

Destabilization of methane hydrates: a risk analysis

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David Archer
Department of the Geophysical Sciences
University of Chicago
d-archer@uchicago.edu

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Abstract

A huge reservoir of carbon resides as methane in clathrate deposits on the sea floor and associated with permafrost soils. On geologic time scales of thousands of years and longer, this reservoir seems precarious, because the hydrate ice floats in water, and melts at Earth surface conditions. Eventually the hydrates could release as much carbon as we release from fossil fuels. On an anthropogenic time scale of the coming century, however, estimates of methane release from hydrates are generally small relative to the climate forcing from fossil fuel CO₂ release. The risk of climate impact in the coming century from the methane hydrate reservoir is speculative but could be comparable to climate feedbacks from the terrestrial biosphere and from decomposition of melting peat deposits.

Major landslides such as the Storegga slide off the coast of Norway could have released at most a gigaton of C as methane to the atmosphere. The potential climate perturbation from a release this size is smaller, although of opposite sign and somewhat longer lived, than the climate impact from a major volcanic eruption.

The nightmare scenario would be the catastrophic release of some large fraction of the enormous methane hydrate reservoir, but no one has proposed a mechanism by which this could take place. The carbon isotopic excursion at the end of the Paleocene has been interpreted as the release of thousands of Gton C from hydrates, but the time scale of the release appears to have been thousands of years, i.e. a chronic release rather than a catastrophic.

Anthropogenic warming may drive a chronic, ongoing release of methane that would raise the steady-state concentration of methane in the atmosphere, and contribute another source of CO₂, which accumulates to impact climate for hundreds of thousands of years. Several simulations have found a greater climate impact from the accumulating CO₂ than from the transient atmospheric methane.

Methane in the Carbon Cycle

Sources of Methane

Juvenile Methane

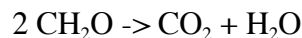
Methane, CH₄, is the most chemically reduced form of carbon. In the atmosphere and in parts of the biosphere controlled by the atmosphere, oxidized forms of carbon are most stable, such as CO₂, the carbonate ions in seawater, and CaCO₃ minerals. Methane is therefore a transient species in our atmosphere; 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 CO₂. The other source of reduced carbon is from photosynthesis, harvesting energy from sunlight. By far the greatest portion of the methane 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 state, such as carbohydrates made up of multiples of the unit CH₂O 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.

Biogenic Methane

Biogenic methane is a product of organic matter degradation. Microbial respiration tends to utilize the partner electron acceptor which will maximize the energy yield from the organic matter. In the presence of molecular oxygen, O₂, oxic respiration is the most energetically lucrative, and this is the pathway that is followed. With the depletion of O₂, respiration proceeds using electron acceptors in the order NO₃⁻, Mg²⁺, Fe²⁺, then SO₄²⁻. Of these, SO₄²⁻ has potentially the highest availability, because seawater contains high concentrations of SO₄²⁻. Fresh water has less SO₄²⁻, and so methanogenesis begins earlier in fresh water systems. Once these electron acceptors have been depleted, two pathways produce methane. These pathways can be distinguished by their isotopic signatures of δ¹³C and δD in the methane [Whiticar and Faber, 1986]. In sulfate-depleted salt water, the dominant pathway is the reduction of CO₂ by molecular hydrogen, H₂. H₂ 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]. In fresh waters, the dominant pathway appears to be by the splitting of acetate into CO₂ + CH₄. Acetate, CH₃COO⁻, can be produced from molecular hydrogen, H₂, and CO₂ [Hoehler et al., 1999]. The H₂ is produced by fermentation of organic matter [Hoehler et al., 1998].

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, by the reaction



[Martens et al., 1998]. A higher carbon conversion efficiency could result from the input of reducing power as hydrogen.

In sediments, biogenic methane production at the Blake Ridge is inferred to take place hundreds of meters below the depth where SO₄²⁻ is depleted, as indicated by linear gradients in SO₄²⁻ and CH₄ as they march toward their mutual annihilation [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., 2004; D'Hondt et al., 2002]. Biological activity has been inferred to take place as deep as 800 meters below the sea floor [D'Hondt et al., 2004; D'Hondt et al., 2002; Wellsbury et al., 2002].

Thermogenic Methane

As temperatures increase to about 110° C degrees [Milkov, 2005], methane is produced from photosynthetically-produced organic matter abiologically. This thermogenic methane is distinguished by carbon isotopic values of about -30‰ [Whiticar and Faber, 1986], in contrast with the much lighter values, -60 to -110‰ of biogenic methane. Thermogenic methane is often associated with petroleum deposits. 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 on Earth derive from biogenic methane, but the Gulf of Mexico is an example of a clathrate system dominated by thermogenic methane [Milkov, 2005].

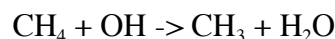
Thermogenic methane is also accompanied by other small organic compounds such as ethane [Milkov, 2005]. In addition to serving as a tracer for the origin of the methane, these compounds affect the thermodynamics of clathrate formation. Pure methane forms Type I structural hydrates, while the inclusion of a few percent of ethane or H₂S favors Type II structure. Type II hydrates are stable to 5-10° C warmer, or perhaps 100 meters deeper in the geothermal gradient in warmer temperatures [Sloan, 1998].

Radiative Impacts of Methane Release

Atmospheric Release

CO₂ is the dominant anthropogenic greenhouse gas in the atmosphere, because the anthropogenic perturbation to the CO₂ concentration is much larger than the anthropogenic change in CH₄. However, the higher concentration of CO₂ means that on a per-molecule basis, CO₂ is a less potent greenhouse gas than CH₄ by about a factor of 24 [Wuebbles and Hayhoe, 2002]. **Figure 1** shows the radiative impact of changes in CO₂ and CH₄ concentrations. The most significant practical distinction between the gases is that CO₂ is more concentrated in the atmosphere than is methane. For this reason, the strongest absorption bands of CO₂ already absorb most of the outgoing longwave light from the ground. An increase in CO₂ concentration tends to make the absorption bands a bit wider, but they cannot get any more intense. Methane is less concentrated than CO₂, 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 CO₂, by about a factor of 24 [Wuebbles and Hayhoe, 2002]. The radiative impact of CH₄ follows the concentration to roughly the 1/3 power, while the CO₂ 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 CO₂ from present-day, and 10 times present methane would be equivalent to about a doubling of CO₂.

Once methane is released to the oxic, sunlit atmosphere, it oxidizes to CO₂ on a time scale of about 8 years. Ultimately, the oxidizing power comes from O₂, but the reactive compound OH is a necessary intermediate, following the reaction



where CH_3 produced is a reactive radical compound, quickly reacting with water vapor and other gases to form ultimately CO_2 . OH is produced by photolysis, the absorption of light energy by the severing of a chemical bond. Ozone photolyzes in the troposphere to yield OH, as does H_2O_2 and NO_2 . In the absence of sunlight, such as in ice cores, no OH is produced, and CH_4 and O_2 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 calculated as

$$\text{Inventory [mol]} = \text{Emission flux [mol/year]} / \text{Atmospheric lifetime [years]}$$

One unknown in this equation is how strongly the methane lifetime may depend on the methane source flux. If the methane oxidation rate were strictly limited by the supply rate of OH, then the lifetime should increase linearly as methane increased, and the steady-state concentration would increase as the emission flux squared. The concentration of OH, and hence the lifetime of methane, could also be affected by anthropogenic emissions of combustion products such as the nitrogen oxides NO_x , hydrocarbons, and carbon monoxide. The large anthropogenic changes in the concentrations of these compounds in the atmosphere appear to have cancelled each other out, however, so that the OH concentration, and the methane lifetime, seem to largely unaffected [Wang and Jacob, 1998].

The other aspect of methane concentration behavior in the atmosphere is the response to a spike of methane emission. If the methane is released on a time scale that is short compared to the atmospheric lifetime, the resulting methane concentration in the atmosphere follows a time-trajectory, and can reach much higher values than typical steady-state values. We will refer to this as a “catastrophic” methane release, as opposed to a “chronic” release. In the case of an instantaneous release, the concentration of methane increases instantaneously, and decays back to a long-term mean concentration on an e-folding time scale of the atmospheric lifetime, currently 8 years. The record of methane recorded in an ice core represents a time-average of longer duration than the atmospheric lifetime, so that the maximum concentration reached just after an emission event would be smoothed out. The current inventory of methane in the atmosphere is about 3 Gton C. Therefore, the release of 1 Gton of methane catastrophically to the atmosphere would raise the methane concentration by 33%. 10 Gton C would triple atmospheric methane.

Radiative Impact of Methane Oxidized in the Ocean

Once the methane is oxidized to CO_2 , it still acts as a greenhouse gas, albeit with less intensity. CO_2 equilibrates between the atmosphere and the ocean on a time scale of hundreds of years [Archer, 2005]. Depending on the magnitude of the CO_2 release, i.e. the pH perturbation of the ocean, the equilibrium between the atmosphere and the ocean finds 15-30% of the CO_2 release remains 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 CO₂ in the atmosphere than at equilibrium, and the excess CO₂ will invade the ocean. Methane oxidized in the ocean will increase the inventory of CO₂ in the ocean, leading to gradual degassing of 15-30% over the coming centuries. The final distribution of the CO₂ between the atmosphere and ocean will be the same regardless of whether the source of the CO₂ is in the atmosphere or the ocean.

Excess CO₂ 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, CO₂ accumulates. For this reason, the impact of a slow, ongoing methane release might be to have greater radiative forcing from the accumulated CO₂ than from the increased methane concentration, even while the methane release is ongoing (Figure 2 from [Archer and Buffett, 2005], see also [Harvey and Huang, 1995]).

There exists an alternate pathway for methane oxidation which does not produce CO₂, but rather bicarbonate ion HCO₃⁻. This is anaerobic oxidation of methane, referred to as AOM [Boetius *et al.*, 2000],



The fate of the released alkalinity is often to precipitate as CaCO₃. Authigenic CaCO₃ has been used as a tracer for the locations of CH₄ emissions at Hydrate Ridge [Teichert *et al.*, 2003; Teichert *et al.*, 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 CaCO₃ slabs, which tend to seal off the methane emission [Sager *et al.*, 1999].

The Geology of Methane Clathrate

Methane Production

The majority of the clathrate deposits on Earth are composed of biogenic methane, as indicated by its isotopic composition and the lack of other short hydrocarbons such as ethane. Most of the organic matter raining to the sea floor decomposes in the 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, in a bacterially mediated reaction called anaerobic oxidation of methane or AOM [Boetius *et al.*, 2000; Nauhaus *et al.*, 2002; Nauhaus *et al.*, 2005]. The stoichiometry of this reaction is



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; Borowski *et al.*, 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 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].

Methane Transport

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

$$T [s] = \Delta x^2 [m^2] / D [m^2 / s]$$

where D is a diffusion coefficient, of order 10^{-9} , 10^{-6} , and 10^{-4} m²/s for a solute, for heat, and for pressure, respectively. A thermal signal can propagate approximately 100 m in about 300 years (Figure 3). Solutes such as dissolved methane diffuse more slowly, while a pressure perturbation, such as would result from melting of hydrate to methane bubbles, diffuses away more quickly.

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 in active margins expel water more quickly than 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 [Aoki *et al.*, 2000; Flemings *et al.*, ; Hovland *et al.*, 1997]. Lateral flow steered by sediment permeability predicts expulsion of fluid near the base of the continental slope off of 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 fluid effluent from the sediment into the ocean generates a structure known as a mud volcano [Dimitrov, 2002]. There are approximately 1800 mud volcanos around the world, above and below sea level, mostly centered in a belt called the mud volcano belt beginning in the Mediterranean Sea and winding across Asia to Indonesia. Submarine mud volcanoes are often associated with methane clathrates (see below).

Gas Migration

In addition to pore water flow, methane is able to move as a gas under at least some conditions. 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 column, 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 in stratigraphic deposits (they refer to them as “basin”) 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 and Spiess, 2004; Zuhlsdorff *et al.*, 2000]. Seismic studies often show “wipeout zones” where the BSR is missing, and all of the layered structure of the sediment column above the missing BSR is smoothed out. These are interpreted to be areas where gas has broken through the structure of the sediment to escape to the ocean [Hill *et al.*, 2004; Riedel *et al.*, 2002; Wood *et al.*, 2002]. Bubbles associated with

seismic wipeout zones are observed within the depth range which should be within the hydrate stability zone, assuming that the temperature of the sediment column is the steady-state expression of the local average geothermal gradient [Gorman *et al.*, 2002]. This observation has been explained by assuming that upward migration of the fluid carries with it heat, maintaining a warm channel where gas can be transported through what would otherwise be thermodynamically hostile territory [Taylor *et al.*, 2000; Wood *et al.*, 2002].

Physical Chemistry of Methane Hydrate

Thermodynamics

If the methane dissolved 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 **Figure 4**. At atmospheric pressure, hydrate is never stable at earth surface temperatures. At water depths of 100 m, hydrate would form at about -20°C , while at 500 meters depth, the melting temperature approaches in situ temperatures. This minimum stability depth is somewhat shallower in the high-latitude oceans, about 200 meters in the Arctic Ocean, because the upper water column is colder (**Figure 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 meters [Buffett, 2000], but hydrate has been inferred to exist shallower than that, sealed into “ice-bonded” permafrost [Dallimore and Collett, 1995].

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 [Circone *et al.*, 2000]. The dissolution of hydrates appears to be diffusion controlled [Rehder *et al.*, 2004].

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.*, 2000; Clennell *et al.*, 1999; 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].

Mechanisms of Methane Release

Deep Ocean Temperature change

The time-dependence of changes in the inventory of methane in the clathrate 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.*, in press] and from modeling [Archer *et al.*, 2004] that the temperature of the deep sea is sensitive to the climate of the earth's surface. In general, the time scale for changing the temperature of the ocean increases with depth. 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 Arctic ice cap. Temperatures in the North Atlantic appear to be sensitive to changes in ocean circulation such as Dansgaard Oeschger events [Dansgaard *et al.*, 1989].

As described above, the top of the hydrate stability zone is at 200-600 meters 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 1,000 years the temperature signal should have propagated about 180 meters in the sediment (Figure 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 Gas Migration section), a landslide or a pockmark-type explosion, 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.

Pockmarks

The sediment surface of the world's ocean has holes in it called pockmarks [Hill *et al.*, 2004], interpreted to be the result of catastrophic escape of gas to the ocean. Pockmarks off of Norway are accompanied by authigenic carbonate 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 km² example on the Blake Ridge [Kvenvolden, 1999]. Even though the methane from an individual pockmark is released in one catastrophic event, the amount of methane released by each explosion is probably small relative to the amount of methane in the atmosphere, so pockmark methane emission is most significant as an ongoing "chronic" source rather than single "catastrophic" releases. The Blake Ridge explosion probably released less than 1 Gton C in methane (assuming a 500 meter thick layer of 4% methane yields 1 Gton).

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]. Submarine landslides are especially prevalent in river deltas, because of the high rate of sediment delivery, and submarine canyons. The tendency for slope failure can be amplified if the sediment accumulates more quickly than the excess porosity can be squeezed out. This can lead to instability of the sediment column, causing periodic Storegga landslides off the coast of Norway (see below), in the Mediterranean Sea [Rothwell *et al.*, 2000] or potentially off the East coast of the United States [Dugan and Flemings, 2000].

Warming temperatures or sea level changes may trigger the melting of clathrate deposits, provoking landslides [Driscoll *et al.*, 2000; Vogt and Jung, 2002] [Kvenvolden]. [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/m². The origin of these estimates is discussed in the section on the Storegga Slide, below.

Fate of Methane Released as Bubbles

Methane released from sediments in the ocean may reach the atmosphere directly, or it may dissolve in the ocean. Bubbles are not generally a very efficient means of transporting methane through the ocean to the atmosphere. [Rehder *et al.*, 2002] compared the dissolution kinetics of methane and argon, and found enhanced lifetime of methane bubbles below the saturation depth in the ocean, about 500 meters, 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 magnitude of the surface dissolution inhibition seems small; in the [Rehder *et al.*, 2002] study a 2 cm bubble dissolves in 30 meters above the stability zone, and only 110 meters below the stability zone. Acoustic imaging

of the bubble plume from Hydrate Ridge showed bubbles surviving from 600-700 meters 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 in Siberia [Shakhova *et al.*, 2005; Washburn *et al.*, 2005; Xu *et al.*, 2001] or during time periods of lower sea level [Luyendyk *et al.*, 2005]. If the rate of methane release is large enough, the rising column of seawater in contact with the bubbles may saturate with methane, or the bubbles can be larger, potentially increasing the escape efficiency to the atmosphere.

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 ballasting itself with 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 [Boudreau *et al.*, 2005; Gardiner *et al.*, 2003] 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 ROV, 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.

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 time scales for gas evasion from the surface ocean would be about 3-5 meters per day. A surface mixed layer 100 m deep would approach equilibrium (degas) in about a month. Even a 1000-meter 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.

Stratigraphic-type Sedimentary Hydrate Deposits

The most common clathrate 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. 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. Following the terminology of Milkov [2002], we will refer to these as stratigraphic-type hydrate deposits.

Most of the clathrate deposits on earth correspond to the stratigraphic type, and hence the estimates of the global inventory of clathrates are based on the physics or on the observed distribution of these types of deposits. The estimates can be compared according to two metrics. One is the area of the sea floor where clathrates 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.

One aspect is the area of the sea floor, between 500 and 3000 meters depth, that has clathrate deposits. MacDonald [1990] for example assumed a high-clathrate 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 meters of the sea floor. Milkov [2004], in addition to pointing out the Borowski 30% estimate, also cites that only 3.5% of ODP cores actually contained hydrate historically. He points out that this proportion is clearly biased low by the avoidance of drilling through clathrate zones for much of the history of ODP. Milkov views Borowski's 30% as an upper limit, and takes 10% as his best estimate of the high-clathrate slope area fraction.

The Buffett and Archer [2004] model predicts nonzero column inventories of methane hydrate or bubbles in 55% of the area between 500-3000 meters, but in much of that area the abundance of methane is unmeasurably small. (Its presence is of interest thermodynamically, however.) If we take $>0.25\%$ as a detectability cutoff, we would say that that 30% of the sea floor contains methane. If we use if $>0.5\%$ clathrate as the cutoff, then 15% of the area contains methane in hydrate or bubbles.

Many studies estimate the area containing clathrates is to use 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 meters (from the sediment diagenesis model [Archer *et al.*, 2002] used in Buffett and Archer [2004], and from Gornitz and Fung [1994]). Gornitz and Fung [1994] used

high chlorophyll concentrations from CZCS 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 like sedimentary organic carbon maps. The areas of the sea floor represented by the CZCS cutoffs was 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 clathrates 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. 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]. 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 clathrate formation.

The other part of a global methane inventory estimate, on which different studies disagree, is the volume fraction of methane hydrate within the porewater, averaged over the depth range of the hydrate stability zone. *Kvenvolden* [1988] assumed 10%. The modeling studies of *Buffett and Archer* [2004] and *Klauda and Sandler* [2005] essentially tuned their model so that the boundary conditions for Blake Ridge reproduce a variety of estimates that point to values of 2-4% [*Borowski*, 2004; *Paull et al.*, 2000]. Values from Hydrate Ridge are lower, closer to 1%. Our model also predicts low hydrate volume here because the water depth is so shallow, and the hydrate stability zone thin. *Milkov*, 2004 #2726] argues that a volume fraction of 1.2% is the best estimate for the global average as well. The current data is probably too sparse to distinguish between 1% and say 3% as a global average clathrate porewater volume fraction, but the 10% volume fraction assumed in earlier studies like the influential *Kvenvolden* [1988] now seems to be high.

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]. Disturbingly, 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 3,000 Gton C in hydrate (plus 2,000 Gton C in bubbles).

Klauda and Sandler [2005] report that in their model, sediments with >0.4% organic carbon contained at least 0.5% clathrate. According to my own reckoning, 37% of the sea floor between 500-3000 meters contains >0.4% organic carbon. *Klauda and Sandler* [2005] thus have 37% of the sea floor covered with at least 0.5% hydrate pore fraction. The *Buffett and Archer* [2004] predicts 15% of the sea floor should have this much (0.5%) clathrate. This accounts for a factor of 2 difference between the studies.

Klauda and Sandler [2005] show that the hydrate fraction predicted by their model for the Blake Ridge looks reasonable, averages of 2-4%, similarly to the *Buffett and Archer* [2004] model. There is certainly no factor of ten difference here. The depth of

the hydrate stability zone is well known, and can also not account for this difference. The bottom line is that I am unable to account for the huge inventory predicted by *Klauda and Sandler* [2005] relative to *Buffett and Archer* [2004] and other estimates summarized by *Milkov* [2004].

There are a few other issues between the two papers, one of which is advection of pore water. Advection in *Klauda and Sandler* [2005] is just compaction. In the *Buffett and Archer* [2004] model, compaction-driven flow was augmented by an additional component of vertical fluid flow. We assumed it to be symmetric, flowing upward in half of the area, and at the same rate downward in the other half of the area. The hydrate fractions predicted by the model are average of the two locations although the downwelling vertical flow almost never contained much hydrate. In our model, if the external fluid flow is not used, the global inventory of methane hydrate drops to about 700 Gton C. To compare the *Klauda and Sandler* [2005] and *Buffett and Archer* [2004] models properly, this 700 Gton C is the estimate most comparable to the model used by *Klauda and Sandler* [2005]. Now the studies differ by a factor of 100.

Another issue is the efficiency of carbon conversion to methane. We assumed 25%, which is higher than the geologically-based estimate of 8% [*Raiswell and Berner*, 1987]. By conservation of oxidation state, 50% would be a maximum upper limit unless methanogenesis is fueled at least in part by hydrogen input. *Klauda and Sandler* [2005] do not mention this parameter, and it appears that they assume 100% conversion. This would have the effect of increasing the area of high-clathrate sediments, and the average concentration of hydrates in these areas. Both models compare well with concentrations from Blake Ridge, however, so differences in concentration cannot account for the difference. Perhaps lower fluid velocities and higher methane flux compensate for each other to some extent. The area of clathrate sediments predicted by *Klauda and Sandler* [2005] area is larger than *Buffett and Archer* [2004], but only by a factor of two. The large difference between *Klauda and Sandler* [2005] and *Buffett and Archer* [2004] global estimates remains a mystery.

The uncertainty in the area of high-clathrate sediments can be derived from the uncertainties in the area and concentration estimates. The high-clathrate sediment areas predicted by the studies range from 10% [*MacDonald*, 1990; *Milkov*, 2004], to 15% [*Buffett and Archer*, 2004], to 30% from sulfate profiles [*Borowski et al.*, 1999], up to 37% [*Klauda and Sandler*, 2005]. My guess is that the *Klauda* estimate is high; most sediments with only 0.4% organic carbon do not contain detectable hydrates. Excluding this estimate still leaves perhaps factor of two to three uncertainty in the area of high-clathrate sediment. Estimates of the average clathrate concentrations within the high-clathrate area range from 1% to about 3%, perhaps resulting in another factor of three uncertainty. The *Milkov* [2004] global inventory estimate combines low but not unreasonable possibilities for the high-clathrate sediment area (10%) and the global average hydrate concentration (1% porewater volume). Higher-end but not unreasonable values of these two parameters generate an estimate in accord with [*Buffett and Archer*, 2004]. The data seem strong enough to say that the *Kvenvolden/MacDonald* “consensus” value of 10,000 Gton is probably too high. The very high 78,000 Gton estimate from *Klauda and Sandler* is inexplicable. 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 continuing improvements in techniques for estimating the concentration of methane, both as hydrate and as bubbles, ideally ultimately by seismic methods that can be used regionally, and by continued deep core sampling within hydrate regions, 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 (CO_2 , HCO_3^- , and CO_3^{2-}) is about 38,000 Gton C. This sounds comfortably larger than the hydrate reservoir, but an addition of 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 $2 \cdot 10^{17}$ moles of oxygen, which could be completely depleted by reaction with about 1000 Gton C in methane.

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 clathrate deposits that are abundant at shallow depths in the sediment column, closer to the sea floor. These "structural-type" deposits could be vulnerable to temperature-change driven melting on a faster time scale than the stratigraphic deposits are expected to be.

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

Collett and Kuuskraa [1998] estimate that 500 Gton C might reside as hydrates in the Gulf sediments, but Milkov [2001] estimates only 5 Gton C. In the CCSM model under doubled CO_2 (after 80 years of 1%/year CO_2 increase, from C. Bitz, personal communication), waters at 500 meters depth in the Gulf warm about 0.75°C , and 0.2° at 1000 meters. In situ temperatures at 500 meters are much closer to the melting temperature, so the relative change in the saturation state is much more significant at 500 meters than deeper. The equilibrium temperature change in the deep ocean to a large, 5000 Gton C fossil fuel release could be 3°C [Archer *et al.*, 2004]. Milkov and Sassen [2003] subjected a 2-dimensional model of the hydrate deposits in the Gulf to a 4°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.* [2001b] find no molecular fractionation of gases in near-surface hydrate

deposits that would be indicative of partial dissolution, and suggests that the reservoir may in fact be growing.

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

Mud Volcanos

As described above, mud volcanos are produced by focused upward fluid flow into the ocean. Mud volcanos 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 clathrate deposits, with authigenic carbonates, and with pockmarks [Dimitrov and Woodside, 2003] indicative of anoxic methane oxidation. [Milkov, 2000] estimates that mud volcanoes contain at most 0.5 Gton C of methane in hydrate; about 100 times his estimate of the annual supply. Most of the submarine oceanic mud volcanoes are in the Mediterranean Sea [Huguen *et al.*, 2004].

Land Deposits

Permafrost is defined in terms of temperature: a two-year mean temperature of less than 0° 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 [Camill, 2005; Payette *et al.*, 2004]. 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 in a process called thermokarst [Nelson *et al.*, 2002], and buildings fall down [Stockstad, 2004]. This process has had a dizzying impact on the subarctic landscape [Kolbert, 2005; Pearce, 2005; Stockstad, 2004]. Model projects 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].

Peat Decomposition

Permafrost soils contain relict organic matter which survived decomposition because of the freezing temperatures. Fossil mastadons, still edible after all these years, are examples of this phenomenon. 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 CO₂ and CH₄ [Liblik *et al.*, 1997; Rivkina *et al.*, 2004; Rivkina *et al.*, 2000]. Soil that has been frozen for thousands of years still contains viable populations of methanotrophic bacteria [Rivkina *et al.*, 2004]. The flux of methane to the atmosphere also depends on the location of the water table, which controls the thickness of the oxic zone [Bubier *et al.*, 2005; Bubier *et al.*, 1995; 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.

Melting Hydrates

There is also the possibility that ongoing methanogenesis has produced methane which has been trapped in methane clathrate 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 clathrates under any reasonable temperature. However, if the pore space is closed, sealed, by ice most likely, then the lithostatic pressure will come to bear on the pore spaces, and any region of high-purity methane in the gas phase will be stable for clathrates. High-pressure reservoirs such as this are routinely exploited by the gas mining concerns, to eject gas from the subsurface reservoir to the surface. In fact, 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 meters, and inferred invisible pore-water hydrate crystals as shallow as about 120 meters, in solidly ice-bonded sediment which perhaps elevates the local methane pressure? [Dallimore and Collett, 1995]. The stability zone is below ~250 meters here. Total amounts of clathrate 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 [Gavrilov *et al.*, 2003; Hubberten and Romanovskii, 2001; Romankevich, 1984]. The ice complex is a sealed horizon of ice that was formed when sea level was as much as 120 meters lower than today, during the last glacial interval. Liquid ground water flowing through the permafrost froze, creating a sealed layer up to 60-80 meters thick, onshore and offshore under as much as 100 meters 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°C is perhaps 10°C warmer than the surface air temperature the locations were previously exposed to. A geotherm projected down from 0°C intersects the melting temperature at a much shallower depth than would a geotherm from the initial 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 [Gavrilov *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 Figure 6 in [Hubberten and Romanovskii, 2001]). Entire islands have melted within historical times in the past centuries [Romankevich, 1984]. Emission of clathrate-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]. 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).

Hydrates as Fossil Fuel

Hydrates may serve as a significant but not unlimited source of fossil energy. Estimates of the total inventory of methane in clathrate 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. 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] and mud volcanos [Milkov, 2000]. Milkov [Milkov and Sassen] estimates 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 a field called Messoyakha, in which 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_2) 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, in a field called Mallik [Chattopadhyay et al., 2005; Kerr, 2004]. Hydrates here are in a sandstone layer 1000 meters 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 perhaps hydrate methane could supply order 10% of methane extraction rate in order 10 years, by analogy to coal-bed methane 30 years ago [Graul, 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 clathrate reservoir. Most of the hydrates are probably impractical to extract.

Methane hydrates are probably not a renewable resource, but a one-use reservoir. The production rate of methane in stratigraphic deposits such as Blake Ridge is slow enough that the build-up time for methane is millions of years [Davie and Buffett, 2001]. Methane in the permafrost-associated regions such as Mallik and Messoyakha is hundreds of thousands of years old. Some of the hydrates in structural deposits such as the Gulf of Mexico may be replenished more quickly than that by leaking from a subsurface field [Sassen et al., 2001a], but in this case, the subsurface field is itself a non-renewable resource.

The possibility of geological hazard from methane drilling has been discussed in a general way [Chatti et al., 2005; Graul, 2001; Kvenvolden, 1999] but the likelihood of methane extraction causing slope instability still seems rather speculative. Some have considered replacing CH₄ hydrates with CO₂ hydrates, sequestering CO₂ and maintaining the stability of the continental slope in the process [Warzinski and Holder, 1998]. The Storegga slide (next section) was investigated in order to determine the safety of extracting gas from the Ormen Lange gas field within the Storegga slide area.

Observations From the Past

The Storegga Landslide

Observations

The largest exposed submarine landslide in the ocean is the Storegga Slide in the Norwegian continental margin [Bryn et al., 2005; Mienert et al., 2000; Mienert et al., 2005]. The slide excavated on average the top 250 meters of sediment over an 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, 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 clathrate deposits as indicated by a seismic BSR [Bunz and Mienert, 2004; Mienert et al., 2005; Zillmer et al., 2005a; Zillmer et al., 2005b] corresponding to the base of the HSZ at 200-300 meters, and pockmarks [Hovland et al., 2005] indicating gas expulsion from the sediment.

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 clathrate 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 for deeper in the water column [Vogt and Jung, 2002]; the stability zone is shown increasing by about 10 meters for sediments in water depth below about 750 meters. Shallower sediments are more impacted by 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 (Figure 6 from [Mienert *et al.*, 2005]). The slide started at a few hundred meters water depth, just off the continental slope, just where Mienert calculates the maximum change in HSZ. Sultan *et al.* [2004] predict that warming in the near-surface sediment would provoke hydrate to dissolve by increasing the saturation methane concentration. This form of dissolution differs from heat-driven direct melting, however, in that it produces dissolved methane, rather than methane bubbles. Sultan *et al.* assert that melting to dissolved methane increases the volume, but I believe this is not the conventional wisdom. Dissolved methane in porewater meters below the sea floor is unlikely to escape to the atmosphere very efficiently.

The amount of methane released by the slide has not been estimated in the literature that I have found, but we can do a simple calculation. The volume of sediment moved was about 2500 km³ [Haflidason *et al.*, 2004]. Assuming 1% hydrate by pore water volume were released from this volume of slide, 50% porosity, we calculate a methane inventory of about 0.8 Gton of C. Paul [Paul, 1978] predicted 5 Gton C methane released. If 0.8 Gton C CH₄ reached the atmosphere all at once, it would raise the atmospheric concentration by about 0.4 ppm of methane, relative to a present-day concentration of about 1.7 ppm. The radiative impact of this methane depends on the methane concentration at that time, higher if the methane were released into a low-methane atmosphere. Taking the present-day concentration as conceptually mid-way between the lower glacial and the higher future values, we get an increased trapping of heat at a rate of about 0.2 W/m². This radiative forcing would subside over a time scale of a decade or so, as the pulse of released methane was oxidized to CO₂, and the atmospheric methane concentration relaxed toward the long-term steady state value. The radiative impact of the Storegga landslide would be an order of magnitude smaller than the eruption of a large volcano, such as the Mt. Pinatubo eruption (0.2 W/m² rather than 2), but it would last for longer (10 years rather than 2).

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, no δ¹³C anomaly was detected at the 8.2kyr event boundary. The

shutdown of convection in the North Atlantic would have, if anything, cooled the overlying waters. No one has made any connection in the literature between these two apparently coincidental incidents in the climate record, that I am aware.

Implications

Much of our knowledge of the Storegga landslide is due to research sponsored by the Norwegian oil industry, who are interested in tapping the Ormen Lange gas field within the headlands of the Storegga slide, but are concerned about the geophysical hazard of gas extraction [Bryn *et al.*, 2005]. The Norwegian oil industry does not want to trigger another Storegga landslide. The conclusion that rapid glacial sediment loading is a cause of the slides would seem to indicate that drilling should be safe until another ice age were to start depositing new sediment on the sea floor. On the other hand, the modeling results of Mienert *et al.*, [Mienert *et al.*, 2005] in Figure 4 raise a suspicion that warming and melting of hydrates had something to do with the slide. 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 range from 1-5 Gton C, which is significant but not apocalyptic. The increase in tsunami hazard might be equally concerning.

Paleocene Eocene Thermal Maximum

Observations

About 55 million years ago, the $\delta^{13}\text{C}$ in the ocean and on land spiked 2.5-5 ‰ negative on a time scale of less than 10 kyr, then recovered in parallel on a time scale of ~140 kyr [Kennett and Stott, 1991] (Figure 7 from [Zachos *et al.*, 2001]). The $\delta^{18}\text{O}$ of CaCO_3 form at intermediate depths in the ocean spiked negative 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 record the $\delta^{13}\text{C}$ spike a bit before the benthics do, suggesting that the carbon spike invaded the deep ocean from the atmosphere [Thomas *et al.*, 2002]. Similar events, although less well documented, have been described from other times in geologic history [Hesselbo *et al.*, 2000; Jenkyns, 2003].

Inferences

The spike in $\delta^{18}\text{O}$ can only be attributed to temperature change in the water column. Planktonic $\delta^{18}\text{O}$ can also be fractionated by changes in freshwater forcing, but benthics are less susceptible to this sort of local noise. $\delta^{18}\text{O}$ can be affected by fractionated ice sheets, but there were no ice sheets at this time. $\delta^{18}\text{O}$ can also be affected by reactions with rocks, but not on short time scales such as this one. The inferred temperatures at paleo-depth of several kilometers rose from 8° to about 14° C.

The lightening of the carbon isotope is attributed to the release of isotopically light carbon. If we knew the isotopic value of the released carbon, and the size of the carbon reservoir that is diluting it, we could calculate how much carbon was released. One issue

is the magnitude of the carbon isotopic shift. The surface change recorded in CaCO_3 in soils [Koch *et al.*, 1992] and in planktonic foraminifera [Thomas *et al.*, 2002] is consistently twice as big a change as is the value in the deep sea. One possibility is that the land values were impacted by changes in hydrology: water stress leads to transport-limited CO_2 uptake which changes the fractionation factor [Bowen *et al.*, 2004]. This explanation seems to me somewhat speculative, and it doesn't account for the planktonic foraminifera, but it is likely that the land fractionation is probably less reliable a record of the whole-biosphere average than is the deep ocean.

We can estimate the change in the carbon inventory of the ocean by specifying an atmospheric pCO_2 value, a mean ocean temperature, and insisting on equilibrium with CaCO_3 [Zeebe and Westbroek, 2003]. The ocean was warmer, prior to the PETM event, than it is today. Climate modelers assume atmospheric pCO_2 values of about 560 ppm at this time [Huber *et al.*, 2002]. The present-day inventory of CO_2 in the ocean is about 40,000 Gton C. According to my simple thermodynamic calculations, 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 (Figure 8). Candidate sources include methane, which can range in its isotopic composition from -30 to -110 ‰. If a typical value of -60 ‰ is assumed, we calculate that 2,000 Gton C is required to explain the isotopic anomaly. If the methane were thermogenic -30 ‰, then 4,000 Gton would be required.

Buffett and Archer [Buffett and Archer, 2004] find that the steady-state clathrate reservoir size in the ocean is extremely sensitive to the temperature of the deep sea. At the temperature of Paleocene time, they predict less than a thousand Gton C in the ocean. As the ocean temperature decreases, the stability zone gets thinner and covers less area. The concentration of hydrate in the model is extremely sensitive to the thickness of the stability zone, because methane diffusion is faster, so more organic carbon respiration is required, so more carbon concentration is required, so the area decreases. 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 (supported by the presence of North Slope fossil fuels). 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 water column, it would be found in planktonic tropical forams before benthic, as observed in the ocean cores (which come from places outside the Arctic). Bubbles release from the sea floor mostly dissolve before reaching the atmosphere (see section), and half the methane reservoir is bubbles [Buffett and Archer, 2004], so it is more difficult 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. The area of the volcanic complex appears to be about 50,000 km² and the depth range in the sediment about 2 km. If this volume contains 1% organic carbon, it would contain 1250 Gton C. CaCO₃ could also release CO₂, of a heavier isotopic composition. It seems like a stretch, but it is possible that the volcanic intrusion could have released enough carbon to account for the isotopic data.

Comets are not well constrained in their isotopic compositions, but cometary dust tends to be about -45 ‰ [Kent *et al.*, 2003]. Kent calculates 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 sounds like it would be a stretch to ask for thousands of Gton C from a comet. 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 this 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 slow.

Acidification of the ocean by invasion of CO₂ caused an extinction of calcifying organisms in the ocean [Kennett and Stott, 1991] and a whole-ocean shoaling of the depth of CaCO₃ preservation [Zachos *et al.*, 2005]. The magnitude of the CCD shift is 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 CH₄ and CO₂. Schmidt and Shindell [2003] calculated that the steady-state atmospheric CH₄ 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 go away a few decades after the excess emission ceased. At this point the temperature anomaly would die away, namely, 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 CO₂ is the more likely greenhouse warmer rather than CH₄. (It could be that the time scale for the pCO₂ to reach steady state might be different than the time scale for the isotopes to equilibrate, analogous to the equilibration of the surface ocean by gas exchange: isotopes take longer. However, in the [Kump and Arthur, 1999] model results, pCO₂ seems to

take longer to equilibrate than $\delta^{13}\text{C}$. The first-order result is that the CO_2 and $\delta^{13}\text{C}$ timescales are much more similar than the CH_4 and $\delta^{13}\text{C}$ time scales would be.)

A warming of 5°C would require somewhere between one and two doublings of the atmospheric CO_2 concentration, if the climate sensitivity is in the range of $2.5 - 5^\circ\text{C}$. Beginning from 600 ppm, we would increase the pCO_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 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 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.

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. 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 (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 $2-4^\circ$, based on paleoclimate records and model results [Martin *et al.*, in press]. The warming during the PETM was 5° , and this was from a higher initial CO_2 , so that a further spike of only 2000 Gton (based on methane isotopic composition) would have only a tiny radiative impact, much less than 5° .

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‰ , if the rest were volcanic carbon at -7‰ . The implication would be that the clathrate reservoir at that time did not amplify the initial carbon release (analogous to our fossil fuel CO_2) by more than 10%. However, there are no strong ideas for where that other

9000 Gton C could have come from. Volcanoes are too slow, comets are too small, organics in sediments are too small.

Perhaps the land $\delta^{13}\text{C}$ shift is correct, 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 CO_2 . The *Archer and Buffett* [2005] model predicted a regime in model space where the clathrate 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 you get periodic meltdowns. Tauntingly, there are several tiny “after shocks” of the PETM, all about 2 million years apart, one of which has been called ELMO [Lourens *et al.*, 2005]. The trouble then is that the model, tuned to periodic meltdowns during the PETM, predicts that the clathrate reservoir today, larger because the ocean is colder, should periodically melt down even more severely today.

Perhaps some external agent of warming, not CO_2 , drove temperatures up, releasing clathrate carbon, some instability in the sun perhaps, something unexpected. 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 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 CO_2 to the atmosphere [Archer, 2005]. However, in my opinion, 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 clathrate reservoir in the immediate future.

Santa Barbara Basin and the Clathrate Gun Hypothesis

Kennett et al. [2003] and *Nisbet* [2002] think that methane from hydrates is responsible for the initial deglacial rise in the Greenland methane record. [Kennett *et al.*, 2000] found episodic negative $\delta^{13}\text{C}$ excursions in benthic foraminifera in the Santa Barbara Basin which they interpreted 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] argued that these results could have arisen from contamination or subsequent diagenetic overprints. The interhemispheric gradient of methane says that the deglacial increase in atmospheric methane arose from high Northern latitudes [Dallenbach *et al.*, 2000]. This could be due to high-latitude hydrate deposits or methanogenesis from thawing organic matter decomposition or from wetlands. 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. Hydrate methane release might account for some of the deglacial methane rise, they conclude. 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.

Risks for the Future

We have defined a catastrophic methane release as one which occurs on a time scale that is short relative to the atmospheric lifetime of methane, about a decade, generating a spike in atmospheric methane concentration that lasts about a decade. Methane has a stronger impact on the radiative balance of the earth, per molecule, than CO₂, because of its lower concentration.

The nightmare scenario would be the catastrophic release of a large fraction of the thousands of Gton C in the ocean hydrate reservoir. No one has proposed a mechanism by which such a nightmare catastrophe could take place. The largest landslide in the sea floor record appears to be the Storegga slide deposits off the coast of Norway. This slide could have released about 1 Gton C of methane. Perhaps half of the methane in sediments exists as bubbles, the other half as hydrate [Davie and Buffett, 2001]. Bubbles have a small chance of escaping to the atmosphere, unless they are released in shallow water, as for example in the Siberian margin [Shakhova et al., 2005]. Even if 1 Gton C of methane reached the atmosphere catastrophically, the climate impact of this would be relatively small.

The other issue is the climate impact of ongoing, chronic methane release resulting from anthropogenic warming. 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.

On geologic time scales, the strongest climate impact appears to be from the CO₂ that released methane oxidizes to. Methane is transient while CO₂ accumulates, and persists to affect climate for hundreds of thousands of years. Methane oxidized within the ocean will equilibrate with the atmosphere within a few hundred years. Even during a time period when the ongoing methane emission is accelerated, the largest climate impact may come from the accumulating CO₂ concentration. Ultimately, after thousands of years, the methane hydrate reservoir may release as much carbon as fossil fuel emissions.

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Table

Chronic releases	Inventory	Vulnerable Inventory	Fate of the Methane
Peat Decomposition	350-450	20% over 100 years	0.7 Gton / yr to atmosphere, triples pCH ₄
Gulf of Mexico	5-500	2 Gton over centuries	Released to water column, small potential impact on atmospheric CH ₄
Stratigraphic-type Deposits	1000-6000	Any release would take millennia	Effects would be most pronounced on geological timescales. Radiative effect of accumulating CO ₂ > effect of transient methane.
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

Figure Captions

Figure 1. Radiative impacts of atmospheric methane and CO₂ concentrations: the outgoing longwave radiation flux over midlatitude winter conditions, from the Modtran model, with a web interface at <http://geosci.uchicago.edu/~archer/cgimodels/radiation.html>. The sensitivities to methane and CO₂ 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 CO₂. The leveling off of this curve is due to saturation of absorption bands.

Figure 2. Model projection of the radiative impact of a fossil fuel CO₂ release over the coming 100 kyr, from *Archer and Buffett* [2005]. (a) The warming from the CO₂ (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 CO₂ and methane releases. The methane direct effect is smaller than the original CO₂ radiative forcing, and it is also smaller and much shorter-lived than the radiative effect of the oxidized methane as CO₂, gauged the difference between the anthropogenic CO₂ 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, CO₂.

Figure 3. Diffusive time scale as a function of distance, for heat, pressure, and solutes.

Figure 4. The methane stability zone in surface sediments. Hydrate solubility temperature is given by the long-dashed line. Offshore water column temperatures are from *Levitus* [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.

Figure 5. 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.

Figure 6. Modeling results from [*Mienert et al.*, 2005] of hydrate stability in the vicinity of the Storegga slide off the coast of Norway. The landslide occurred several thousand years after clathrate destabilization by warming of the water column.

Figure 7. Carbon and oxygen isotopic excursion known as the Paleocene Eocene Thermal Maximum, from [*Zachos et al.*, 2001].

Figure 8. Size of the implied PETM carbon release as a function of its carbon isotopic composition.

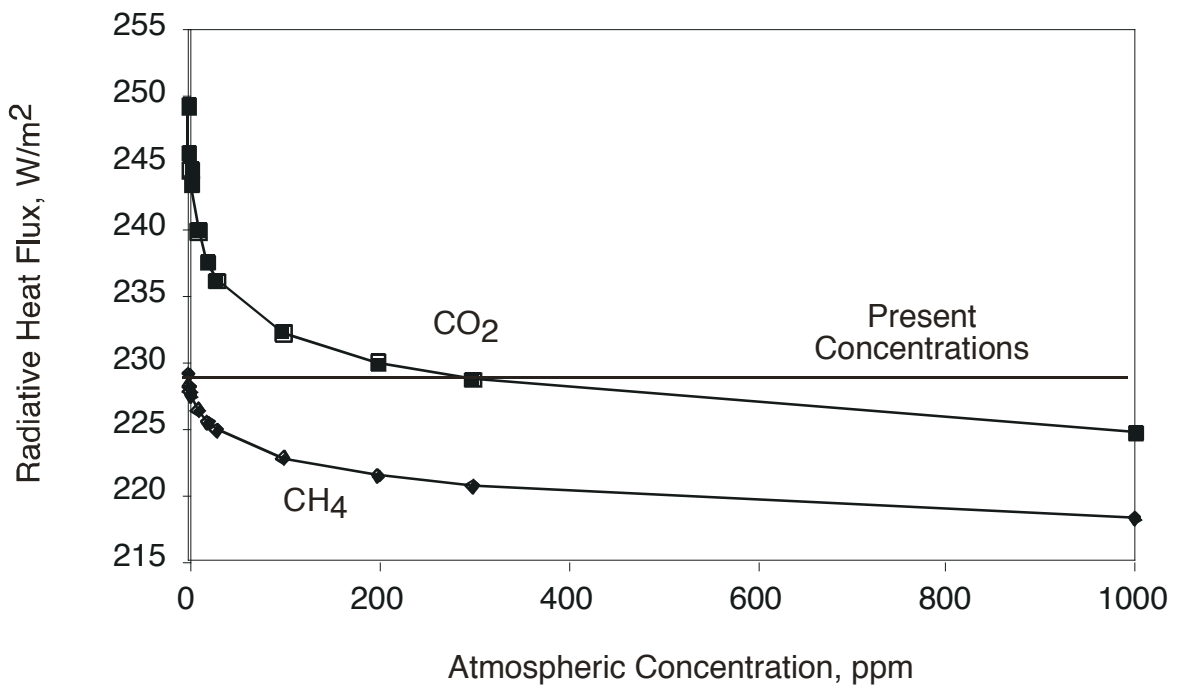


Figure 1

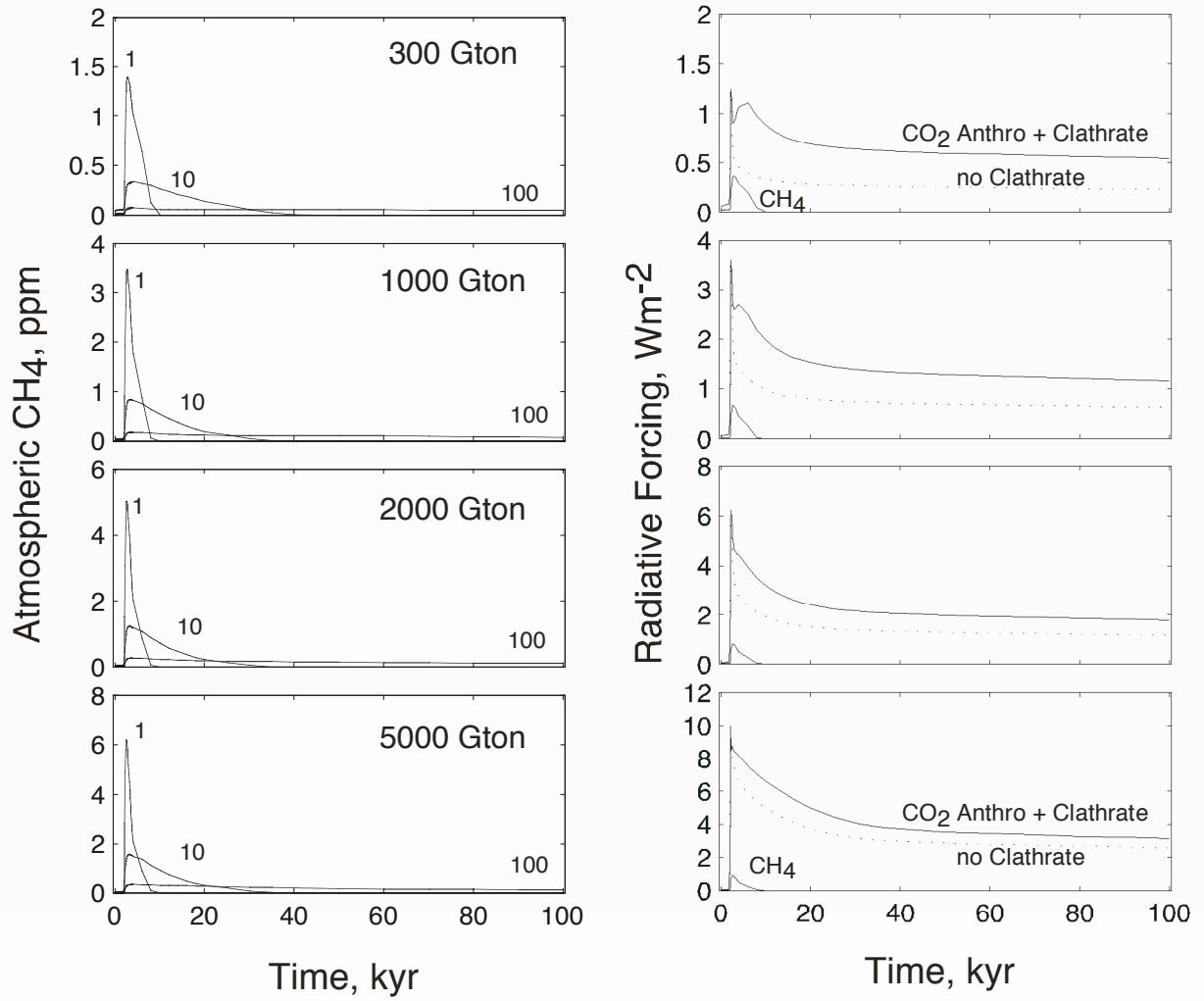


Figure 2

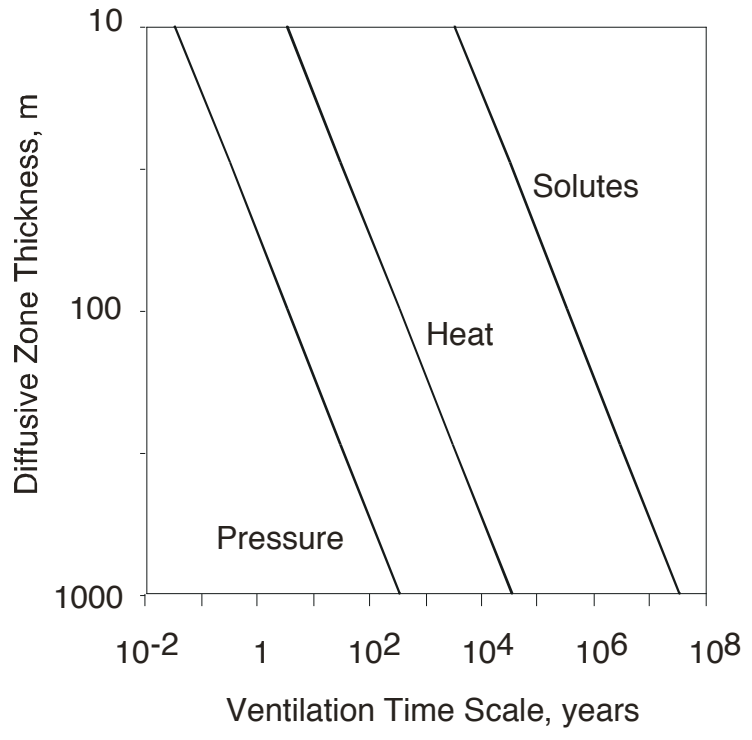


Figure 3

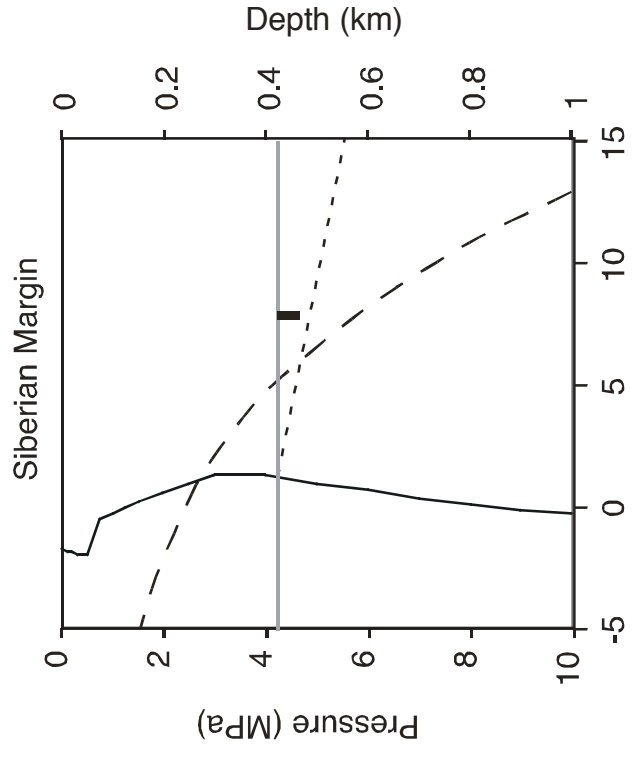
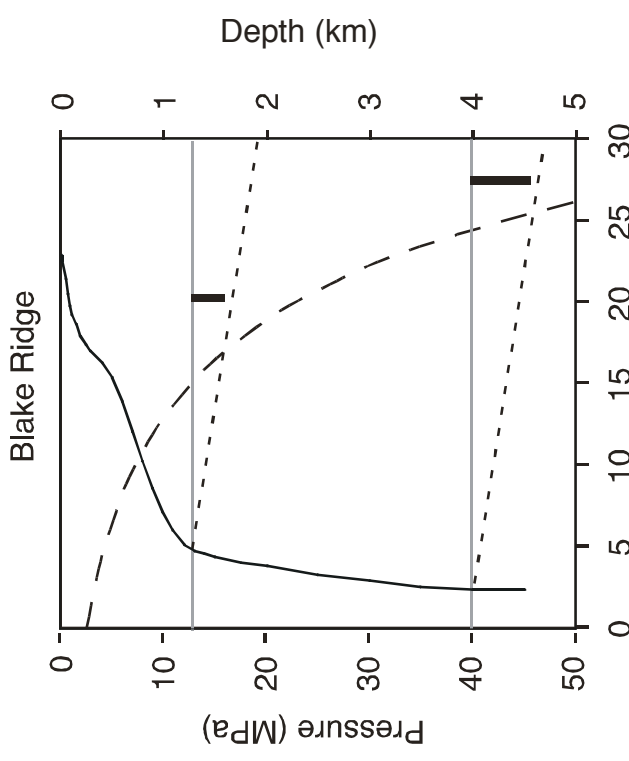
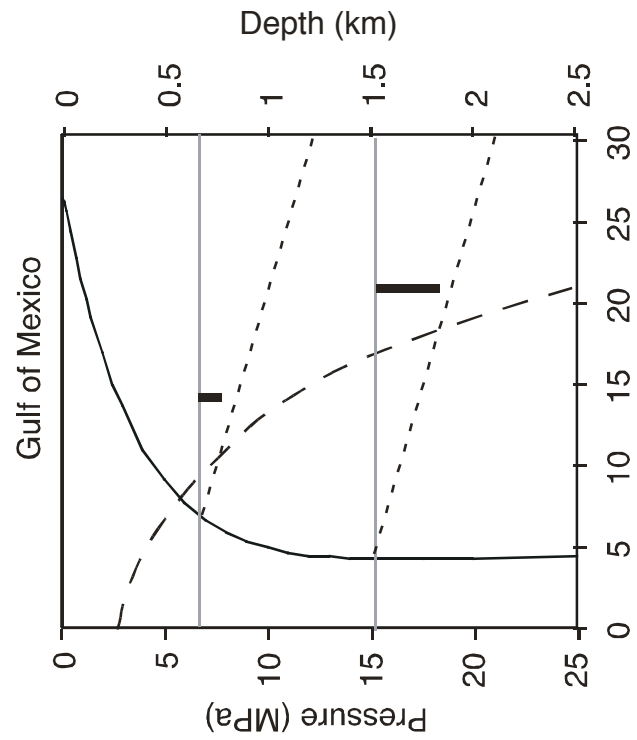
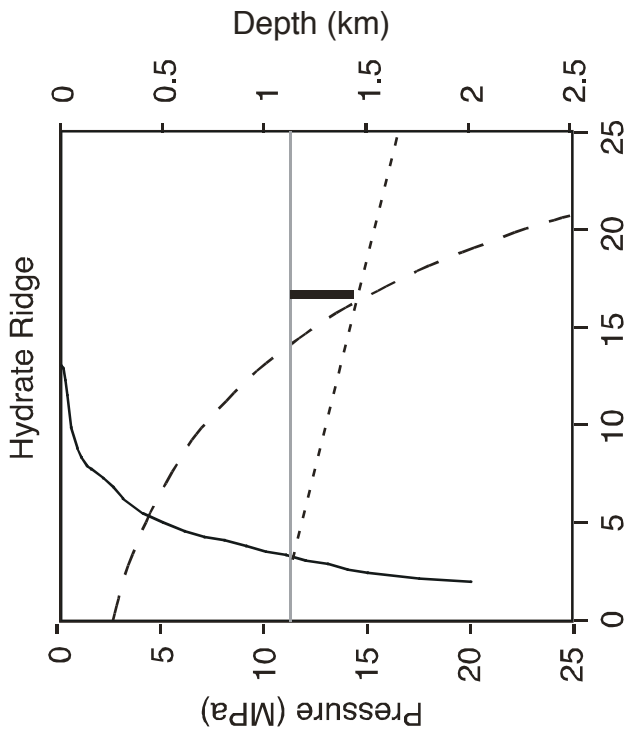


Figure 4

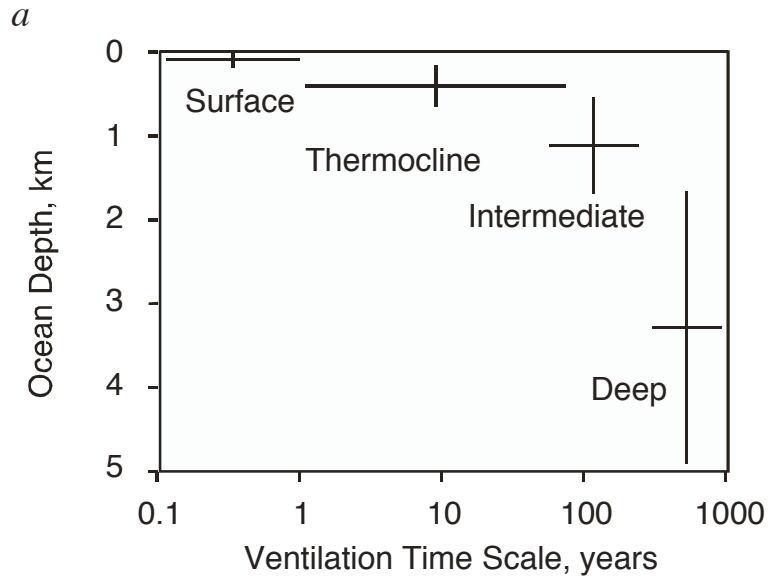


Figure 5

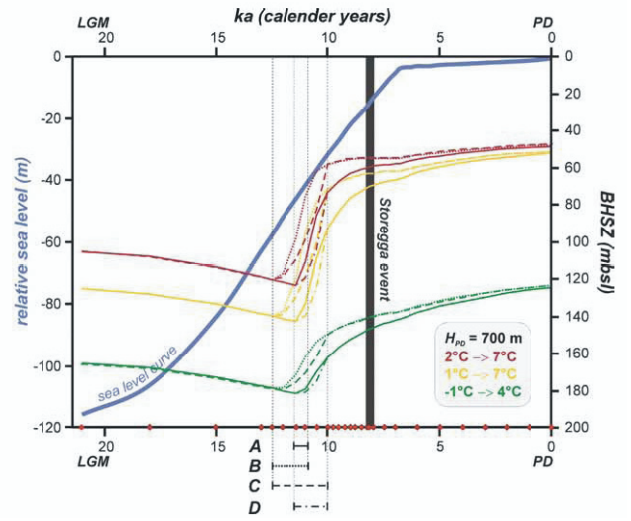
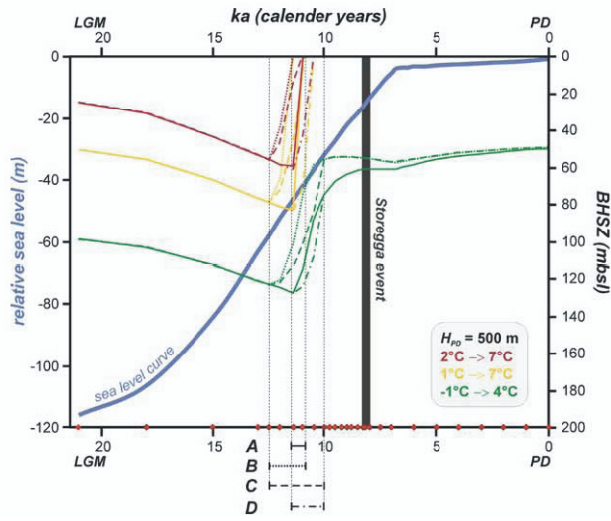


Figure 6

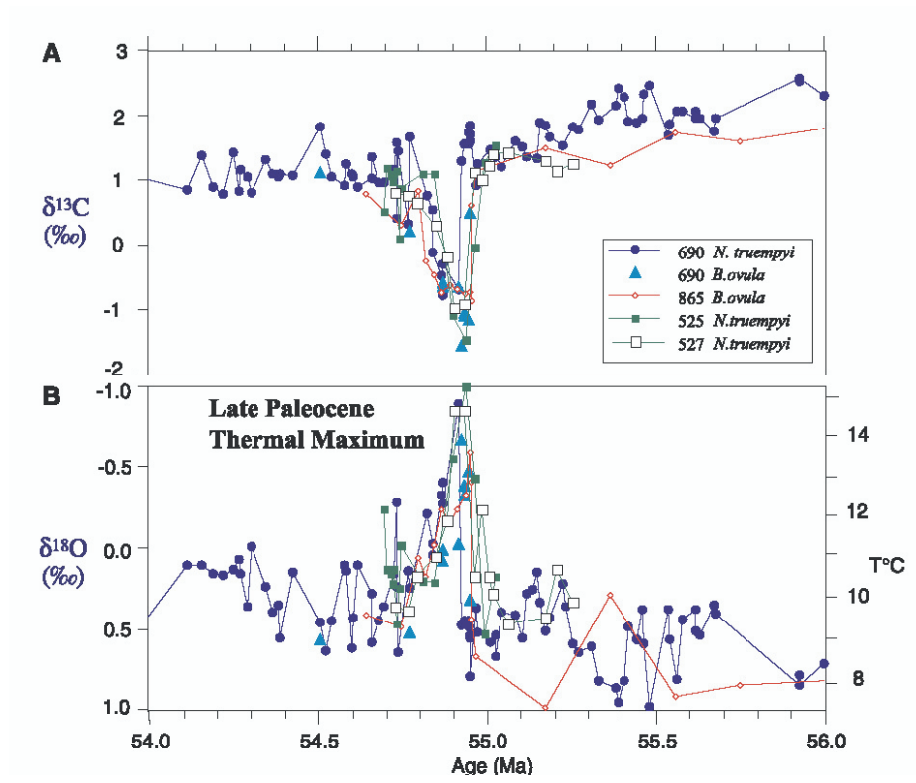


Figure 7

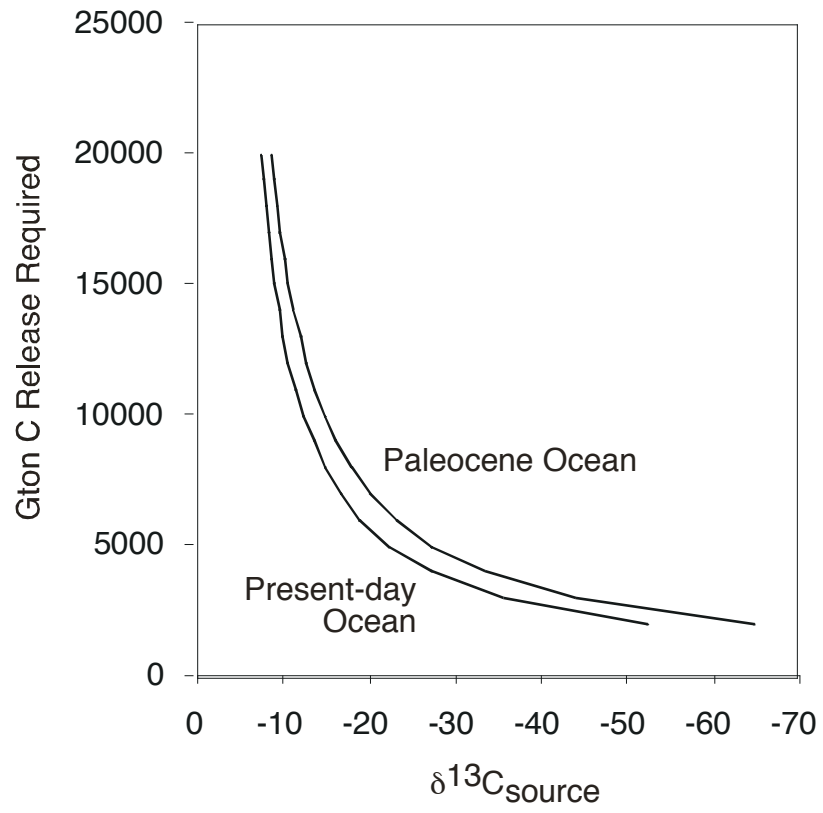


Figure 8