REVIEW

Gas hydrates: past and future geohazard?

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Gas hydrates are ice-like deposits containing a mixture of water and gas; the most common gas is methane. Gas hydrates are stable under high pressures and relatively low temperatures and are found underneath the oceans and in permafrost regions. Estimates range from 500 to 10 000 giga tonnes of carbon (best current estimate 1600–2000 GtC) stored in ocean sediments and 400 GtC in Arctic permafrost. Gas hydrates may pose a serious geohazard in the near future owing to the adverse effects of global warming on the stability of gas hydrate deposits both in ocean sediments and in permafrost. It is still unknown whether future ocean warming could lead to significant methane release, as thermal penetration of marine sediments to the clathrate–gas interface could be slow enough to allow a new equilibrium to occur without any gas escaping. Even if methane gas does escape, it is still unclear how much of this could be oxidized in the overlying ocean. Models of the global inventory of hydrates and trapped methane bubbles suggest that a global 3°C warming could release between 35 and 940 GtC, which could add up to an additional 0.5°C to global warming. The destabilization of gas hydrate reserves in permafrost areas is more certain as climate models predict that high-latitude regions will be disproportionately affected by global warming with temperature increases of over 12°C predicted for much of North America and Northern Asia. Our current estimates of gas hydrate storage in the Arctic region are, however, extremely poor and non-existent for Antarctica. The shrinking of both the Greenland and Antarctic ice sheets in response to regional warming may also lead to destabilization of gas hydrates. As ice sheets shrink, the weight removed allows the coastal region and adjacent continental slope to rise through isostacy. This removal of hydrostatic pressure could destabilize gas hydrates, leading to massive slope failure, and may increase the risk of tsunamis.

Keywords: gas hydrates; geohazards; climate change; ocean; permafrost

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1. Introduction

The importance of gas (methane) hydrates in the global climate systems has only been realized in the last two decades. Gas hydrates form when there is an adequate supply of water and methane at relatively low temperatures and high pressures. They are affected by the sediment type and textures as well as seawater salinity. Increasing temperatures and/or lowering pressures can cause gas hydrates to break down, releasing the trapped methane. Gas hydrates were first recognized nearly 200 years ago, by the British scientist Sir Humphrey Davy, who discovered that, if a mixture of gas and water is exposed to high pressure and low temperature, it turns into a solid compound called gas hydrate or clathrate (Henriet & Mienert 1998). He found this by producing in 1810 an ice-like substance (chlorine hydrate) by effervescing chlorine gas through water under elevated pressure. However, during the following century, gas hydrate was perceived as nothing more than a chemical oddity, and as such it did not receive much attention. In the 1930s, however, the oil and gas industry found that the formation of gas hydrate, or as they called it dirty ice, clogged natural gas pipelines during cold weather. In the 1950s, the first two structures of gas hydrates were described. But it was not until the 1970s that Russian scientists, based upon theoretical models, postulated that there must be vast quantities of natural gas hydrate deposits on our planet (e.g. Vasil'ev *et al.* 1970; Trofimuk *et al.* 1973, 1975, 1979; Tucholke *et al.* 1977). This theory was confirmed when seafloor samples were recovered in the Black Sea by Russian vessels (Yefremova & Zhizhchenko 1974), Blake Ridge (Harrison & Curiale 1982; Shipley & Didyk 1982) and off Central America by the Deep Sea Drilling Project (Stoll *et al.* 1971). It was also observed that methane was the predominant gas trapped in naturally occurring gas hydrates (figures 1 and 2). Since then, many countries have set up national research programmes for the investigation of gas hydrate, owing to their geohazard and economic implications. The most important are run by Japan, Canada, the USA, Germany and India (Henriet & Mienert 1998; Milkov & Sassen 2002).

2. Gas hydrate structure

Gas hydrates are non-stoichiometric compounds, which means water molecules (the so-called structural molecules) form cage-like structures in which gas molecules are enclosed as guest molecules (figure 1). For this reason, they are also called cage compounds or clathrates (Lat. 'clatratus' for cage). Generally speaking, a gas hydrate can contain different types of gas molecules in separate cages, depending on the mixture of gas molecules in the direct environment. In addition to CH_4 in naturally occurring gas hydrates, these gases will mostly be H_2S, CO_2 and, less frequently, other hydrocarbons.

Hydrates normally form in one of three different repeating crystal structures (figure 2). Both structures I and II crystallize to a cubic (isometric) system, whereas the third structure (also denominated H) crystallizes to a hexagonal system, like ice (von Stackelberg & Müller 1954; Sloan 1998). The structure of gas hydrate can be seen as a packing of polyhedral cages. All three structures occur naturally. Structure I is most frequent. Its unit cell consists of eight cages
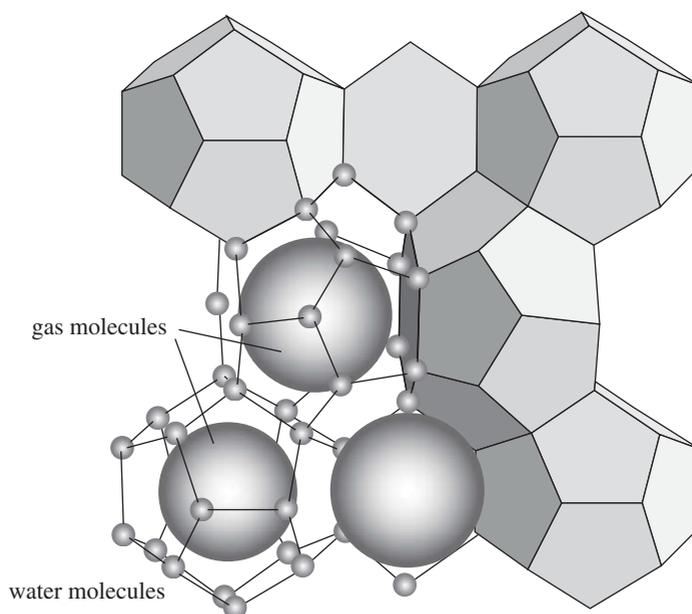
Figure 1. Typical structure of gas hydrate with water molecules linked together to form a cage trapping a gas molecule such as methane within.

of two different types. Structure I cages can enclose gas molecules that are smaller in diameter than propane molecules, such as CH_4, CO_2 or H_2S. Therefore, the natural occurrence of this crystal structure mainly depends on the presence of biogenic gas, as commonly found in sediments of the ocean floor. A unit cell of structure II consists of 24 cages, i.e. 16 small cages and eight large ones. The latter are larger than those of structure I. Hence, structure II contains natural mixtures of gases with molecules larger than ethane and smaller than pentane. It is usually confined to areas where a thermogenic formation of gas takes place in the sediment. H is a more complicated structure (Sloan 1998). Apart from smaller cages, it contains a cage type, which requires very large gas molecules such as methyl cyclohexane.

3. Where are gas hydrates found?

We have compiled a map of the currently published possible locations of gas hydrate deposits based on the original dataset of Kvenvolden & Lorenson (2001), Ginsburg & Soloviev (1998) and Lorenson & Kvenvolden (2007). The gas hydrate locations are based on both physical samples and seismic evidence taken over the last 20 years (see figure 3). Samples of gas hydrate have been taken at approximately 20 different sites, while at another 80 sites the existence of gas hydrate has been suggested by seismic evidence, in the form of bottom-simulating reflectors (BSRs). BSRs are seismic reflectors with a negative reflection coefficient (Henriet & Mienert 1998; Haacke *et al.* 2008). They occur at the interface between sediment containing methane hydrate and sediment containing free methane gas; it is the gas that produces the negative reflector. This is because below
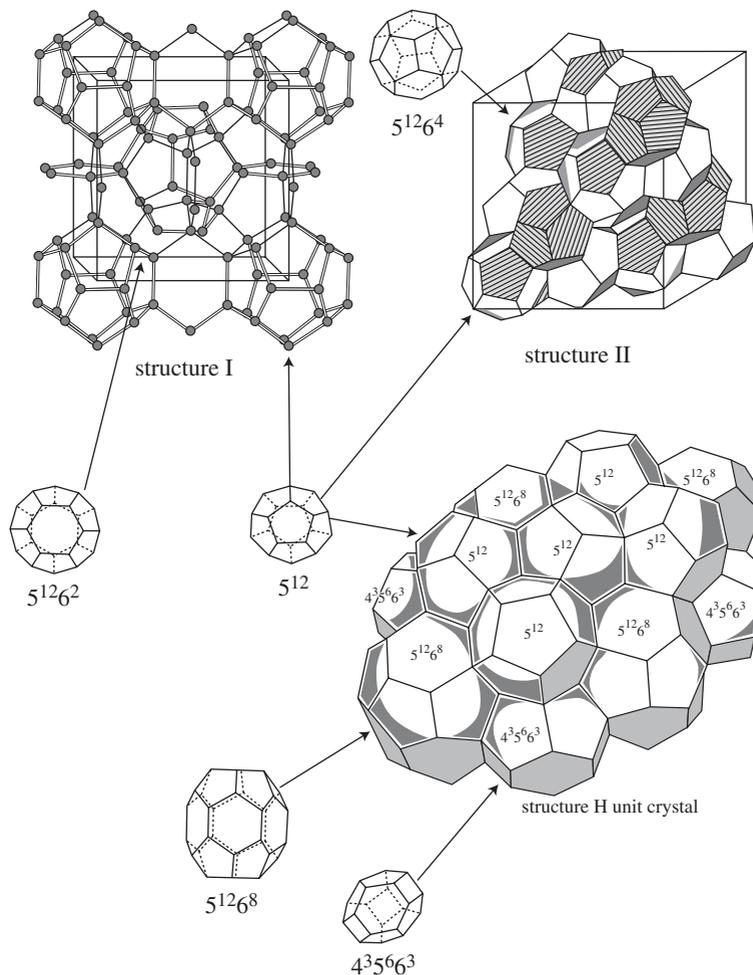
Figure 2. Illustration of the three different gas hydrate cage structures; within each cage one gas molecule can be held. (Adapted from Sloan (1998).)

a certain depth in ocean sediment the geothermal gradient makes the sediment too warm to support the solid gas hydrates, so any methane produced below this depth is trapped as a layer of gas beneath the solid gas hydrate layer. The BSR structures exist roughly parallel to the seafloor morphology along isotherms, hence their name (figure 4; Shipley *et al.* 1979). They do not necessarily follow the trend of stratigraphic horizons, but may intersect them. Haacke *et al.* (2008) provide an excellent model of the formation of the BSR. The BSR can occur in depths of several hundred metres below seafloor, indicating the lower boundary of gas hydrate stability. Consequently, gas hydrate can be assumed to exist above the BSR, otherwise the free gas below the BSR would have migrated upwards. However, gas chimneys have been found in which large quantities of gas can exist surrounded by gas hydrate with no BSR signature (Wood *et al.* 2002). Figure 3 indicates that gas hydrates are found along most continental shelf and slope regions and in many permafrost areas.
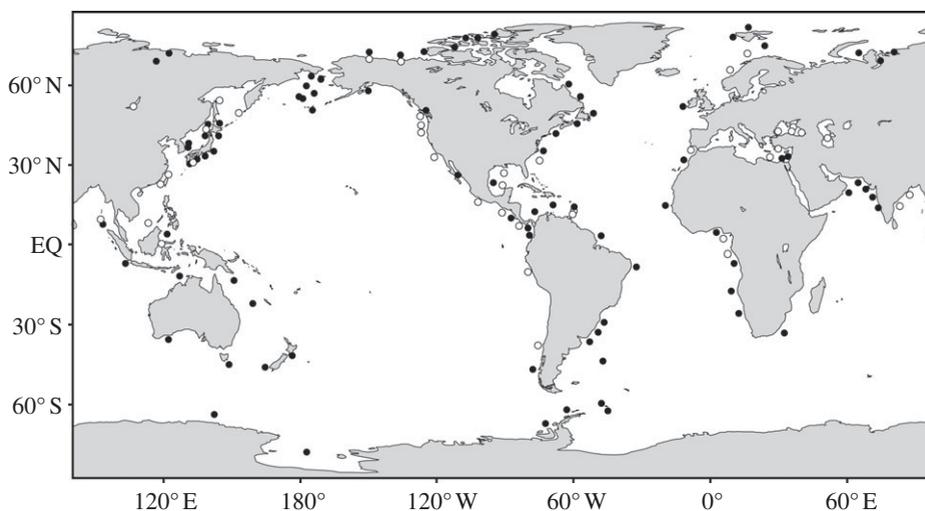
Figure 3. Global map of where gas hydrate reserves have been found; compiled by using data in Kvenvolden & Lorenson (2001), Ginsburg & Soloviev (1998) and Lorenson & Kvenvolden (2007). Solid points are locations where the presence of gas hydrates has been inferred, e.g. by the presence of a BSR, while the open points are location where actual samples of gas hydrates have been recovered.

Seafloor samples have confirmed the existence of gas hydrates in sediments above BSRs (Abegg *et al.* 2007, 2008). Most gas hydrate samples have been obtained either by drill ships (e.g. DSDP, ODP and IODP) or by research vessels from shallow sediment (Kvenvolden 1995, 1998). Once exposed to atmospheric temperature and pressure conditions, gas hydrate is unstable and dissociates. For this reason, it is likely that the presence of gas hydrate was not noticed in samples taken in the past. The only way to study gas hydrate samples in the laboratory is to either use pressurized sampling devices or to ensure extremely quick sampling and processing on board, preserving the gas hydrate in liquid nitrogen. Gas hydrate can occur in various forms, ranging from finely dispersed lumps to massive, pure layers, which are several centimetres thick (Kvenvolden 1998). Other structures may consist of layers that are wedge-shaped, interbeddings with thicknesses only in the 1–10 s mm or irregularly branching gas hydrate that completely dissolves the original sedimentary structure and leads to a formation of clastic sediments (Kvenvolden 1995, 1998). Gas bubbles migrating upward from the seafloor have been observed by submersibles (Sauter *et al.* 2006) and have also been recorded in the water column by means of echo sounder systems (Westbrook *et al.* 2009); these have been taken as evidence of near-ocean floor gas hydrate deposits.

4. How much gas hydrates is there?

The original estimates for the total amount of gas hydrate stored on Earth were between $10\,000$ and $11\,000\,\text{GtC}$ ($2 \times 10^{16}\,\text{m}^3$) (MacDonald 1990; Kvenvolden 1998). If correct, this would mean that there was over 10 times the amount of
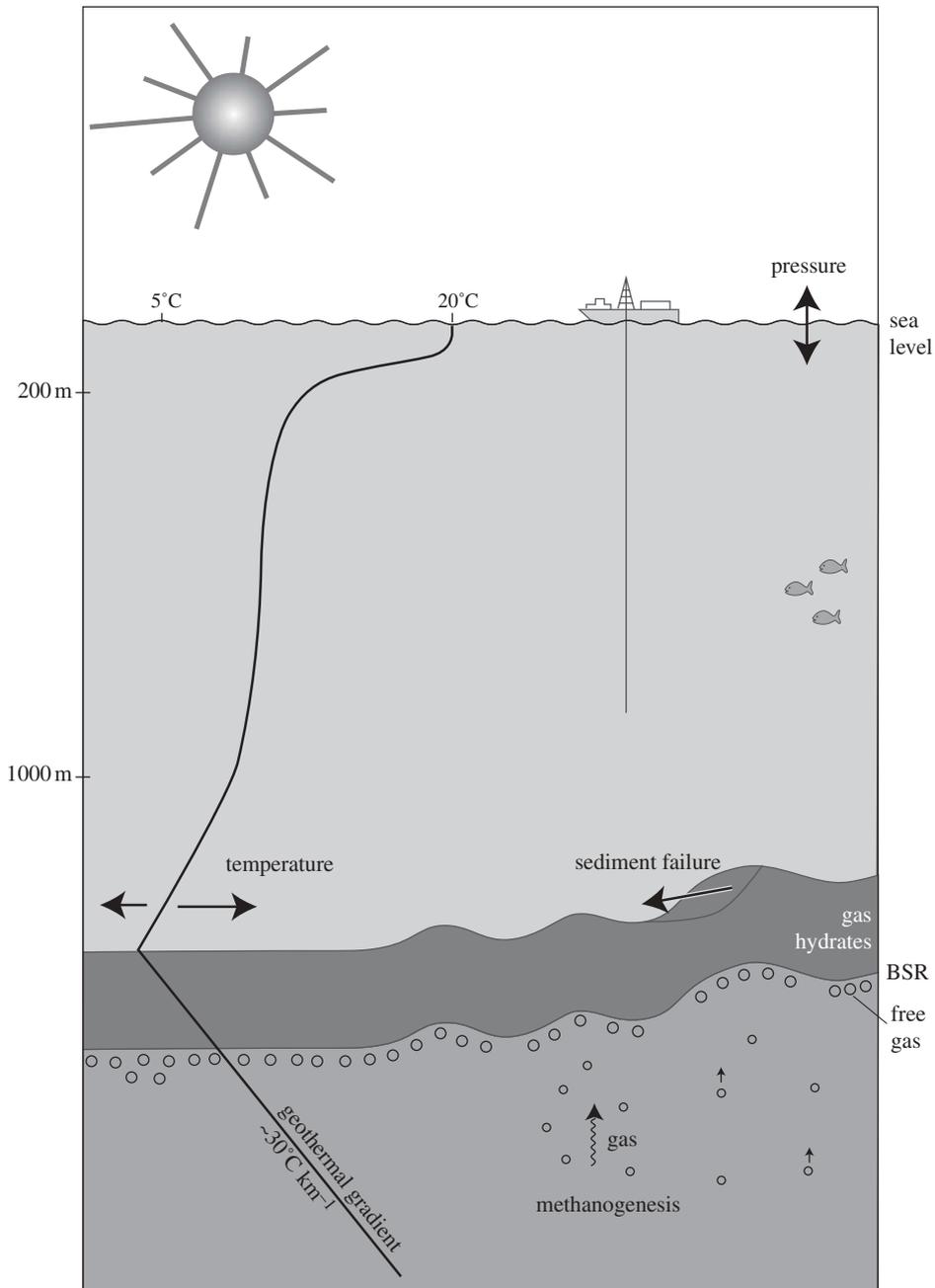
Figure 4. This shows the two controls on the location of the gas hydrate layer, temperature and pressure. Temperature is controlled by the ocean bottom water temperature and the geothermal gradient at any given location. Pressure is controlled by sea level and sediment failures. Many gas hydrate reserves have been identified by their BSR. This is the free gas trapped below the solid gas hydrate layer which shows up clearly on seismics and follows the sediment surface not the structures, as the gas hydrate layer is controlled by pressure and temperature and not lithology (permission grant for use by M. Maslin).

carbon stored in gas hydrates as in the atmosphere and would exceed by far the amount of carbon stored in other fossil fuel reservoirs. However, despite the size of the oceanic methane hydrate reservoir still being poorly understood, improved knowledge has led to an order of magnitude drop of current estimates (Milkov 2004). The highest estimates (e.g. $3 \times 10^{18}\,\mathrm{m}^3$; Trofimuk *et al.* 1973) were based on the assumption that hydrates littered the entire floor of the deep ocean. However, improvements in our understanding of hydrate chemistry and sedimentology have revealed that they only form in a narrow range of depths (continental shelves), only at some locations within their potential depth range (10–30% of the gas hydrate saturation zone), and are typically found at low concentrations (0.9–1.5% by volume) at sites where they do occur. Recent estimates constrained by direct sampling suggest the global inventory lies between 1×10^{15} and $5 \times 10^{15}\,\mathrm{m}^3$ (Milkov 2004). This estimate, corresponding to 500–2500 GtC, is smaller than the 5000 GtC estimated for all other fossil fuel reserves but substantially larger than the approximately 230 GtC estimated for other natural gas sources (USGS World Energy Assessment Team 2000). These estimates are supported by an alternative approach of Buffett & Archer (2004), who used a mechanistic model to predict the distribution of methane hydrate in marine sediments, and used this to predict the sensitivity of the steady-state methane inventory to changes in the deep ocean. Their best estimate yields 3000 GtC in marine hydrate and another 1800 GtC in bubbles. They have refined this estimate with more detailed modelling. Archer *et al.* (2009) predict a combined total of methane hydrate and bubbles in the ocean today of between 1600 and 2000 GtC. Of interest, they find that most of the hydrate in the model is in the Pacific Ocean, owing to the lower oxygen levels that enhance the preservation of organic carbon. In contrast, the permafrost reservoir has not been modelled in detail and has been estimated at about 400 GtC in the Arctic (MacDonald 1990), but no estimates have been made of possible Antarctic reservoirs (figure 5). Despite the lowering of estimates over the last decade, these are still extremely large amounts. For comparison, total atmospheric carbon is around 760 GtC (IPCC 2007).

Lower abundances of hydrates do not rule out their economic potential, but a lower total volume and apparently lower concentration at most sites do suggest that only a limited percentage of the deposits may provide an economically viable resource (Milkov & Sassen 2002). Potential economic exploration of gas hydrates, however, raises two major issues.

— Production and use of gas (methane) hydrate releases the greenhouse gas carbon dioxide.
— Production technology that is cost-effective, environmentally friendly and safe has yet to be developed, for either marine or permafrost gas hydrate.

Fossil fuel reservoirs are sufficient for at least the next century. Hence, only a few countries—such as Japan, which does not have any significant deposits of oil and natural gas—are implementing sizeable programmes concerning an economic production of gas hydrate. Production of oceanic gas hydrate may seem most attractive because of the relatively large quantities available compared with permafrost regions; however, large-scale recovery of oceanic gas hydrates
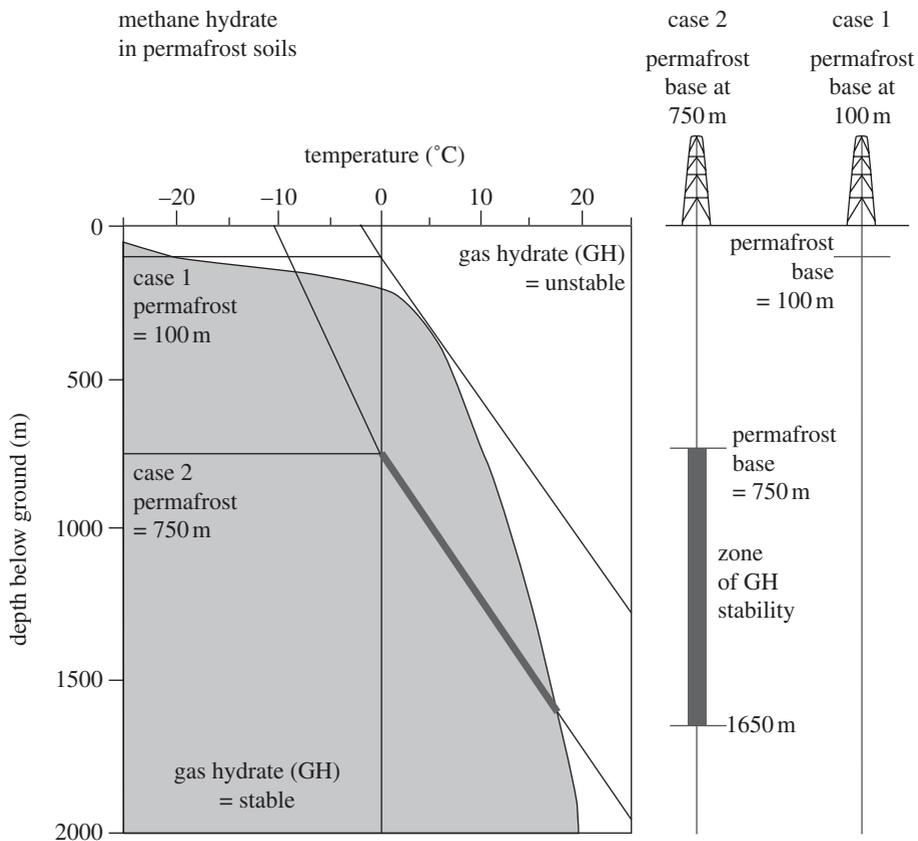
Figure 5. Phase diagram for permafrost sediments (redrawn from Kvenvolden & Lorenson (2001) and http://www.gashydrate.de), showing that the temperature gradients are considerably lower than in the ocean (figure 6). For example, the temperature can be expected to change by 1.3°C per 100 m within the permafrost zone, compared with 2°C per 100 m in layers below the permafrost zone. The ambient temperature and the thickness of the frozen layer are of paramount importance for the stability of gas hydrate. If the permafrost base is located at a depth of 100 m or less (case 1), the physical conditions will not be adequate for a formation of gas hydrate. The situation is different in case 2, where the permafrost basis is located at greater depth. In polar regions, methane hydrate can occur at depths ranging from 150 to 1650 m.

is unlikely to be achieved in the short term for several reasons: (i) low concentration of gas in the sediment, even though every cubic metre of gas hydrate can produce $164 \, m^3$ of methane, at atmospheric conditions, the highest concentrations of oceanic gas hydrates quoted are 17–20% by volume of the pore space, which equates to as little as 3 per cent sediment volume, (ii) the conditions for production are far more complicated than in permafrost regions, and (iii) the geohazards involved as well as the impact on the environment are difficult to assess. Small-scale production of methane from permafrost gas hydrate already occurs at the Messoyakh field, in western Siberia (Krason 2000) and has been trialled at Mallik, on the Mackenzie delta, northern Canada (Dallimore et al. 2005).

5. Formation and break down of gas hydrates

Clathrates/hydrates are not chemical compounds as the sequestered molecules are never bonded to the lattice. The formation and decomposition of hydrates are first-order phase transitions, not chemical reactions. Their detailed formation and decomposition mechanisms are still not well understood on a molecular level (Gao *et al.* 2005*a*,*b*). Gas hydrate can only form if there are sufficient amounts of gas and water combined with high pressure and/or low temperatures. The required pressure and temperature for stability can be influenced by the type of gas incorporated into the hydrate. Hydrates of H_2S, CO_2 and higher hydrocarbon hydrates can exist at higher temperatures, whereas nitrogen hydrates and all hydrate formation in the presence of dissolved salts require lower temperatures. Naturally occurring gas hydrates can be based on various gases. Nitrogen hydrates have been inferred for parts of the Greenland ice sheet, while CO_2 hydrates have been suggested to exist on other planets. The most common type of gas hydrate on Earth is methane hydrate and the conditions required for its stability can occur in permafrost soil (figure 5) and marine sediments (figure 6).

Apart from adequate temperature and pressure conditions, gas hydrate formation is dependent on sufficient gas, primarily CH_4, being available. Most of the methane found in the oceans is produced by decomposition of organic components or by bacterial reduction of CO_2 in sediments. Sometimes, it may also be a product of thermo-catalytic alteration processes in deeper sediments. CH_4 production is highest at the continental margins. Here, high plankton productivity and a high amount of continental in-wash yield large amounts of organic matter, which is the basis for gas production in the sediment. Gas hydrate is, therefore, found on any passive and active margins (Dale *et al.* 2008). However, there are also deposits in the Caspian Sea, the Black Sea, the Mediterranean, Lake Constance and Lake Baikal.

Because the stability of gas hydrates is related to high pressure and relatively low temperatures, any change in these two parameters can increase or decrease the stability of the gas hydrate (Archer 2007). For example, if either the pressure is reduced or the temperature increased, the gas hydrate will change phase from a solid to a gas and liquid. In the marine environment, the ocean temperature can vary owing to circulation changes and general changes in regional and global temperatures. For example, during the last glacial period, ocean temperatures were significantly lower so gas hydrates could form at shallower depth. Indeed, it has been argued that warming at the end of the ice age did destabilize a large quantity of gas hydrates leading to the observed peaks in atmospheric methane as seen in the ice-core record (e.g. Kennett *et al.* 2003; Maslin & Thomas 2003; Maslin *et al.* 2004). It has, therefore, been argued that warmer ocean temperatures predicted owing to global warming will cause gas hydrate dissociation and may lead to a significant increase in atmospheric methane.

The major influence on hydrate stability in permafrost regions is temperature. Regional temperatures can rise and fall, for example, between ice age and non-ice age periods. Current and future global warming is a concern as its warm effects are thought to be largest in the high latitudes (IPCC 2007). However, marine transgressions can also cause catastrophic release of gas hydrates from permafrost regions, as demonstrated for the Beaufort Sea by Paull *et al.* (2007)
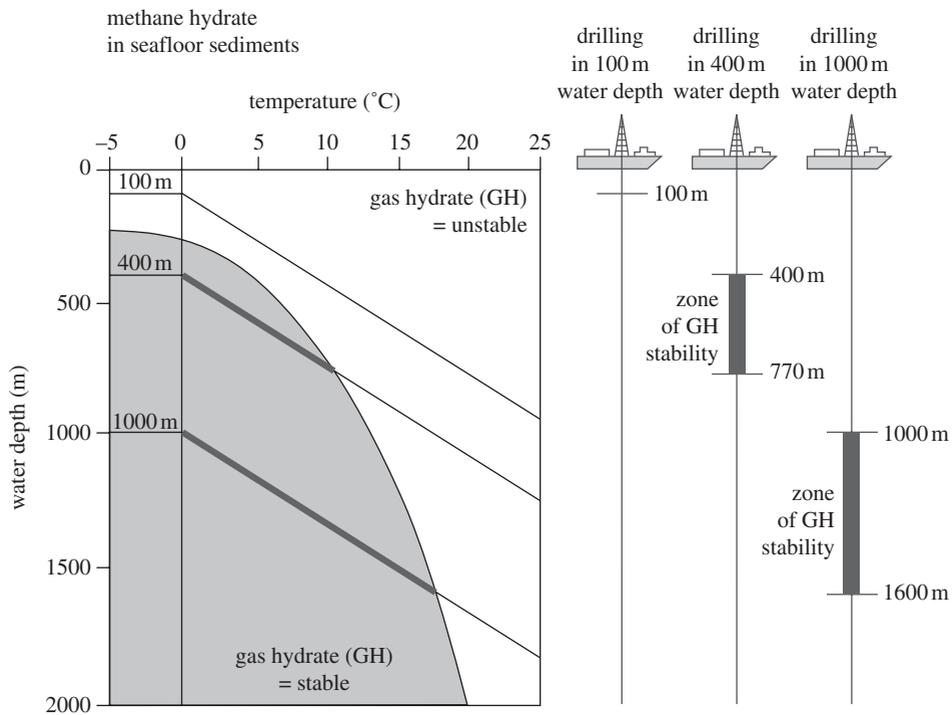
Figure 6. Phase diagram for ocean sediments (redrawn from Kvenvolden & Lorenson (2001) and http://www.gashydrate.de), showing the physical conditions (temperature and pressure) required for the stability of methane hydrate in a marine environment. Assuming a constant temperature of 0°C, e.g. in polar regions, methane hydrate cannot be stable at a water depth of 100 m. It may occur in a seafloor, which is more than 400 m below sea level. The thickness of the hydrate zone will depend on the temperature gradient. However, with an increasing depth below the seafloor, temperatures get too high for a formation of gas hydrate, so that one can find free gas and water. Given an average temperature increase of 3°C per 100 m sediment depth, when drilling at a water depth of 300 m, we can expect to find a 300 m thick hydrate layer. At 1000 m water depth, the layer will be 600 m thick. If, however, sediments are characterized by a stronger increase in temperature, which can be the case, e.g. at active continental margins (4–6°C per 100 m depth), the hydrate zone will generally be thinner. Gas hydrate has been found in sediments up to 1100 m below the seafloor.

and for the East Siberian Arctic Seas by Shakhova *et al.* (2010). This is because the land temperature can be below −20°C, but salty oceanic water can be no colder than about −1.8°C before freezing (Maslin & Thomas 2003). So, if sea level rises and floods permafrost areas, these will encounter a thermal shock of at least 20°C warming, which could lead to considerable break down of gas hydrates.

Marine gas hydrate stability can also be affected by pressure changes. Increased sea level will increase the hydrostatic pressure and will stabilize gas hydrates to a deeper depth, while lowering sea level will reduce the pressure on the sediment causing gas hydrates to become unstable (Paull & Dillon 2001; Paull *et al.* 2003). Another way of removing pressure from underlying sediments is by marine sediment failure. When the overlying sediment column collapse occurs and sediment moves down slope there is a reduction in weight of the sedimentary
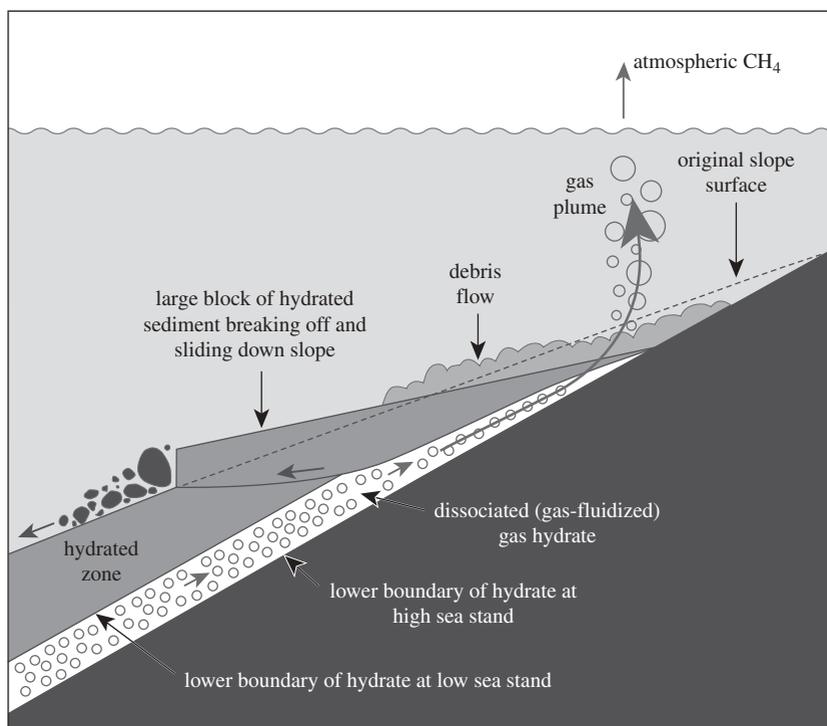
Figure 7. Champagne cork effect: illustration of what happens when a slope failure occurs above a gas hydrate layer and how large quantities of gas can be released. (Adapted from Kvenvolden (1998).)

column; as upper layers have been removed, this decrease in pressure could cause gas hydrates to dissociate. This can be rapid as pressure effects can be transferred through the sediment quickly and thus can enlarge the sediment collapse as large quantities of hydrate turn to gas (figure 7).

6. Hydrate and past climate changes

Identification of large-scale release of methane gas from the collapse of gas hydrate deposits in the past may be postulated on the basis of two criteria. First is the identification of features associated with hydrate dissociation and gas release, large features such as pockmarks and seabed slumps as well as smaller scale features such as fluid venting chimneys (e.g. Haflidason *et al.* 2004; Paull *et al.* 2008). The second is changes in regional and global records of carbon isotopes. This is because hydrate methane has extremely depleted $\delta^{13}C$ values ($-40‰$ to $-100‰$ PDB, average approx. $-60‰$ PDB; MacDonald 1990; Dickens *et al.* 1997; Kvenvolden 1998; Buffett 2000; Maslin & Thomas 2003) compared with average sea water (approx. $0‰$ PDB). Three case studies are briefly reviewed below with evidence of large-scale methane hydrate release in the past.

(a) Carbon isotope excursion at the Cretaceous–Tertiary boundary

One of the characteristic features of the Cretaceous–Tertiary (K/T) boundary extinction event is a marked but short-lived change or boundary excursion in the stable isotopic composition of carbon in carbonate sediments deposited at the time of the event (see references in Day & Maslin (2005)). Planktonic foraminifera δ^{13}C records indicate a significant shift to light or depleted values, meaning that the sediment is enriched in the light isotope ^{12}C. Similar, short-lived ^{12}C enrichments have been identified at several other turnover events in the history of life on Earth, such as the Palaeocene–Eocene thermal maximum or PETM (Dunkley Jones *et al.* 2010) and the Permian–Triassic mass extinction. The difference between the K/T boundary carbon isotope excursions (CIEs) and others such as the PETM should also be considered. At the K/T boundary, planktonic foraminifera indicate surface water ^{12}C enrichment, while the benthic foraminifera show an enrichment of the bottom water in ^{13}C. In contrast at the PETM both the surface and deep water become enriched in ^{12}C (e.g. Dunkley Jones *et al.* 2010), which has implications concerning speed of gas hydrate destabilization and the effects of an impact on ocean productivity. Day & Maslin (2005) presented a plausible mechanism linking a large impact, such as Chicxulub, to significant continental sedimentary slope failure and gas hydrate release. Calculations of both the duration and intensity of syn- and post-impact-related seismicity suggest that there was a sufficient forcing to cause widespread sediment liquifaction and failure along tens of thousands of kilometres of continental slope. They have calculated the potential storage of gas hydrates based on known environmental conditions during the Cretaceous, which suggests that slope failures caused by the Chicxulub impact could have led to the release of between 300 and 1300 GtC (best estimate approx. 700 GtC) of methane from the destabilization of gas hydrates. This would produce a global CIE of between -0.5‰ and -2‰ (best estimate approx. -1‰). This compares well with the observed change of -1‰ in the planktonic foraminifera records across the K/T boundary. This large release of methane may also account for the recently reconstructed very high atmospheric pCO$_2$ levels after the K/T boundary as our estimated gas hydrate releases could have increased atmospheric carbon dioxide by a maximum of 600–2300 ppm (best estimate approx. 1200 ppm).

(b) Palaeocene–Eocene thermal maximum

The PETM (approx. 55.5 Ma) was first identified in the geological record by its expression in deep-sea sediment cores of the Southern Ocean as a rapid paired negative excursion in carbon and oxygen isotopes, coincident with a dramatic extinction event in benthic foraminifera (Kennett & Stott 1991). First attributed to major ocean circulation changes (Kennett & Stott 1991), for a number of years the magnitude and rate of the PETM CIE proved resistant to explanation with a conventional understanding of atmosphere–ocean–biosphere carbon cycling. On the basis of relatively simple but compelling mass balance arguments, Dickens *et al.* (1995) first proposed a role for the massive global-scale dissociation of oceanic sediment-hosted methane hydrate deposits in generating such prominent negative CIEs in the geological record. These reservoirs of strongly ^{13}C-depleted carbon (δ^{13}C approx. -60‰), with their inherent sensitivity to environmental temperature and pressure perturbations, have the potential to explain both

the rapidity and the magnitude of global negative CIEs, such as observed across the PETM. The catastrophic methane hydrate destabilization hypothesis has also gained some support from seismic and sedimentological evidence for large-scale PETM slope failure along the western margin of the Atlantic basin (Katz *et al.* 1999).

The last 15 years has seen a great deal of research focus on the PETM, largely driven by the potential analogues with modern anthropogenic climate change. This has investigated the primary sedimentary record of the PETM, including the magnitude of the CIE (e.g. Zachos *et al.* 2007), the refinement of age models for the duration of the event (e.g. Rohl *et al.* 2007), the associated climatic perturbation (e.g. Sluijs *et al.* 2006; Zachos *et al.* 2006), evidence for ocean circulation changes (e.g. Thomas *et al.* 2003; Nunes & Norris 2006), the profound impacts on oceanic carbonate chemistry (e.g. Zachos *et al.* 2005; Zeebe & Zachos 2007) and the effects of the event on benthic (e.g. Thomas & Shackleton 1996), planktic (e.g. Gibbs *et al.* 2006) and terrestrial ecosystems (e.g. Gingerich 2006). It has also seen a number of climate and carbon cycle modelling studies attempting to integrate the available proxy data into a coherent view of Earth-system behaviour across the event (e.g. Bice & Marotzke 2002; Panchuk *et al.* 2008; Zeebe *et al.* 2009). The current synthesis, although with significant continuing uncertainties, appears to consist of an approx. 4‰ negative CIE in the oceanic dissolved inorganic carbon pool, a global temperature anomaly of 5–6°C, a rapid (less than 10 kyr) onset and total PETM duration of approx. 170 kyr, and a carbon input within the range 4000–7000 GtC with some contribution, but perhaps not the dominant one, from methane hydrates. For further discussion of the PETM, see Dunkley Jones *et al.* (2010).

(*c*) *A forcing role for methane in the Quaternary glacial to interglacial cycles*

The Quaternary glacial cycles are characterized by a saw-tooth pattern within which the methane and temperature record are in close agreement (e.g. Brook *et al.* 1996). This, among other evidence, has led various authors to suggest a role for methane hydrate release in the forcing of Quaternary climate change (see Kennett *et al.* (2003) and references therein). Temperature and sea-level oscillations, associated with the changing climate signals, fit the model of hydrate phase shift and hence dissociation. However, whether methane hydrates have played a role in Quaternary climate change is a topic which has sparked much debate (e.g. Sowers 2006; O'Hara 2008).

Unfortunately, this problem is extremely difficult to investigate as the main sources of evidence are subject to varying degrees of uncertainty and error. The ice-core methane record is subject to uncertainty over differences between ice age and gas age as well as the age distribution, as opposed to a discrete age, of a gas bubble (Spahni *et al.* 2003). Investigating past occurrence of events which may be related to hydrate dissociation and methane release, such as submarine slope failures and the occurrence of pockmarks, is an extremely expensive affair and accurate age-constraint difficult. Despite these difficulties, recent work has focused on compiling databases of mass movement occurrence in order to assess the relationships with climate and the methane record (Maslin *et al.* 2004; Owen *et al.* 2007). It has been noted previously that submarine mass movements appear to occur more frequently during periods of rapid
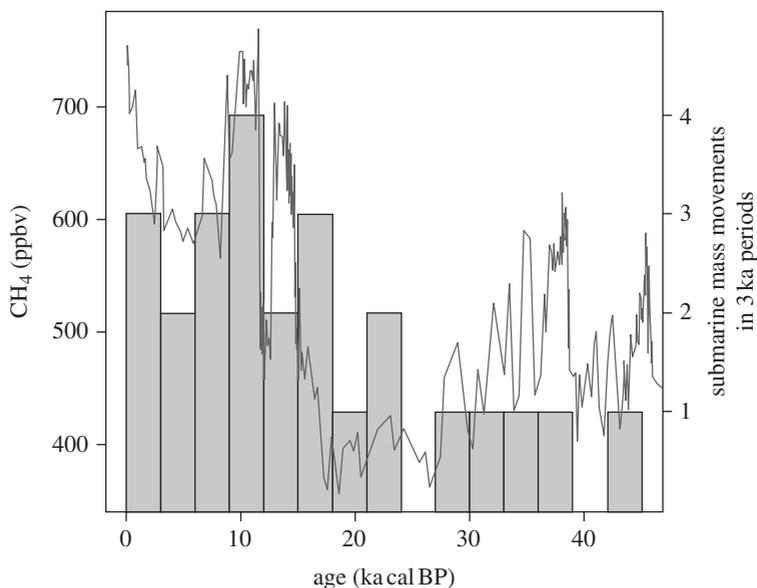
Figure 8. GISP2 methane concentration (Brook *et al.* 1996; Blunier & Brook 2001) with North Atlantic submarine mass movement occurrence during the last 45 ka plotted as a histogram in 3 ka periods. (Adapted from Owen *et al.* (2007).)

climatic change (e.g. Maslin *et al.* 2004, 2005, 2006; Owen *et al.* 2007; Lee 2009; Camerlenghi *et al.* 2010). The general consensus is that this is primarily due to changes in the sedimentary regime (with associated effects on pre-conditioning, trigger mechanisms and pore pressure) rather than a result of gas hydrate dissociation (Masson *et al.* 2010). However, this does not rule out a role for mass movements in releasing methane, previously stored either within or beneath the hydrate layer, into the atmospheric system, nor does it preclude a role for gas hydrates in slope instability.

Figure 8 shows the occurrence of North Atlantic submarine mass movements plotted with GISP2 atmospheric methane concentration for the last 45 ka. A key point to note is the lack of individual mass movements included within figure 8; this is due to the difficulty of accurately dating these events. An attempt has been made to magnify any trends by grouping events into 3 ka periods. The pre-boreal methane peak coincides with the period with most observed mass movements, and the increased occurrence of mass movements at the glacial to interglacial transition is associated with the Bølling methane peak. However, owing to dating uncertainties and the small sample number, any meaningful statistical analysis of these data is impossible. It is possible to attempt to reconstruct the palaeo-methane budget by analysing the isotopic composition of ice-core methane record. Sowers (2006) investigates GISP2 δD-CH$_4$ at a stated temporal resolution of approx. 35 years. Methane hydrates appear to have a more distinctive δD signature than they do δ^{13}C, especially in comparison with global wetlands. Hydrates have a mean δ^{13}C value of -62.5‰, extremely similar to values of -62‰ and -56.8‰ to -58.9‰ for boreal and tropical wetlands, respectively; contrasting this δD-CH$_4$ values are -190‰ and -360‰ to -380‰ for hydrates and wetlands, respectively (Whiticar & Schaefer 2007).
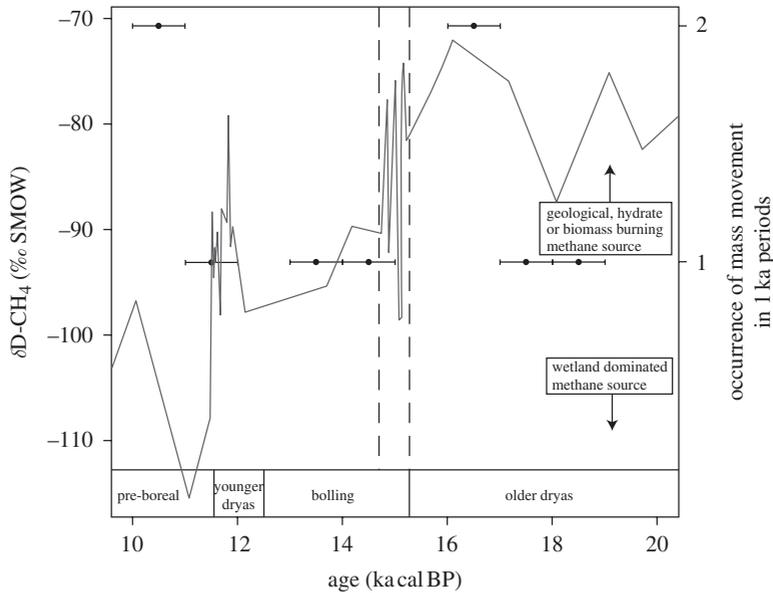
Figure 9. GISP2 δD-CH$_4$ record (Sowers 2006) with occurrence of North Atlantic submarine mass movements in 1 ka periods for the period 10–20 ka cal BP, the last glacial to de-glacial transition. (Adapted from Owen *et al.* (2007).)

GISP2 δD-CH$_4$ and submarine mass movement occurrence for the period 10–20 ka cal BP are shown in figure 9. During the glacial period, the δD-CH$_4$ record is isotopically heavier, as would be expected with a greater role expected for geological, hydrate or biomass burning methane sources. Progressing towards the Holocene, the record is isotopically lighter as tropical and boreal wetlands assume a greater role. If methane hydrates were to release large volumes of methane gas into the atmospheric system, the δD-CH$_4$ record would be expected to show a marked increase in the occurrence of ^{2}H, becoming isotopically heavier. We are in agreement with previous authors (e.g. Sowers 2006; Whiticar & Schaefer 2007) who state that there is no evidence of, the so-called 'smoking gun', catastrophic hydrate dissociation. However, we also feel that the oscillating δD-CH$_4$ values observed at the older Dryas–Bølling transition are intriguing and seem to indicate a complex period for the methane budget, with a potential for pulses of ^{2}H-enriched methane disrupting the gradual decrease in isotopic weight caused by the shift to wetland-source-dominated atmospheric methane. Intriguingly, this period, 14.7–15.2 ka cal BP, is also a period within which one might expect to observe an increased occurrence of submarine slope failures associated with the deglaciation of mid- to high-latitude margins. The current data on submarine mass movement occurrence do not support this, as shown in figure 8, with the greatest occurrence some 3 ka nearer the present. It is possible that our dataset is biased to more recent failures, which may obscure the record of older events and it is also true that, on the whole, the dating of these events is not as accurate as we would wish. Which two points lead us to the conclusion that until we have more accurate dating of submarine mass movement occurrence, coupled with a larger database of events, it will not be possible to accurately assess their role as possible sources of methane.

7. Future global gas hydrate hazards

The future geohazard risks of gas hydrates can be divided into global and regional threats. In terms of global threats, as both marine and permafrost gas hydrate reservoirs are sensitive to environmental changes, they will be affected by global warming. Global warming prediction by the IPCC (2007) suggests that, by the year 2100, global mean surface temperature could rise by between 1.1°C and 6.4°C (best estimate 4°C) and global mean sea level could rise at least 28–79 cm, more if the melting of Antarctica and Greenland accelerates. These predictions include the warming of both the oceans and the permafrost regions, which could cause significant dissociation of gas hydrates, releasing unknown amounts of methane into the atmosphere. As methane is a very strong greenhouse gas, 21 times more powerful than carbon dioxide, gas hydrates have become one of the major concerns of global warming (Heimann 2010). We believe that our current best estimate is that there is 1600–2000 GtC (Archer *et al.* 2009) of methane stored beneath the ocean, and there may be another 400 GtC (MacDonald 1990) in the Arctic permafrost regions compared with only 760 GtC in the atmosphere.

The general IPCC (2007) climate prediction quoted above masks regional differences, which may have a much greater impact on gas hydrate stability. First, the temperature increase in the high latitudes is expected to be much larger than this average valve given. Liggins *et al.* (2010) suggest that permafrost areas in the Northern Hemisphere could undergo up to a 12°C warming by 2100. This will have a significant detrimental effect on the stability of gas hydrates trapped in permafrost regions and will have important local affects, which are discussed in §8. However, as we do not have a reliable estimate of the amount of methane stored in and under permafrost gas hydrates in the Arctic and no estimate at all for the Antarctic, it is impossible to quantify the magnitude of any methane release. There are, however, worrying signs. Detailed work by Shakhova *et al.* (2010) has shown a large increase in the methane being released by the subsea permafrost on the East Siberian Arctic Shelf. They suggest the annual outgassing from this region is now about 8 Tg (0.008 GtC), which is the same as the methane emissions for the rest of the world ocean (IPCC 2007). Shakhova *et al.* (2010) suggest that the subsea permafrost lid on gas hydrate reserves around the world is extremely vulnerable to regional warming.

Climate models also predict an increase in intermediate water temperature (IPCC 2007). This is an important consideration as it is the intermediate ocean waters between about 200 and 1500 m water depth which bathe the sediment most likely to contain gas hydrates. This predicted warming of the intermediate ocean depth will tend to destabilize the marine gas hydrates. The small predicted future sea-level rise of up to 1 m may increase the hydrate stability slightly but is completely insufficient to counter the warming. However, to destablize gas hydrates through increased temperatures, the increased warmth must penetrate through the gas hydrate layer to the phase transition at the hydrate–gas boundary at the base. Thermal diffusivity is a relatively slow process and related to the temperature gradient, the hydrate depth and sediment composition (Clennell *et al.* 1999; Henry *et al.* 1999). It could, therefore, be possible for the destabilized gas hydrate at the base of the hydrate layer to become gas and migrate up into the stable zone and re-form hydrate. Archer *et al.* (2009) used models to estimate not only the gas hydrate inventory discussed above but also the possible future

release. They also calculated that between 35 and 940 GtC of methane could escape owing to global warming of 3°C. This is a huge range of uncertainty reflecting the problems discussed above. Archer *et al.* (2009) show that their estimate is highly dependent on the assumption of how much of the newly formed gas can escape the sediment into the water column and then into the atmosphere. They also predict that the maximum calculated methane release would add a maximum additional 0.5°C to global warming.

8. Future regional gas hydrate hazards

(*a*) *Permafrost regions*

In the high-latitude and high-altitude areas, permafrost exists where it is so cold that the ground is frozen solid to a great depth. During the summer months, only the uppermost layer of the permafrost gets warm enough to melt, and this is the so-called active layer. In Sweden, active layer thickening at rates of 0.7–$1.3\,\mathrm{cm\,yr^{-1}}$ has been observed over the last 29 years and in the last decade rates have accelerated to $2\,\mathrm{cm\,yr^{-1}}$ (Åkermann & Johansson 2008). Future predictions suggest there will be an increase in the thickness of the active layer of the permafrost or, perhaps in some areas, the complete disappearance of the so-called discontinuous permafrost over the next century (Lawrence *et al.* 2008). The thermal shock of this warming will destabilize gas hydrates trapped beneath the active layer. This widespread loss of permafrost and the loss of structural integrity owing to dissolution of gas hydrates will produce a huge range of local problems, such as triggering erosion or subsidence, and changing hydrological processes. These changes in sediment cohesiveness may reduce the stability of slopes and thus increase incidence mass movement such as soil creep, landslides and avalanches. A more dynamic cryosphere may increase the natural hazards for people, structures and communication links. Already buildings, roads, pipelines (such as the oil pipelines in Alaska) and communication links are being threatened. There is also the very remote possibility that methane could be explosively released and, in the right circumstances, would burn, posing a serious highly localized threat. Recent research carried out in the Siberian Arctic has shown that millions of tons of methane are already being released with concentrations in some regions reaching up to 100 times above normal (Shakhova *et al.* 2007, 2008).

(*b*) *Marine risks*

Both the occurrence of gas hydrate deposits and predicted oceanic warming vary regionally so there will be particular areas more vulnerable to gas hydrate destablization. Moreover, ocean temperature changes can be caused by variations in the location of key ocean currents. Westbrook *et al.* (2009) have shown large plumes of methane gas bubbles emanating from the seabed west of Svalbard. They suggest that this is due to the breakdown of gas hydrates caused by a shift and warming of the West Spitzbergen current. These localized gas plumes could have safety implications for both shipping and marine oil/gas production. If sufficient methane is released in relatively shallow water, the gas could produce negative buoyancy and could cause boats/ships to founder. A more likely problem

is the increased risk to oil and gas platforms in deeper water, i.e. between 200 and 1500 m water depth. The localized increase in intermediate water temperatures could cause gas hydrate to breakdown, which may lead to significant sediment failure (see below) and/or outgassing, both of which could be detrimental to the structural safety of the platforms and those working on them. Of course, these risks will be significantly increased if economic exploitation of marine gas hydrate deposits is initiated.

(*c*) *Catastrophic submarine slope failures*

When enclosed in sedimentary pore space, gas hydrates can act like cement, compacting and stabilizing the seafloor (Grozic 2010). The degree of strengthening is a function of temperature, strain rate, particle size, density and cage occupancy (Winters *et al.* 2004). However, if formed in deposits that are still unconsolidated, gas hydrate prevents the normal increase of compaction with increasing lithostatic pressure. If exposed to lower pressure and/or increased temperature, the gas hydrate decomposes. If this occurs, the compactness of the seafloor decreases, which may lead to submarine slope failures. Seismic, bathymetric and side-scan sonar mapping of the seafloor has shown that these mass movement deposits, of various sizes and morphologies, characterize all continental slopes. For instance, near slide scars one can often find seismic evidence of gas and fluid pathways up through the sediment column. The seafloor itself shows crater-like depressions, the so-called pockmarks that indicate fluid or gas venting (e.g. Hustoft *et al.* 2009).

Sediments fail when the downslope force (shear stress) exceeds the resisting force (shear strength). Sediments deposited in a state where shear strength is greater will be stable. However, an alteration of this state through either a reduction in shear strength or an increase in shear stress can lead to failure. At the upper shelf edge, there are slopes of more than 4°. Submarine slope failures probably appear if such a slope moves out of equilibrium and into an unstable state, and there are many means by which this can occur: one of which being gas hydrate dissociation. Stable sediments, strengthened at depth by a hydrate layer, may become unstable if the hydrate layer dissociates, weakening the sedimentary column and allowing either gravimetric forces or a relatively minor trigger (such as a low-magnitude earthquake) to initiate slope failure. One important factor seems to be the expansion of the released gas, which increases with decreasing water depth. For example, at 650 m water depth, the volume of released gas and water is almost three times the original gas hydrate volume. Gas hydrate decomposition at the upper shelf edge can result in an enormous pore pressure that leads to a massive loss of compactness while the large pore space makes the sediment highly deformable. This only occurs if there is no consistent venting of the methane gas. The free gas and hydrate layer which result in the BSRs, with their slope-parallel trend, are another potential pre-conditioning factor for submarine slope failure. When gas hydrates dissociate, they will be weak layers parallel to the slope.

There is some evidence that gas hydrate decomposition has contributed to the cause of a number of massive slides over the last 45 ka (Maslin *et al.* 1998, 2004; Owen *et al.* 2007; Lee 2009; Maslin 2009). Although it is extremely difficult to link hydrates directly to these geological slope failures, one such event is the Cape Fear slide, on the US Atlantic margin, for which methane hydrates, along with salt

diapirism, are believed to have played a significant role (Hornbach *et al.* 2007). One of the most famous submarine slope failures in which gas hydrates are implicated is the Storegga slide off Norway, which has a known volume of 3000 km³ and occurred about 8100 years ago (Bouriak *et al.* 2000; Bryn *et al.* 2003; Haflidason *et al.* 2004, 2005). This slide is known to have produced a tsunami impacting Norway, the Faeroes, Scotland and Northern England with a run-up of up to 20 m (Bondevik *et al.* 2005). More recently, the 1998 Sissano tsunami, which resulted in the loss of more than 2000 lives, may have also been caused by a submarine slope failure (Tappin *et al.* 2001).

Global warming via gas hydrate destabilization may pose a potential threat to continental slope sediment stability. If significant parts of the Greenland and Antarctica ice sheets melt (Hansen *et al.* 2008), the removal of the weight of ice from the continent initiates a slow movement upwards. This isostatic rebound can be seen in the British Isles, which are still recovering from the last ice age which ended 10 000 years ago. Scotland, on which the British ice sheet sat, is recovering at a rate of $3\,\mathrm{mm\,yr}^{-1}$, while England is still sinking at a rate of $2\,\mathrm{mm\,yr}^{-1}$. This coastal recovery or isostatic rebound means the relative sea level around the continental shelf reduces, removing the weight and thus pressure of the sea water on the marine sediment. In some cases, pressure removal may be a more efficient way of destabilizing gas hydrates than temperature increases and hence there is a potential risk of slumping on the continental shelf around Greenland and the Antarctic, which could lead to tsunamis being generated. There is already evidence that Arctic sea ice is in retreat (Boé *et al.* 2009; Wang & Overland 2009) and the Greenland and Antarctic ice sheets shrinking (e.g. Thomas 2001; Wingham *et al.* 2006). Hence, regional gas hydrate hazards must be considered and studied in more depth to assess the potential risks.

9. Conclusions

At the moment, it is difficult to assess the potential future geohazard represented by gas hydrates owing to a lack of knowledge. For example, we are unsure how much methane is stored in and below gas hydrates. For ocean sediments, estimates range from 500 to 10 000 GtC (best estimate 1600–2000 GtC) stored, while our current estimates of gas hydrate storage in the Arctic region are very poor (approx. 400 GtC) and non-existent for Antarctica. We do not know whether increased future temperatures could lead to significant methane release from ocean sediments, as thermal penetration of marine sediments to the clathrate–gas interface could be slow enough to allow a new equilibrium to occur without any gas escaping. Even if methane gas does escape, it is still unclear how much of this could be oxidized in the overlying ocean. Our best estimate by Archer *et al.* (2009), using state-of-the-art modelling, has a huge potential range from 35 to 940 GtC. The destabilized gas hydrate reserves in permafrost areas seem more certain as climate models predict that high-latitude regions will be disproportionately affected by global warming with temperature increases of up to 12°C predicted for much of North America and Northern Asia. There is already new evidence of significant methane release from subsea permafrost on the East Siberian Arctic Shelf (Shakhova *et al.* 2010). But our current estimates of gas hydrate storage in the Arctic region are very poor and

non-existent for Antarctica. Hence, more research is required to (i) quantify the amount of methane stored in and below gas hydrate deposits and (ii) increase our understanding of the possible limits of stability of these deposits, before we can successfully evaluate the future risk they pose to both the local and global environment.

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