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METHANE HYDRATES AND CLIMATIC EFFECTS

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Introduction

Natural gas hydrates are crystalline solids that occur widely in marine sediment of the world's continental margins. They are composed largely of methane

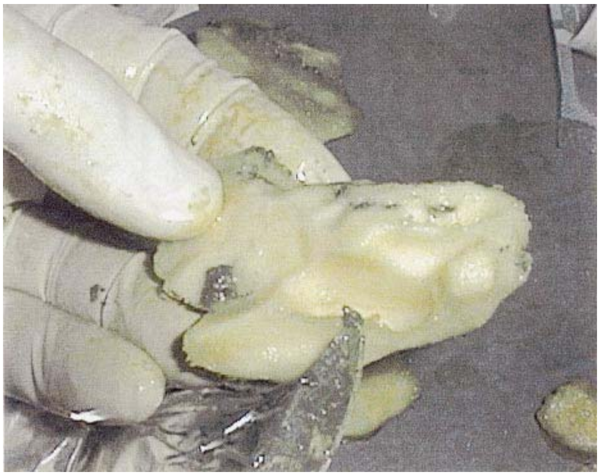

Figure 1 A piece of natural gas hydrate from the Gulf of Mexico. (Photograph courtesy of I. MacDonald, Texas A&M University.)

and water, frozen in place in the sediment under the dual conditions of high pressure and frigid temperatures at the sediment–water interface (**Figure 1**). When the breakdown of the gas hydrate (also known as clathrate) occurs in response to reduced hydrostatic pressure (e.g., sea level fall during glacial periods), or an increase in bottom-water temperature, it causes dissociation of the solid hydrate at its base, creating a zone of reduced sediment strength that is prone to structural faulting and sediment slumping. Such sedimentary failure at hydrate depths could inject large quantities of methane (a potent greenhouse gas) in the water column, and eventually into the atmosphere, leading to enhanced greenhouse warming. Ice core records of the recent geological past show that climatic warming occurs in tandem with rapid increase in atmospheric methane. This suggests that catastrophic release of methane into the atmosphere during periods of lowered sea level may have been a causal factor for abrupt climate change. Massive injection of methane in sea water following hydrate dissociation during periods of warm bottom temperatures are also suspected to be responsible for major shifts in carbon-isotopic ratios of sea water and associated changes in benthic assemblages and hydrographic conditions.

Hydrate Stability and Detection

Gas hydrate stability requires high hydrostatic pressure (>5 bars) and low bottom-water temperature ($<7^{\circ}$C) on the seafloor. These requirements dictate that hydrates occur mostly on the continental slope and rise, below 530 m water depth in the low latitudes, and below 250 m depth in the high latitudes. Hydrated sediments may extend from these depths to *c.* 1100 m sub-seafloor. In higher latitudes, hydrates also occur on land, in association with the permafrost.

Rapidly deposited sediments with high biogenic content are amenable to the genesis of large quantities of methane by bacterial alteration of the organic matter. Direct drilling of hydrates on the Blake Ridge, a structural high feature off the US east coast, indicated that the clathrate is only rarely locally concentrated in the otherwise widespread field of thinly dispersed hydrated sediments. The volume of the solid hydrate based on direct measurements on Blake Ridge suggested that it occupies between 0 and 9% of the sediment pore space within the hydrate stability zone (190–450 m sub-seafloor). It has been estimated that a relatively large amount, *c.* 35 Gt (Gigaton $= 10^{15}$ g), of methane carbon was tied up on Blake Ridge, which is equal to carbon from about 7% of the total terrestrial biota.

Hydrates can be detected remotely through the presence of acoustic reflectors, known as bottom simulating reflectors (BSR), that mimic the seafloor and are caused by acoustic velocity contrast between the solid hydrate above and the free gas below. However, significant quantities of free gas need to be present below the hydrate to provide the velocity contrast for the presence of a BSR. Thus, hydrate may be present at the theoretical hydrate stability depths even when no BSR is observed. Presence of gas hydrate can also be inferred through the sudden reduction in pore-water chlorinity (salinity) of the hydrated sediments during drilling, as well as through gas escape features on land and on the seafloor.

Global estimates of methane trapped in gas hydrate reservoirs (both in the hydrate stability zone and as free gas beneath it) vary widely. For example, the Arctic permafrost is estimated to hold anywhere between 7.6 and 18 000 Gt of methane carbon, while marine sediments are extrapolated to hold between 1700 and 4 100 000 Gt of methane carbon globally. Obtaining more accurate global estimates of methane sequestered in the clathrate reservoirs remains one of the more significant challenges in gas hydrate research.

Another major unknown, especially for climatic implications, is the mode of expulsion of methane from the hydrate. How and how much of the gas escapes from the hydrate zone and how much of it is dissolved in the water column versus escaping into the atmosphere? In a steady state much of the methane diffusing from marine sediments is believed to be oxidized in the surficial sediment and the water column above. However, it is not clear what happens to significant volumes of gas that might be catastrophically released from the hydrates when they disintegrate. How much of the gas makes it to the atmosphere (in the rapid climate change scenarios it is assumed that much of it does), or is dissolved in the water column?

Hydrate dissociation and methane release into the atmosphere from continental margin and permafrost sources and the ensuing accelerated greenhouse heating also have important implications for the models of global warming over the next century. The results of at least one modeling study play down the role of methane release from hydrate sources. When heat transfer and methane destabilization process in oceanic sediments was modeled in a coupled atmosphere–ocean model with various input assumptions and anthropogenic emission scenarios, it was found that the hydrate dissociation effects were smaller than the effects of increased carbon dioxide emissions by human activity. In a worst case scenario global warming increased by 10–25% more with clathrate destabilization than without. However, these models did not take into account the associated free gas beneath the hydrate zone that may play an additional and significant role as well. It is obvious from drilling results on Blake Ridge that large volumes of free methane are readily available for transfer without requiring dissociation.

Hydrate Breakdown and Rapid Climate Change

The temperature and pressure dependency for the stability of hydrates implies that any major change in either of these controlling factors will also modify the zone of hydrate stability. A notable drop in sea level, for example, will reduce the hydrostatic pressure on the slope and rise, altering the temperature–pressure regime and leading to destabilization of the gas hydrates. It has been suggested that a sea level drop of nearly 120 m during the last glacial maximum (*c.* 30 000 to 18 000 years BP) reduced the hydrostatic pressure sufficiently to raise the lower limit of gas hydrate stability by about 20 m in the low latitudes. When a hydrate dissociates, its consistency changes from a solid to a mixture of sediment, water, and free gas. Experiments on the mechanical strength behavior of hydrates has shown that the hydrated sediment is markedly stronger than water ice (10 times stronger than ice at 260 K). Thus, such conversion would create a zone of weakness where sedimentary failure could take place, encouraging low-angle faulting and slumping on the continental margins. The common occurrence of Pleistocene slumps on the seafloor have been ascribed to this catastrophic mechanism and major slumps have been identified in sediments of this age in widely separated margins of the world.

When slumping occurs it would be accompanied by the liberation of a significant amount of methane trapped below the level of the slump, in addition to the gas emitted from the dissociated hydrate itself. These emissions are envisaged to increase in the low latitudes, along with the frequency of slumps, as glaciation progresses, eventually triggering a negative feedback to advancing glaciation, encouraging the termination of the glacial cycle. If such a scenario is true then there may be a built-in terminator to glaciation, via the gas hydrate connection.

In this scenario, the negative feedback to glaciation, can initially function effectively only in the lower latitudes. At higher latitudes glacially induced freezing would tend to delay the reversal, but once deglaciation begins, even a relatively small increase in atmospheric temperature of the higher latitudes could cause additional release of methane from near-surface sources, leading to further warming. One scenario suggests that a small triggering event and liberation of one or more Arctic gas pools could initiate massive release of methane frozen in the permafrost, leading to accelerated warming. The abrupt nature of the termination of the Younger Dryas glaciation (some 10 000 years ago) has been ascribed to such an event. Modeling results of the effect of a pulse of 'realistic' amount of methane release at the glacial termination as constrained by ice core records indicate that the direct radiative effects of such an emission event may be too small to account for deglaciation alone. However, with certain combinations of methane, CO_2, and heat transport changes, it may be possible to simulate changes of the same magnitude as those indicated by empirical data.

The Climate Feedback Loop

The paleoclimatic records of the recent past, e.g., Vostock ice core records of the past 420 000 years from Antarctica, show the relatively gradual decrease in atmospheric carbon dioxide and methane at the onset of glaciations. Deglaciations, on the other hand, tend to be relatively abrupt and are associated with equally rapid increases in carbon dioxide and methane. Glaciations are thought to be initiated by Milankovitch forcing (a combination of variations in the Earth's orbital eccentricity, obliquity and precession), a mechanism that also can explain the broad variations in glacial cycles, but not the relatively abrupt terminations. Degassing of carbon dioxide from the ocean surface alone cannot explain the relatively rapid switch from glacials to interglacials.

The delayed response to glacially induced sea level fall in the high latitudes (as compared with low latitudes) is a part of a feedback loop that could be an effective mechanism for explaining the rapid warmings at the end of glacial cycles (also known as the Dansgaard-Oeschger events) in the late Quaternary. These transitions often occur only on decadal to centennial time scales. In this scenario it is envisioned that the low-stand-induced slumping and methane emissions in lower latitudes lead to greenhouse warming and trigger a negative feedback to glaciation. This also leads to an increase in carbon dioxide degassing for the ocean. Once the higher latitudes are warmed by these effects, further release of methane from near-surface sources could provide a positive feedback to warming. The former (methane emissions in the low latitudes) would help force a reversal of the glacial cooling, and the latter (additional release of methane from higher latitudes) could reinforce the trend, resulting in apparent rapid warming observed at the end of the glacial cycles (see **Figure 2**).

The record of stable isotopes of carbon from Santa Barbara Basin, off California, has revealed rapid warmings in the late Quaternary that are synchronous with warmings associated with Dansgaard-Oeschger (D-O) events in the ice record from Greenland. The energy needed for these rapid warmings could have come from methane hydrate dissociation. Relatively large excursions of $\delta^{13}C$ (up to 5 ppm) in benthic foraminifera are associated with the D-O events. However, during several brief intervals the planktonics also show large negative shifts in $\delta^{13}C$ (up to 2.5 ppm), implying that the entire water column may have experienced rapid ^{12}C enrichment. One plausible mechanism for these changes may be the release of methane from the clathrates during the interstadials. Thus, abrupt warmings at the onset of D-O events may have been forced by dissociation of gas hydrates modulated by temperature changes in overlying intermediate waters.

For the optimal functioning of the negative–positive feedback model discussed above, methane would have to be constantly replenished from new and

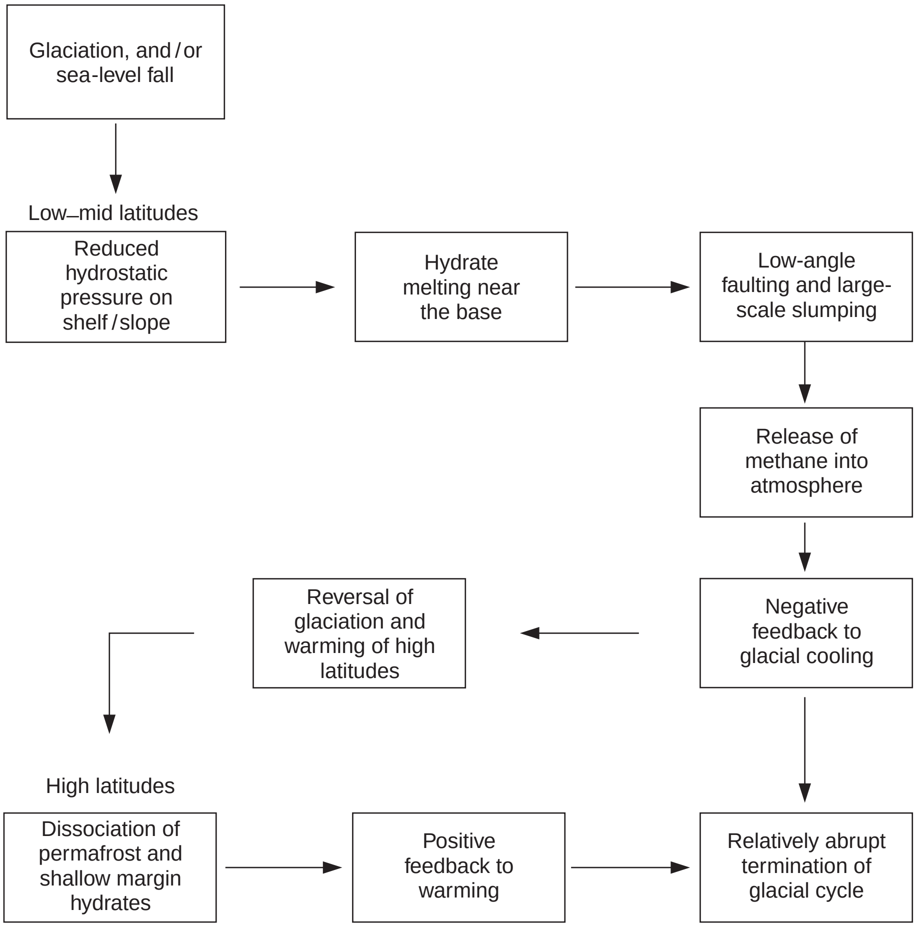

Figure 2 The negative–positive feedback loop model of sea level fall, hydrate decomposition, and climate change (reversal of glaciation and rapid warming) through methane release in the low and high latitudes. (Adapted with permission from Haq, 1993.)

larger sources during the switchover. Although as a greenhouse gas methane is nearly 10 times as effective as carbon dioxide, its residence time in the atmosphere is relatively short (on the order of a decade and a half), after which it reacts with the hydroxyl radical and oxidizes to carbon dioxide and water. The atmospheric retention of carbon dioxide is somewhat more complex than methane because it is readily transferred to other reservoirs, such as the oceans and the biota, from which it can re-enter the atmosphere. Carbon dioxide accounts for up to 80% of the contribution to greenhouse warming in the atmosphere. An effective residence time of about 230 years has been estimated for carbon dioxide. These retention times are short enough that for cumulative impact of methane and carbon dioxide through the negative–positive feedback loop to be effective methane levels would have to be continuously sustained from gas hydrate and permafrost sources. The feedback loop would close when a threshold is reached where sea level is once again high enough that it can stabilize the residual clathrates and encourage the genesis of new ones.

Several unresolved problems remain with the gas hydrate climate feedback model. The negative–positive feedback loop assumes a certain amount of time lag between events as they shift from lower to higher latitudes, but the duration of the lag remains unresolved, although a short duration (on decadal to centennial time scales) is implied by the ice core records. Also, it is not clear whether hydrate dissociation leads to initial warming, or warming caused by other factors leads to increased methane emissions from hydrates. Data gathered imply a time lag of *c.* 50 (± 10) years between abrupt warming and the peak in methane values at the Bølling transition (around 14 500 years Bp), although an increase in methane emissions seems to have begun almost simultaneously with the warming trend (± 5 years). However, this does not detract from the notion that there may be a built-in feedback between increased methane emissions from gas hydrate sources and accelerated warming. If smaller quantities of methane released from hydrated sediments are oxidized in the water column, initial releases of methane from dissociated hydrates may not produce a significant positive shift in the atmospheric content of methane. However, as the frequency of catastrophic releases from this source increases, more methane is expected to make it to the atmosphere. And, although the atmospheric residence time of methane itself is relatively short, when oxidized, it adds to the greenhouse forcing of carbon dioxide. This may explain the more gradual increase in methane, and is not inconsistent with the short temporal difference between the initiation of the warming trend and methane increase, as well as the time lag between the height of warming trend and the peak in methane values.

Although there is still no evidence to suggest that the main forcing for the initiation of deglaciation is to be found in hydrate dissociation, once begun, a positive feedback of methane emissions from hydrate sources (and its by-product, carbon dioxide) can only help accelerate the warming trend.

Gas Hydrates and the Long-Term Record of Climate Change

Are there any clues in the longer term geological record where cause and/or effect can be ascribed to gas hydrates? One potential clue for the release of significant volumes of methane into the ocean waters is the changes in δ^{13}C composition of the carbon reservoir. The δ^{13}C of methane in hydrates averages *c.* -60 ppm; perhaps the lightest (most enriched in ^{12}C) carbon anywhere in the Earth system. It has been argued that massive methane release from gas hydrate sources is the most likely mechanism for the pronounced input of carbon greatly enriched in ^{12}C during a period of rapid bottom-water warming. The dissolution of methane (and its oxidative by-product, CO_2) in the sea water should also coincide with increased dissolution of carbonate on the seafloor. Thus, a major negative shift in δ^{13}C that occurs together with an increase in benthic temperature (bottom-water warming) or a sea level fall event (reducing hydrostatic pressure) may provide clues to past behavior of gas hydrates.

A prominent excursion in global carbonate and organic matter δ^{13}C during the latest Paleocene peak warming has been explained as a consequence of such hydrate breakdown due to rapid warming of the bottom waters. The late Paleocene–early Eocene was a period of peak warming, and overall the warmest interval in the Cenozoic when latitudinal thermal gradients were greatly reduced. In the latest Paleocene bottom-water temperature also increased rapidly by as much as 4°C, with a coincident excursion of about -2 to -3 ppm in δ^{13}C of all carbon reservoirs in the global carbon cycle. A high resolution study of a sediment core straddling the Paleocene–Eocene boundary concluded that much of this carbon-isotopic shift occurred within no more than a few thousand years and was synchronous in oceans and on land, indicating a catastrophic release of carbon, probably from a methane source. The late Paleocene thermal maximum was also coincident with a major benthic foraminiferal mass extinction and widespread carbonate dissolution and low oxygen conditions on the seafloor. This rapid excursion cannot be explained by conventional mechanisms (increased volcanic emissions of carbon dioxide, changes in oceanic circulation and/or terrestrial and marine productivity, etc.). A rapid warming of bottom waters from 11 to 15°C could abruptly alter the sediment thermal gradients leading to methane release from gas hydrates. Increased flux of methane into the ocean–atmosphere system and its subsequent oxidation is considered sufficient to explain the -2.5 ppm excursion in δ^{13}C in the inorganic carbon reservoir. Explosive volcanism and rapid release of carbon dioxide and changes in the sources of bottom water during this time are considered to be plausible triggering mechanisms for the peak warming leading to hydrate dissociation. Another recent high-resolution study supports the methane hydrate connection to latest Paleocene abrupt climate change. Stable isotopic evidence from two widely separated sites from low- and southern high-latitude Atlantic Ocean indicates multiple injections of methane with global consequences during the relatively short interval at the end of Paleocene. Modeling results, as well as wide empirical data, suggest warm and wet climatic conditions with less vigorous atmospheric circulation during the late Paleocene thermal optimum.

The eustatic record of the late Paleocene–early Eocene could offer further clues for the behavior of the gas hydrates and their contribution to the overall peak warm period of this interval. The longer term trend shows a rising sea level through the latest Paleocene and early Eocene, but there are several shorter term sea level drops throughout this period and one prominent drop straddling the Paleocene–Eocene boundary (which could be an additional forcing component to hydrate dissociation for the terminal Paleocene event). Early Eocene is particularly rich in high-frequency sea level drops of several tens of meters. Could these events have contributed to the instability of gas hydrates, adding significant quantities of methane to the atmosphere and maintaining the general warming of the period? These ideas seem testable if detailed faunal and isotopic data for the interval in question were available with at least the same kind of resolution as that obtained for the latest Paleocene interval.

Timing of the Gas Hydrate Development

When did the gas hydrates first develop in the geological past? The specific low temperature–high pressure requirement for the stability of gas hydrates suggests that they may have existed at least since the latest Eocene, the timing of the first development of the oceanic psychrosphere and cold bottom waters. Theoretically clathrates could exist on the slope and rise when bottom-water temperatures approach those estimated for late Cretaceous and Paleogene (*c.* 7–15°C), although they would occur deeper within the sedimentary column and the stability zone would be relatively slimmer. A depth of *c.* 900 m below sea level has been estimated for the hydrate stability zone in the late Palecene. If the bottom waters were to warm up to 22°C only then would most margins of the world be free of gas hydrate accumulation. The implied thinner stability zone during warm bottom-water regimes, however, does not necessarily mean an overall reduced methane reservoir, since it also follows that the sub-hydrate free gas zone could be larger, making up to the hydrate deficiency.

Prior to late Eocene there is little evidence of large polar ice caps, and the mechanism for short-term sea level changes remains uncertain. And yet, the Mesozoic–Early Cenozoic eustatic history is replete with major sea level falls of 100 m or more that are comparable in magnitude, if not in frequency, to glacially induced eustatic changes of the late Neogene. If gas hydrates existed in the pre-glacial times, major sea level falls would imply that hydrate dissociation may have contributed significantly to climate change and shallow-seated tectonics along continental margins. However, such massive methane emissions should also be accompanied by prominent δ^{13}C excursions, as exemplified by the terminal Paleocene climatic optimum.

The role of gas hydrate as a significant source of greenhouse emissions in global change scenarios and as a major contributor of carbon in global carbon cycle remains controversial. It can only be resolved with more detailed studies of hydrated intervals, in conjunction with high-resolution studies of the ice cores, preferably with decadal time resolution. A better understanding of gas hydrates may well show their considerable role in controlling continental margin stratigraphy and shallow structure, as well as in global climatic change, and through it, as agents of biotic evolution.

See also

Methane Hydrates. Paleoceanography, Climate Models in.

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MICROBIAL LOOPS

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Introduction

The oceans contain a vast reservoir of dissolved, organically complex carbon and nutrients. At any given point in time, most of this dissolved organic matter (DOM) is refractory to biological utilization and decomposition. However, a significant flow of material cycles rapidly through a smaller labile pool and supports an important component of the food web based on bacterial production. The recapturing of this otherwise lost dissolved fraction of production by bacteria and its subsequent transfer to higher trophic levels by a chain of small protistan grazers was initially called the microbial loop by Farooq Azam and co-workers in the early 1980s. The following decades have been charecterized by remarkable discoveries of previously unknown life-forms and by major advances in our understanding of trophic pathways and concepts involving the seas' smallest organisms. In modern usage, the term microbial food web incorporates the original notion of the microbial loop within this broader base of microbially mediated processes and interactions.

Perspectives on an Evolving Paradigm

Although early studies date back more than a century, our understanding of the microbial ecology of the seas initially advanced slowly relative to other aspects of biological oceanography largely because of inadequate methods. Prior to the mid-1970s, for example, the simple task of assessing bacterial abundance in sea water was done indirectly, by counting the number of colonies formed when sea water was spread thinly over a nutritionally supplemented agar plate. We know now that about one marine bacterium in a thousand is 'culturable' by such methods. At the time, however, the low counts on media plates, typically tens to hundreds of cells per ml, were consistent with the then held view that sea water would not support a large and active assemblage of free-living bacteria. The role of bacteria was therefore assumed to be that of decomposers of organically rich microhabitats such as fecal pellets or detrital aggregates.

Coincidentally, early deficiencies in phytoplankton production estimates, due to trace metal contaminates and toxic rubber springs in water collection devices, were giving systematic underestimates of primary production, particularly in the low-nutrient central regions of the oceans that we now know to be dominated by microbial communities. For such regions, the low estimates of bacterial