonzero column inventories of methane hydrate or bubbles in 16% of the area between 500–3000 m, but in much of that area the abundance of methane is unmeasurably small. (Its presence is of interest thermodynamically, however.) If we take  $>0.25\%$  over 200 m as a detectability cutoff, the model predicts 13% of the sea floor to fit that definition.

Many studies estimate the area containing hydrates based on the organic carbon concentration of surface sediments. The critical cutoff organic carbon concentration is typically taken as 1% (Kvenvolden, 1999) or 0.5% (Harvey and Huang, 1995), which correspond respectively to about 15% or 30% of the area of sea floor between 500 and 3000 m (based on results from the sediment diagenesis model (Archer et al., 2002) used in Buffett and Archer (2004)). Gornitz and Fung (1994) used high chlorophyll concentrations from Coastal Zone Color Scanner images as correlates to the 0.5–1% organic carbon concentration in sediments. This assumption neglects the role of depth and oxygen in determining the organic carbon degradation, but the satellite data generates a map that looks very similar to sedimentary organic carbon maps. The areas of the sea floor represented by the Coastal Zone Color Scanner cutoffs were 13% and 32%, similar to the organic carbon areas for  $>1\%$  and  $>0.5\%$ . The surface organic carbon method is appealing because of the general correspondence between surface organic carbon and seismic indications of hydrates below, but there are some caveats. The critical quantity in the Buffett and Archer (2004) model is the advective flux of organic carbon to the methanogenesis zone, which increases with increasing carbon concentration, but also depends on sedimentation rate, a boundary condition which must be accounted for in

some way. Using sediment surface organic carbon concentrations neglects the possibility that conditions might have changed in the millions of years it takes for surface sediments to be advected to the methanogenesis zone (Fehn et al., 2000). Changes in ocean temperature could alter the critical organic carbon concentration for hydrate formation in the past (Buffett and Archer, 2004). In spite of these caveats, sediment organic carbon concentrations capture the general trend from oligotrophic to eutrophic, nearshore to pelagic, in the ocean that also drive methane hydrate formation.

Another metric by which global methane inventory estimates can be compared is the volume fraction of methane hydrate within the porewater, averaged over the depth range of the hydrate stability zone. Kvenvolden (1988) assumed 10%. Milkov (2004) argues for a value of 1.2%. The Buffett and Archer (2004) predicts about 1.5%. Data from the Blake Ridge range from 2–4% (Paull et al., 2000; Borowski, 2004). Values from Hydrate Ridge are lower, closer to 1%. The current data is probably too sparse to distinguish between 1% and say 3% as a global average hydrate porewater volume fraction, but the 10% volume fraction assumed in earlier studies like the influential paper by Kvenvolden (1988) now seems to be high, if Blake Ridge or Hydrate Ridge is taken to be representative of the broader ocean.

There are two studies, Buffett and Archer (2004), and Klauda and Sandler (2005), based on mechanistic models of the sedimentary methane cycle. Both studies are based on the 1-D column model of Davie and Buffett (2001). The two studies differ in their global estimates by a factor of twenty. Klauda and Sandler (2005) estimate 76 000 Gton C in hydrate, while Buffett and Archer (2004) predict 3000 Gton C in hydrate (plus 2000 Gton C in bubbles). Both studies show a reasonable fit to data from the Blake Ridge. The difference can be traced to differences in the sediment accumulation rate, and carbon conversion efficiencies, by the two studies. The Klauda and Sandler (2005) calculation assumes a uniform accumulation rate of sediment, throughout the entire ocean, of 10 cm/yr, too high for the deep sea by an order of magnitude and more. For this reason, the Klauda and Sandler (2005) model predicts that most of the hydrates in the ocean ought to exist in abyssal sediments, rather than restricted to the continental margins, as observed (in seismic studies, for example).

Uncertainty in the areal coverage of methane hydrate sediment contributes a factor of three uncertainty in our estimate of the global hydrate reservoir size. The average hydrate fraction is also unknown to within a factor of three, resulting in perhaps a factor of ten overall uncertainty. A potential range of hydrate inventories must span about 500–3000 Gton C, with the inclusion of bubble methane adding perhaps a similar amount. The uncertainty range will be reduced in the future by (1) improvement in techniques for estimating the concentration of methane, both as hydrate and as bubbles, ideally by seismic methods that provide regional coverage, and (2) by continued deep-core sampling within hydrate re-

gions, to constrain the variability in methane concentrations.

For comparison, the inventory of fossil fuels, mostly coal, is thought to be about 5000 Gton C (Rogner, 1997), comparable to the hydrate reservoir. The inventory of dissolved oxidized carbon in the ocean ( $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) is about 38 000 Gton C. This sounds comfortably larger than the hydrate reservoir, but an addition of  $\text{CO}_2$  of this magnitude on a fast time scale would be a sizable perturbation to the pH of the ocean (Archer et al., 1997). The ocean contains about  $2 \times 10^{17}$  moles of oxygen, which could be completely depleted by reaction with about 1000 Gton C in methane.

## 2.6 Structural-type sedimentary hydrate deposits

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

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

Collett (1998) estimate that 500 Gton C might reside as hydrates in the Gulf sediments, but Milkov and Sassen (2001) estimate only 5 Gton C. In the Community Climate System Model model under doubled  $\text{CO}_2$  (after 80 years of 1%/year  $\text{CO}_2$  increase, from C. Bitz, personal communication), waters at 500 m depth in the Gulf warm about  $0.75^\circ\text{C}$ , and  $0.2^\circ$  at 1000 m. In-situ temperatures at 500 m are much closer to the melting temperature, so the relative change in the saturation state is much more significant at 500 m than deeper.

The equilibrium temperature change in the deep ocean to a large, 5000 Gton C fossil fuel release could be  $3^\circ\text{C}$  (Archer et al., 2004). Milkov and Sassen (2003) subjected a 2-dimensional model of the hydrate deposits in the Gulf to a  $4^\circ\text{C}$  temperature increase and predicted that 2 Gton C from hydrate would melt. However, there are no observations to suggest that methane emission rates are currently accelerating. Sassen et al. (2001) find no molecular fractionation of gases in near-surface hydrate deposits that would be indica-

tive of partial dissolution, and suggests that the reservoir may in fact be growing.

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

### 2.6.1 Mud volcanoes

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

## 2.7 Land deposits

The term permafrost is intended to distinguish whether water is frozen, but it is defined in terms of temperature: a two-year mean annual temperature below  $0^\circ\text{C}$ . It has been estimated that permafrost covers 20% of the terrestrial surface of the Earth. High-latitude northern permafrost is observed to be warming (Smith et al., 2005) and thawing (Payette et al., 2004; Camill, 2005). Ice near the surface can melt in the summer, in what is called the “active zone”. Observations show that the active zone is getting thicker (Sazonova et al., 2004). When surface ice melts, soils collapse to form terrain called thermokarst (Nelson et al., 2002), and buildings fall down (Stockstad, 2004). This process has had a dizzying impact on the subarctic landscape (Stockstad, 2004). Models project 30–40% increase in active zone thickness by 2100 (Stendel and Christensen, 2002), and a comparable decrease in the total area of permafrost soils (Anisimov and Nelson, 1996). Melting is projected to be most intense in the marginal permafrost zone in the south (Anisimov and Nelson, 1996) and along the Arctic ocean (Nelson et al., 2002).

### 2.7.1 Peat decomposition

Permafrost soils contain relict organic matter that survived decomposition due to the freezing temperatures. Fossil mammoths, still edible after all these years, are examples of this phenomenon (Herz, 1904). Peat deposits are a substantial reservoir of carbon, are estimated to be 350–450 Gton C (Stockstad, 2004). With a thaw will come accelerated decomposition of this organic matter, increasing the flux of CO<sub>2</sub> and CH<sub>4</sub> (Liblik et al., 1997; Rivkina et al., 2000, 2004). Soil that has been frozen for thousands of years still contains viable populations of methanotrophic bacteria (Rivkina et al., 2004). The flux of methane from peat soils to the atmosphere also depends on the location of the water table, which controls the thickness of the oxic zone (Bubier et al., 1995, 2005; Liblik et al., 1997). If 20% of the peat reservoir converted to methane, released over 100 years, this would release 0.7 Gton C per year, doubling the atmospheric methane concentration.

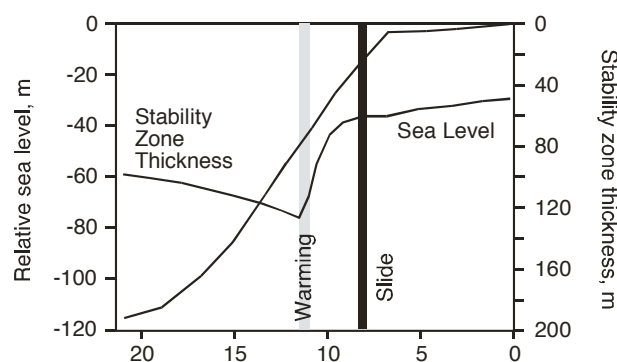
### 2.7.2 Melting hydrates

There is also the possibility that methane is trapped in permafrost-associated hydrate deposits, and might potentially be released upon melting of the permafrost. Permafrost soil need not necessarily be continuous filled ice, it must simply be below the freezing point of pure water. If the pores are open, in contact with the atmosphere, the pressure in the pore spaces will be hydrostatic with the fluid being the atmosphere. In this case, it will be virtually impossible to achieve high enough pressures of methane to form hydrates under any reasonable temperature. However, if the pore space is sealed, by ice or clay for example, then the lithostatic pressure will come to bear on the pore spaces. Mappable natural gas deposits are often at high pressure, demonstrating the impingement of the lithostatic pressure on the hydrostatic pressure. The higher lithostatic pressure is conducive to hydrate formation in places where methane is found.

The Messoyakh gas field, producing gas for 13 years in Western Siberia, is thought to be mostly hydrate (Krasov, 2000). A profile of permafrost from the Mackenzie Delta showed massive, visible hydrate at ~350 m, and implied the presence of invisible pore-water hydrate crystals as shallow as about 120 m, in solidly ice-bonded sediment (Dallimore and Collett, 1995). The stability zone is below ~250 m here.

Total amounts of hydrate methane in permafrost soils are very poorly known, with estimates ranging from 7.5 to 400 Gton C (estimates compiled by Gornitz and Fung (1994)).

There is a special case called the ice complex in Siberia (Romankevich, 1984; Hubberten and Romanovskii, 2001; Gavrillov et al., 2003). The ice complex is a sealed horizon of ice that was formed when sea level was as much as 120 m lower than today, during the last glacial maximum. Liquid ground water froze as it flowed through the permafrost, cre-



**Fig. 6.** Modeling results replotted from Mienert et al (2005) of hydrate stability in the vicinity of the Storegga slide off the coast of Norway. Sea level rose, associated with the melting of the ice sheets (left axis). The stability zone thickness increased with the rise in sea level, but then decreased because of warming (right axis). This particular model scenario is for a temperature change from  $-1^{\circ}$  to  $4^{\circ}$ C, at 500 m. For all model scenarios, the landslide occurred several thousand years after hydrate destabilization by warming of the water column.

ating a sealed layer up to 60–80 m thick, onshore and offshore under as much as 100 m water depth. Bottom water temperatures are near freezing in these locations, and so they currently do not provide much impetus to melt at the surface, although surface melting may accelerate with future high-latitude warming. However,  $0^{\circ}$ C is considerably warmer than surface air temperatures during glacial times. A geotherm projected down from  $0^{\circ}$ C intersects the melting temperature at a much shallower depth than would a geotherm from a glacial surface temperature. For this reason, most of the melting of the submerged ice complex since deglaciation has been on the bottom of the ice, not on the top.

Melting is also driven by lateral invasion of the coastline, a melt-erosion process called thermokarst erosion (Gavrillov et al., 2003). The ice melts where it is exposed to the ocean along the coast, collapsing the land into the sea and leaving more ice exposed to melting. The Siberian coast has receded by 100–500 km in 7500 years (Hubberten and Romanovskii, 2001), after the sea level finished its deglacial rise (see Fig. 6 in Hubberten and Romanovskii (2001)). Entire islands have melted within historical times (Romankevich, 1984).

Emission of hydrate-melt methane has been documented along the Siberian coastline. Coastal melting has resulted in 2500% supersaturation concentrations of methane relative to the atmosphere in Siberian shelf waters (Shakhova et al., 2005). Two surveys of methane concentration, taken 1 year apart, differed in their methane inventory by a factor of five. Whether this difference is due to differences in water circulation or methane degassing is unknown. Surface waters over the North Slope of Alaska were similarly supersaturated (Kvenvolden, 1999).

**Table 1.** Summary of mechanisms by which methane might escape to the atmosphere.

Chronic releases	Inventory	Potential Release	Impacts
Stratigraphic-type hydrate deposits in the ocean	1000–6000	Any release would take millennia	Effects would be most pronounced on geological timescales. Radiative effect of accumulating CO <sub>2</sub> >effect of transient methane.
Arctic Ocean	Hundreds	CH <sub>4</sub> release ongoing today, but time scale for acceleration is probably decades	Released to water column, could reach atmosphere as CH <sub>4</sub>
Gulf of Mexico	5–500	Any release would take centuries	Released to water column, small potential impact on atmospheric CH <sub>4</sub>
Peat Decomposition	350–450	Say 20% over 100 years	Flux of 0.7 Gton/yr to the atmosphere, triples pCH <sub>4</sub>
Permafrost hydrate melting	Hundreds	Comparable to Peat Decomposition	Comparable to Peat Decomposition
Catastrophic releases			
Landslides		5 Gton from Storegga	Some release as hydrate which can reach the atmosphere, but also bubbles which dissolve in the water column

The potential for methane release to the environment from permafrost hydrate melting has not been extensively discussed, but given the magnitude of the potential hydrate reservoir, and the long time scale for melting, one could imagine a chronic, ongoing release of methane that would rival the release of methane from decomposing peat (Table 1).

## 2.8 Hydrates as fossil fuel

Another pathway by which hydrate carbon might reach the atmosphere to affect climate is if it is combusted as a fossil fuel. Estimates of the total inventory of methane in hydrate deposits globally are very high, but probably only a small fraction of the hydrate reservoir would be extractable (Milkov and Sassen, 2002). The largest methane reservoir, the stratigraphic disseminated deposit, is the least attractive economically. The concentration of methane is generally too low for economical extraction using current technology. The sediments of the Blake Ridge are impermeable (Kvenvolden, 1999), making extraction even more unlikely, while sediments in the Nankai Trough are more permeable and hence easier to extract (Milkov and Sassen, 2002), which the Japanese intend to do (Kerr, 2004). The other class of oceanic deposits is the structurally-focused deposits, such as found in the Gulf of Mexico (Milkov and Sassen, 2001) and mud volcanoes (Milkov, 2000). Milkov and Sassen (2001) estimate that the Gulf of Mexico contains 40 times as much hydrate methane as conventional subsurface reservoir methane in that area.

The most likely near-term targets for methane hydrate extraction are deposits associated with permafrost soils on land

and in the shallow ocean. The Soviets drilled at least 50 wells in the Messoyakha field, in which thermogenic methane is trapped under a dome of 450-m thick permafrost, one-third of it frozen into hydrates (Krasov, 2000). The Soviets extracted gas from Messoyakha for 13 years, injecting hot water and/or solutes (methanol and CaCl<sub>2</sub>) to destabilize hydrate and release methane. Subsequently, an international consortium led by the Japanese drilled a series of wells on the north coast of Alaska, the Mallik field (Kerr, 2004; Chatti et al., 2005). Hydrates here are in a sandstone layer 1000 m down, below mudstones. The hydrate-bearing sediments were more permeable there than had been expected so that methane could be extracted most economically by simply reducing the pressure. Methane moved via fractures, and more fractures could be broken with pressure spiking.

The prognosis for methane hydrate mining is that methane hydrates could supply perhaps 10% of global methane consumption in the coming decades, by analogy to coal-bed methane 30 years ago (Grauls, 2001; Kerr, 2004). Methane hydrates could be a significant source of fossil energy, but not limitless as might be inferred from the large estimates of total methane inventory in the global hydrate reservoir, since most of the hydrates are probably impractical to extract.

The possibility of geological hazard from methane drilling has been discussed in a general way (Kvenvolden, 1999; Grauls, 2001; Chatti et al., 2005) but the likelihood of methane extraction causing slope instability still seems rather speculative. Some have considered replacing CH<sub>4</sub> hydrates with CO<sub>2</sub> hydrates, sequestering CO<sub>2</sub> and maintaining the stability of the continental slope in the process (Warzinski and Holder, 1998). The Storegga slide (next section) was in-

investigated in order to determine the safety of extracting gas from the Ormen Lange gas field within the Storegga slide area.

### 3 Observations from the past

#### 3.1 The Storegga landslide

##### 3.1.1 Observations

One of the largest exposed submarine landslides in the ocean is the Storegga Slide in the Norwegian continental margin (Bryn et al., 2005; Mienert et al., 2000, 2005). The slide excavated on average the top 250 m of sediment over a swath hundreds of kilometers wide, stretching half-way from Norway to Greenland. There have been comparable slides on the Norwegian margin every approximately 100 kyr, roughly synchronous with the glacial cycles (Solheim et al., 2005). The last one, Storegga proper, occurred about 8150 years ago, after deglaciation. It generated a tsunami in what is now the United Kingdom (Smith et al., 2004). The Storegga slide area contains methane hydrate deposits as indicated by a seismic BSR (Bunz and Mienert, 2004; Mienert et al., 2005; Zillmer et al., 2005a, b) corresponding to the base of the hydrate stability zone at 200–300 m, and pockmarks (Hovland et al., 2005) indicating gas expulsion from the sediment.

##### 3.1.2 Inferences

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

The other possibility is the dissociation of methane hydrate deposits by rising ocean temperatures. Rising sea level is also a player in this story, but a smaller one. Rising sea level tends to increase the thickness of the stability zone, by increasing the pressure. A model of the stability zone shows this effect dominating deeper in the water column (Vogt and Jung, 2002); the stability zone is shown increasing by about 10 m for sediments in water depth below about 750 m. Shallower sediments are more impacted by long-term temperature changes, reconstructions of which show warming of 5–6°C over a thousand years or so, 11–12 kyr ago. The landslide occurred 2–3 kyr after the warming (Fig. 6 from Mienert et al. (2005)). The slide started at a few hundred meters water depth, just off the continental slope, just where

Mienert et al. (2005) calculates the maximum change in the hydrate stability zone.

Sultan et al. (2004) claim that warming in the near-surface sediment would provoke hydrate to dissolve by increasing the saturation methane concentration. This form of dissolution differs from heat-driven direct melting, however, in that it produces dissolved methane, rather than methane bubbles. Sultan et al. (2004) assert that melting to produce dissolved methane increases the volume, although laboratory measurements of volume changes upon this form of melting are equivocal, and in any case the volume changes are much smaller than for thermal melting that produces bubbles.

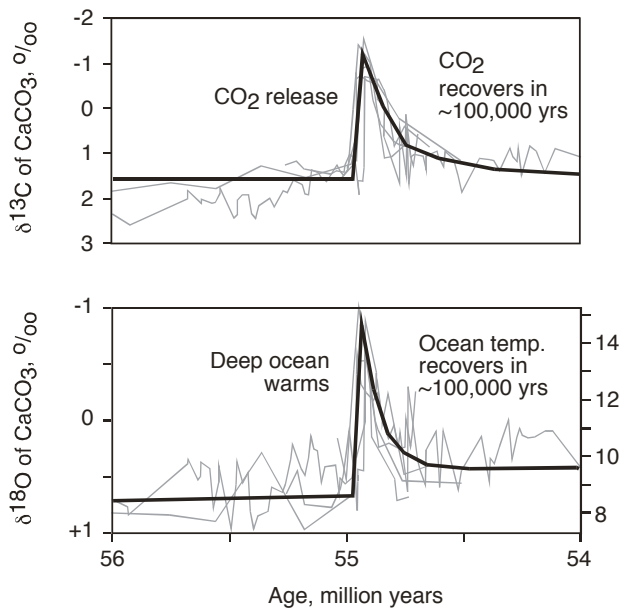
The amount of methane released by the slide can be estimated from the volume of the slide and the potential hydrate content. Hydrate just outside the slide area has been estimated by seismic methods to fill as much as 10% of the pore water volume, in a layer about 50 m thick near the bottom of the stability zone (Bunz and Mienert, 2004). If these results were typical of the entire  $10^4$  km<sup>2</sup> area of the slide, the slide could have released 1–2 Gton C of methane in hydrate. Paul (1978) assumed 10% hydrate fraction and predicted 5 Gton C methane released. If 5 Gton C CH<sub>4</sub> reached the atmosphere all at once, it would raise the atmospheric concentration by about 2.5 ppm of methane, relative to a present-day concentration of about 1.7 ppm, trapping about 0.2 W/m<sup>2</sup> of greenhouse heat. The methane radiative forcing would subside over a time scale of a decade or so, as the pulse of released methane is oxidized to CO<sub>2</sub>, and the atmospheric methane concentration relaxes toward the long-term steady state value. The radiative impact of the Storegga landslide would be comparable in magnitude but opposite in sign to the eruption of a large volcano, such as the Mt. Pinatubo eruption (–2 W/m<sup>2</sup>), but it would last for longer (10 years for methane and 2 for a volcano).

It is tantalizing to a paleoclimatologist to wonder if there could be any connection between the Storegga landslide and the 8.2 kyr climate event (Alley and Agustsdottir, 2005), which is presumed to have been triggered by fresh water release to the North Atlantic. However, ice cores record a 0.75 ppm drop in methane concentration during the 8.2k event, not a rise. The shutdown of convection in the North Atlantic would have, if anything, cooled the overlying waters. Thus there appears to be no link between the 8.2k event and Storegga in either causal direction; methane released by the landslide did not alter the climate, nor did the 8.2k event cause the slide.

##### 3.1.3 Implications

The modeling results of Mienert et al. (2005) in Fig. 4 raise a clear possibility that warming and melting of hydrates had something to do with the slide. On the other hand, several thousand years elapsed between the warming and the landslide. This tends to argue against concern for such events in the coming century. Estimates of potential methane emission





**Fig. 7.** Carbon and oxygen isotopic excursion known as the Paleocene Eocene Thermal Maximum, from (Zachos et al., 2001). The dark line is an generalization of the raw data (light lines), from the south Atlantic and the western Pacific.

from a large landslide range from 1–5 Gton C, which is significant but not apocalyptic. The tsunami hazard might be a comparable cause for concern.

### 3.2 Paleocene Eocene thermal maximum

#### 3.2.1 Observations

About 55 million years ago, the  $\delta^{13}\text{C}$  signature of carbon in the ocean and on land decreased by 2.5–5‰ on a time scale of less than 10 kyr, then recovered in parallel on a time scale of  $\sim 120$ –220 kyr (Kennett and Stott, 1991; Roehl et al., 2006; Farley and Eltgroth, 2003) (Fig. 7 from Zachos et al. (2001)). The  $\delta^{18}\text{O}$  of  $\text{CaCO}_3$  from intermediate depths in the ocean decreased by 2–3‰, indicative of a warming of about 5°C. The timing of the spikes is to a large extent synchronous. Planktonic foraminifera and terrestrial carbon records show a  $\delta^{13}\text{C}$  perturbation a bit earlier than the benthics do, suggesting that the carbon spike invaded the deep ocean from the atmosphere (Thomas et al., 2002). Similar events, also associated with transient warmings although less well documented, have been described from other times in geologic history (Hesselbo et al., 2000; Jenkyns, 2003).

#### 3.2.2 Inferences

The benthic  $\delta^{18}\text{O}$  record is most easily interpreted as a temperature change, at a depth of several kilometers in the ocean, from about 8° to about 14°C, in a few thousand years. Warming is also implied by Mg/Ca ratios in  $\text{CaCO}_3$  (Zachos et al.,

2003). Planktonic  $\delta^{18}\text{O}$  can also be fractionated by changes in freshwater forcing, reflected in salinity, but salinity can be assumed to be regionally more homogeneous in the deep ocean than at the surface. There is usually an offset between the  $\delta^{18}\text{O}$  recorded by foraminifera and the true equilibrium value, called a vital effect, but single-species reconstructions of  $\delta^{18}\text{O}$  tend to reduce the impact of these vital effects. The  $\delta^{18}\text{O}$  of the whole ocean changes when ice sheets grow, but there were no ice sheets at this time.  $\delta^{18}\text{O}$  in chemical reactions with rocks, but not on short time scales such as seen here.

The change in carbon isotopic composition of the carbon in the ocean is attributed to the release of some amount of isotopically light carbon to the atmosphere. However it is not clear where the carbon came from, or how much of it there was. The magnitude of the carbon shift depends on where it was recorded. The surface change recorded in  $\text{CaCO}_3$  in soils (Koch et al., 1992) and in some planktonic foraminifera (Thomas et al., 2002) is twice as large a change as is reported for the deep sea. Land records may be affected by changes in plant fractionation, driven by changing hydrological cycle (Bowen et al., 2004). Ocean records may be affected by  $\text{CaCO}_3$  dissolution (Zachos et al., 2005), resulting in diagenetic imprints on the remaining  $\text{CaCO}_3$ , a necessity to use multiple species, or simple inability to find  $\text{CaCO}_3$  at all.

We can estimate the change in the carbon inventory of the ocean by specifying an atmospheric  $\text{pCO}_2$  value, a mean ocean temperature, and insisting on equilibrium with  $\text{CaCO}_3$  (Zeebe and Westbroek, 2003). The ocean was warmer, prior to the PETM event, than it is today. Atmospheric  $\text{pCO}_2$  was probably at least 560 ppm at this time (Huber et al., 2002). The present-day inventory of  $\text{CO}_2$  in the ocean is about 40 000 Gton C. According to simple thermodynamics, neglecting changes in the biological pump or circulation of the ocean, the geological steady-state inventory for late Paleocene, pre-PETM time could have been on the order of 50 000 Gton C.

The lighter the isotopic value, the smaller the amount of carbon that must be released to explain the isotopic shift (Fig. 8). Candidate sources include methane, which can range in its isotopic composition from  $-30$  to  $-110$ ‰. If the ocean  $\delta^{13}\text{C}$  value is taken at face value, and the source was methane at  $-60$ ‰, then 2000 Gton C would be required to explain the isotopic anomaly. If the source were thermogenic methane or organic carbon at  $\delta^{13}\text{C}$  of about  $-25$ ‰, then 6 000 Gton C would be required.

Buffett and Archer (2004) find that the steady-state hydrate reservoir size in the ocean is extremely sensitive to the temperature of the deep sea. At the temperature of Paleocene time but with everything else as in the present-day ocean, they predict less than a thousand Gton C of methane in steady state. As the ocean temperature decreases, the stability zone gets thinner and covers less area. Their model was able to fit 6000 Gton C in the Arctic Ocean, however, using 6° temperatures from CCSM (Huber et al., 2002) (which may be too

cold) and assuming that the basin had been anoxic (Sluijs et al., 2006).

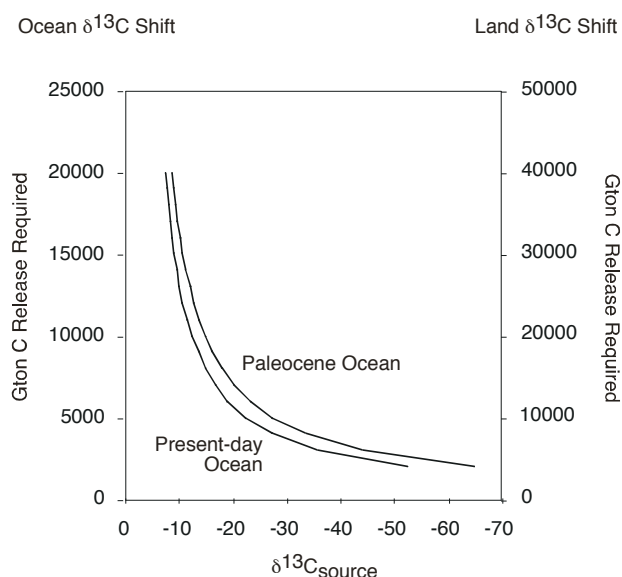
Invoking the Arctic here solves a number of problems. It is easier to imagine a large temperature change in an isolated, polar basin than it is in the whole ocean. This makes it easier to get a large synchronous release such as observed. Also, if methane is released in the Arctic, even if it oxidized in the Arctic water column, in other parts of the ocean the  $\delta^{13}\text{C}$  signature would be found in planktonic forams before benthic, as observed in site 669 near the Antarctic. Bubbles released from the sea floor mostly dissolve before reaching the atmosphere, and half the methane reservoir is bubbles (Buffett and Archer, 2004), so it is not easy to imagine getting methane from the main ocean sediments to the plankton before it reaches the deep sea.

Marine organic matter has an isotopic composition of  $-20\%$ , and would require 6000 Gton to explain the isotopic anomaly. Svensen et al. (2004) proposed that lava intrusions into organic-rich sediments could have caused the isotopic shift. They cite evidence that the isotopic composition of methane produced from magma intrusion should be  $-35$  to  $-50\%$ , requiring therefore 2500–3500 Gton C to explain the isotope anomaly in the deep ocean. If  $\text{CO}_2$  were also released, from metamorphism of  $\text{CaCO}_3$ , the average isotopic composition of the carbon spike would be lower, and the mass of carbon greater. Storey et al. (2007) showed that the opening of the North Atlantic Ocean corresponds in time with the PETM. However, volcanic activity continued for hundreds of thousands of years, leaving still unexplained the reason for the fast ( $<10\,000$  years) carbon isotope excursion.

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

Volcanic carbon has an isotopic composition of  $-7\%$ , requiring a huge carbon release of 20 000 Gton C. Excess carbon emissions have been attributed to superplume cycles in the mantle and flood basalt volcanism (Larson, 1991) However, these events tend to take millions of years to play out (Dickens et al., 1995). Bralower et al. (1997) and Schmitz et al. (2004) find evidence of increased volcanism during the PETM interval, but view the volcanism as rearranging ocean circulation, triggering methane release, rather than a major primary source of carbon itself, presumably because the potential volcanic carbon source is too slow.

Acidification of the ocean by invasion of  $\text{CO}_2$  drove a shoaling of the depth of  $\text{CaCO}_3$  preservation in the Atlantic (Zachos et al., 2005) although curiously not in the Pacific (Zachos et al., 2003). The magnitude of the CCD shift in



**Fig. 8.** Size of the implied PETM carbon release as a function of its carbon isotopic composition. The right-hand axis assumes the  $\delta^{13}\text{C}$  spike of  $-2.5\%$  as observed in most ocean  $\delta^{13}\text{C}$  records. The left-hand axis assumes a global  $\delta^{13}\text{C}$  shift from the paleosol records, about twice that in the ocean (Koch et al., 1992). The mass-balance calculation requires an estimate of the ocean inventory of carbon; we show results assuming the present-day ocean carbon chemistry, and that for a Paleocene ocean assuming equilibrium with 600 ppm atmospheric  $\text{CO}_2$  and with solid  $\text{CaCO}_3$ .

the Atlantic, if taken as representative of the whole ocean, would be suggestive of a large carbon addition, on the order of 5000 Gton C or more (Archer et al., 1997).

A large carbon release is also supported by the warming inferred from the  $\delta^{18}\text{O}$  spike. The temperature can be altered by both  $\text{CH}_4$  and  $\text{CO}_2$ . Schmidt and Shindell (2003) calculated that the steady-state atmospheric  $\text{CH}_4$  concentration during the period of excess emission (ranging from 500–20 000 years) would be enough to explain the temperature change. However, the atmospheric methane concentration anomaly would decay away a few decades after the excess emission ceased. At this point the temperature anomaly would die away, hence as soon as the carbon isotopic composition stopped plunging negative, the oxygen isotopic composition should recover. The carbon isotopic composition should remain light for hundreds of thousands of years (Kump and Arthur, 1999) until it reapproached a steady-state value. The record shows instead that the oxygen and carbon isotopic anomalies recovered in parallel. This suggests that  $\text{CO}_2$  is the more likely greenhouse warmer rather than  $\text{CH}_4$ . It could be that the time scale for the  $\text{pCO}_2$  to reach steady state might be different than the time scale for the isotopes to equilibrate, analogous to the equilibration of the surface ocean by gas exchange: isotopes take longer. However, in the Kump and Arthur (1999) model re-

sults,  $p\text{CO}_2$  seems to take longer to equilibrate than  $\delta^{13}\text{C}$ . The first-order result is that the  $\text{CO}_2$  and  $\delta^{13}\text{C}$  timescales are much more similar than the  $\text{CH}_4$  and  $\delta^{13}\text{C}$  time scales would be.

A warming of  $5^\circ\text{C}$  would require somewhere between one and two doublings of the atmospheric  $\text{CO}_2$  concentration, if the climate sensitivity is in the range of  $2.5\text{--}5^\circ\text{C}$ . Beginning from 600 ppm, we would increase the  $p\text{CO}_2$  of the atmosphere to somewhere in the range of 1200–2400 ppm. The amount of carbon required to achieve this value for hundreds of thousands of years (after equilibration with the ocean and with the  $\text{CaCO}_3$  cycle) would be of order 20 000 Gton C. This would imply a mean isotopic composition of the spike of mantle isotopic composition, not isotopically light methane. The amount of carbon required to explain the observed  $\delta^{18}\text{O}$  would be higher if the initial atmospheric  $p\text{CO}_2$  were higher than the assumed 600 ppm. The only way that a biogenic methane source could explain the warming is if the climate sensitivity were much higher in the Paleocene than it seems to be today, which seems unlikely because the ice albedo feedback amplifies the climate sensitivity today (Pagani et al., 2006).

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

### 3.2.3 Implications

The PETM is significant to the present-day because it is a close analog to the potential fossil fuel carbon release if we burn all the coal reserves. There is about 5000 Gton of C in coal, while oil and traditional natural gas deposits are hundreds of Gton each (Rogner, 1997). The recovery timescale from the PETM (140 kyr) is comparable to the model predictions, based on the mechanism of the silicate weathering thermostat (400 kyr timescale (Berner et al., 1983)).

The magnitude of the warming presents something of a problem. 5000 Gton of fossil fuel release will warm the deep ocean by perhaps  $2\text{--}4^\circ\text{C}$ , based on paleoclimate records and model results (Martin et al., in press). The warming during the PETM was  $5^\circ\text{C}$ , and this was from an atmospheric  $\text{CO}_2$  concentration higher than today, at least 600 ppm and perhaps higher, so that a further spike of only 2000 Gton (based on methane isotopic composition) would have only a tiny radiative impact, not enough to warm the Earth by  $5^\circ\text{C}$ . One

possibility is our estimates for the climate sensitivity is underestimated by a factor of 2 or more. However, one might have expected a decreased climate sensitivity for an ice-free world than for the ice-age climate of today.

Another possibility is that the PETM was driven by two sources of carbon, totaling maybe 10 000 Gton C. At most 10% of this carbon could have had an initial  $\delta^{13}\text{C}$  of  $-60\text{‰}$ , if the rest were volcanic carbon at  $-7\text{‰}$ . The implication would be that the hydrate reservoir at that time did not amplify the initial carbon release (analogous to our fossil fuel  $\text{CO}_2$ ) by more than 10%. However, there are no strong ideas for where that other 9000 Gton C could have come from.

Perhaps the global average  $\delta^{13}\text{C}$  shift was as large as recorded in soils (Koch et al., 1992) and some planktonic foraminifera (Thomas et al., 2002), and perhaps it was thermogenic methane, so the hydrate release could have been 8000 Gton C. In this case we can attribute all of the temperature change to the radiative effect of the released carbon, mostly as the accumulated  $\text{CO}_2$ . The Archer and Buffett (2005) model predicted a regime in model space where the hydrate reservoir would be unstable, periodically melting down. The time period between meltdowns was determined by the time scale of methane accumulation in the reservoir. The critical parameters to the model are the time scale for a melting relaxation to the equilibrium size, and the fraction of the reservoir which melts at all. If most of the reservoir equilibrates quickly, then periodic meltdowns result. Tauntingly, there are several tiny “after shocks” of the PETM, all about 2 million years apart, such as an ELMO event (Lourens et al., 2005). The trouble then is that the model, tuned to periodic meltdowns during the PETM, predicts that the hydrate reservoir today, larger because the ocean is colder, should periodically melt down even more severely today.

Could some external agent of warming, not  $\text{CO}_2$ , have driven temperatures up? The  $\delta^{13}\text{C}$  could be showing us methane release, but the temperature would be attributed to something else, something no one has thought of yet. The difficulty here would be that the decay of the temperature spike follows so closely the decay of the  $\delta^{13}\text{C}$  spike. This tends to steer us back to the path of  $\text{CO}_2$  as the proximate agent of temperature change.

At present, the PETM serves as a cautionary tale about the long duration of a release of new  $\text{CO}_2$  to the atmosphere (Archer, 2005). However, our current understanding of the processes responsible for the  $\delta^{13}\text{C}$  spike is not strong enough to provide any new constraint to the stability of the methane hydrate reservoir in the immediate future.

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

Kennett et al. (2003) and Nisbet (2002) argue that methane from hydrates could be responsible for the initial deglacial methane concentration rise in the Greenland ice core record. Kennett et al. (2000) found episodic negative  $\delta^{13}\text{C}$  excursions in benthic foraminifera in the Santa Barbara Basin,

which they interpret as reflecting release of hydrate methane during warm climate intervals. Biomarkers for methanotrophy are found in greater abundance, and indicate greater rates of reaction, during warm intervals in the Santa Barbara Basin (Hinrichs et al., 2003) and in the Japanese coastal margin (Uchida et al., 2004). Cannariato and Stott (2004) however argued that these results could have arisen from contamination or subsequent diagenetic overprints.

Because methane is a transient chemical species in the atmosphere, a sustained increase in methane concentration would have to be driven by a sustained increase in the chronic methane release rate to the atmosphere. A single catastrophic release of methane might not even be visible in the ice core records. Detailed analysis of the methane record shows a lag of a few hundred years between abrupt warmings and methane rise. This pattern is consistent with a wetland source for methane, but difficult to generate by catastrophic release from hydrates (Brook et al., 2000). The interhemispheric gradient of methane tells us that the deglacial increase in atmospheric methane arose from high Northern latitudes (Dalenbach et al., 2000).

The definitive ruling comes from the isotopic composition of the ice core methane. The isotopic ratio of D/H in ice core methane indicates a freshwater source, rather than a marine source, apparently ruling out much of a role for marine hydrate methane release (Sowers, 2006). The deglacial methane rise could therefore be attributed to methanogenesis from thawing organic matter decomposition or from high-latitude wetlands. Regardless of the source of the methane, the climate forcing from the observed methane record is too weak to argue for a dominant role for methane in the glacial cycles. The climate forcings from changing atmospheric CO<sub>2</sub>, and the albedo forcing from melting ice, had a much stronger impact on the evolution of climate.

## 4 Risks for the future

### 4.1 Capacity for doomsday

There is so much methane as hydrates on Earth that it seems like a perfect ingredient for a climate doomsday scenario. Hydrate is unstable at Earth surface conditions, both because of the low atmospheric methane concentration and because most of the Earth's surface is warmer than the freezing point of methane hydrate at one atmosphere pressure. The hydrate reservoir contains thousands of Gton C of methane, enough that releasing a small fraction of the methane directly to the atmosphere, within a time window that is short relative to the atmospheric lifetime of methane, could increase the methane concentration of the atmosphere by a factor of 100 to 1000 over pre-anthropogenic values. Methane absorbs infrared light between about 1250 and 1350 cm<sup>-1</sup>, a frequency range at which terrestrial radiation is less intense than it is in the absorption band of the CO<sub>2</sub> bending mode,

about 600–700 cm<sup>-1</sup>. A massive increase in methane concentration therefore has a smaller impact on the radiative balance of the Earth than would a comparable increase in CO<sub>2</sub>, but nevertheless the greenhouse forcing from the methane increase could be catastrophic, equivalent to increasing CO<sub>2</sub> by a factor of 10 or more. The methane hydrate reservoir therefore has the potential to warm Earth's climate to Eocene hothouse-type conditions, within just a few years. The potential for planetary devastation posed by the methane hydrate reservoir therefore seems comparable to the destructive potential from nuclear winter or from a bolide impact.

Fortunately, most of the hydrate reservoir seems insulated from the climate of the Earth's surface, so that any melting response will take place on time scales of millennia or longer. Various potential mechanisms for releasing methane in response to climate change, discussed in detail above, are summarized in Table 1.

### 4.2 Permafrost deposits

The Siberian margin is one example of a place where methane hydrate is melting today, presumably at an accelerated rate in response to anthropogenic warming. This is a special case, where subsurface hydrates are exposed to the ocean by lateral erosion of coastline. The coastline is receding at rates of tens of meters per year in parts of Siberia and Alaska, but this is an ongoing process that began with the sea level rise of the deglaciation (Hubberten and Romanovskii, 2001). The melting of hydrates in this region releases methane in an ongoing, chronic way, potentially increasing the steady-state methane concentration of the atmosphere, along with other ongoing anthropogenic methane fluxes. No mechanism has been proposed whereby a significant fraction of the Siberian permafrost hydrates could release their methane catastrophically.

### 4.3 Structural deposits

The most vulnerable hydrate deposits in the ocean appear to be the structural type, in which methane gas flows in the subsurface, along faults or channels, perhaps to accumulate to high concentrations in domes or underneath impermeable sedimentary layers. The structural deposits have two distinguishing characteristics that may affect their potential for methane release. First, they produce "massive" methane hydrates, displacing the sediment to generate large chunks of hydrate, potentially filling tens of percent of the volume of the sediment (Trehu et al., 2004), as opposed to just a few percent as in the stratigraphic-type hydrate deposits. The significance of this is that a large chunk of hydrate is more likely to survive an ascent to the sea surface, if it escapes the sediment column as a result of a submarine landslide (Brewer et al., 2002; Paull et al., 2003) or simply by breaking off from the sediment surface (Macdonald et al., 1994). The other important characteristic of structural hydrate deposits is that

the hydrate can be found at shallower depths in the sediment, in general, than is typical for the stratigraphic-type deposits. Methane hydrates are found at the sediment surface in the Gulf of Mexico (Macdonald et al., 1994) and Hydrate Ridge. Hydrate deposits of these characteristics is also often associated with mud volcanoes.

The proximity of structural hydrate deposits to the waters of the ocean allows them to be affected by anthropogenic warming without waiting thousands of years for heat to diffuse into the sediment column (Fig. 3). However, these deposits are still covered with hundreds of meters of ocean water. Throughout most of the ocean, the stability depth is of order 500–700 m, shoaling to perhaps 200 m in the Arctic. Surface warming is expected to take order a century to reach these depths. Presumably any melting response to this gradual warming would be gradual as well, slower than the atmospheric lifetime of methane and therefore by our definition a chronic methane release rather than a catastrophic one.

#### 4.4 Stratigraphic deposits

Most of the hydrate deposits on Earth are of the stratigraphic-type, which implies that the hydrate is (1) typically dilute and (2) generally located near the base of the stability zone in the sediment, which can be hundreds of meters below the sea floor. Warming of the ocean can propagate into the sediment column, but this thick layer of thermal insulation guarantees that most of the anthropogenic effect on temperature will take thousands of years. Melting of hydrates in response to warming will tend to occur primarily below the stability zone, where bubbles of methane will be produced in a process analogous to the ongoing melting of hydrates to produce the bubble-layer (BSR).

The fate of gas bubbles released in subsurface sediment is still very uncertain. The gas could remain in place, or it could escape through the cold trap of the stability zone, or it could destabilize the sediment column, provoking submarine landslides. A landslide could release methane as hydrate, which may reach the atmosphere, and bubbles, which probably would not. A landslide methane release would certainly be abrupt, but it would not be climatically catastrophic because the amount of methane in any given landslide could only be a tiny fraction of the global methane inventory. A slide the size of the Storegga slide off of Norway could potentially release enough methane to affect climate comparably to a large volcanic eruption, although it would be a warming rather than a cooling, and it would last a decade rather than a few years. As it happens, there was no increase in atmospheric methane during the time interval of the Storegga landslide itself, but rather a decrease associated with the 8.2k climate event, a cooling event triggered by a sudden meltwater release to the ocean.

#### 4.5 Century-timescale response

On the timescale of the coming century, it appears that most of the hydrate reservoir will be insulated from anthropogenic climate change. The exceptions are hydrate in permafrost soils, especially those coastal areas, and in shallow ocean sediments where methane gas is focused by subsurface migration. The most likely response of these deposits to anthropogenic climate change is an increased background rate of chronic methane release, rather than an abrupt release. Methane gas in the atmosphere is a transient species, its loss by oxidation continually replenished by ongoing release. An increase in the rate of methane emission to the atmosphere from melting hydrates would increase the steady-state methane concentration of the atmosphere.

The potential rate of methane emission from hydrates is more speculative than the rate from other methane sources such as the decomposition of peat in thawing permafrost deposits, or anthropogenic emission from agricultural, livestock, and fossil fuel industries, but the potential rates appear to be comparable between these sources.

#### 4.6 Geological-timescale response

On geologic time scales, the strongest climate impact appears to be from CO<sub>2</sub>, the oxidation product of any released methane. Methane is a transient species in the atmosphere, with a lifetime of about a decade. CO<sub>2</sub> accumulates in the atmosphere/ocean/terrestrial biosphere carbon pool, and persists to affect climate for hundreds of thousands of years (Archer, 2005). If a pool of methane is released over a timescale of thousands of years, the climate impact from the accumulating CO<sub>2</sub> concentration may exceed that from the steady-state increase in the methane concentration (Archer and Buffett, 2005), see also Harvey and Huang (1995) and Schmidt and Shindell (2003). After the emission stops, methane drops quickly to a lower steady state, while the CO<sub>2</sub> persists (Schmidt and Shindell, 2003).

If hydrates melt in the ocean, much of the methane would probably be oxidized in the ocean rather than reaching the atmosphere directly as methane. This reduces the century-timescale climate impact of melting hydrate, but on timescales of millennia and longer the climate impact is the same regardless of where the methane is oxidized. Methane oxidized to CO<sub>2</sub> in the ocean will equilibrate with the atmosphere within a few hundred years, resulting in the same partitioning of the added CO<sub>2</sub> between the atmosphere and the ocean regardless of its origin.

Archer and Buffett (2005) find an amplifying positive feedback among atmospheric CO<sub>2</sub>, the temperature of the deep ocean, and the release of carbon from methane hydrate to more atmospheric CO<sub>2</sub>. They find that if the melting kinetics of the reservoir are assumed to be too fast, or the release fraction too high, then the reservoir becomes unstable, melting down spontaneously in ways that are not found in the re-



cent  $\delta^{13}\text{C}$  record. The rate and extent to which methane carbon can escape the sediment column in response to warming is, as we have seen, very difficult to constrain at present. It depends on the stability of the sediment slope to sliding, and on the permeability of the sediment and the hydrate stability zone cold trap to bubble methane fluxes. They find that in a worst-case scenario, after thousands or hundreds of thousands of years, the methane hydrate reservoir could release as much carbon as fossil fuel emissions.

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