Growth and decay of gas hydrates: a forcing mechanism for abrupt climate change and sediment wasting on ocean margins?

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ABSTRACT

High hydrostatic pressure, low bottom-water temperature and the presence of ample natural gas are important prerequisites for gas-hydrate genesis and stability in marine sediments. Sea-level rise and fall, a process that affects hydrostatic pressure, is therefore a prime factor in controlling the growth and decay of gas hydrates along continental margins. Gas hydrates (largely methane and water) solidify and grow when sea-level rises appreciably and hydrostatic pressure on the margins is enhanced. Major sealevel falls, such as those caused by glaciation, reduce hydrostatic pressure, leading to decomposition of the hydrates. The substitution of solid hydrate with water and free gas develops a zone of weakened sediment strength at the lower limit of the hydrate which becomes more susceptible to faulting and slumping.

Breakdown of gas hydrates and ensuing slumps can conceivably release large amount of methane into the atmosphere. If the previous eustatic fall were glacially forced, addition of large quantities of methane from low-latitude gas hydrate fields could provide a negative feedback to glacial cooling, leading to the reversal of the course of glaciation. As climates in high latitudes ameliorate, additional methane could be released from the near-surface sources of shallow marine areas and the permafrost on land, providing a positive feedback to the warming trend, eventually tenninating the glacial cycle relatively rapidly. The model of potential negative-positive climatic feedback associated with gas-hydrate destabilization is based on several ideas put forward earlier and is discussed at length. It is underscored that gas hydrates may play important roles in modifying the stratigraphic patterns along continental margins and in forcing abrupt climatic change.

INTRODUCTION

Gas hydrates, also known as clathrates, are solid, ice-like, crystalline phase of natural gas and water that become stable under either very low temperature, or moderately low temperature and high pressure conditions (fig. 1). These prerequisites are met in the permafrost on land and in the seafloor sediments on the outer continental margins. Most gas hydrates are composed predominantly of methane (99%), but hydrates with significant amount of other gases, such as

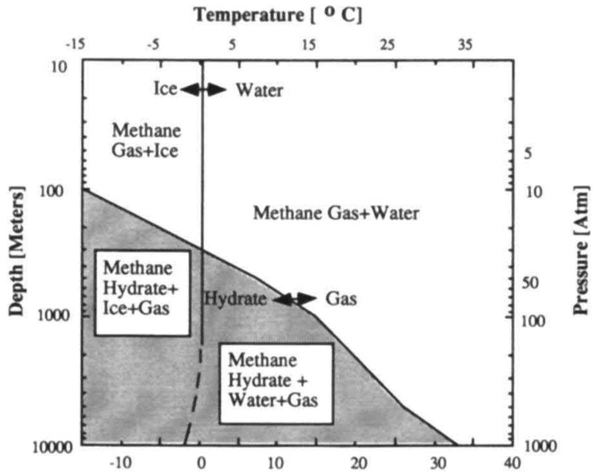

Fig. 1. A gas hydrate phase diagram. The figure shows temperature and pressure (or depth) dependent boundaries between hydrate (shaded area) and free gas, and between ice and water. Redrawn from Kvenvolden (1988).

carbon dioxide and hydrogen sulfide, and smaller quantities of ethane and propane, are also known.The low temperature-high pressure conditions necessary for the stability of gas hydrates in marine sediments are manifested in water depth exceeding 300 m. The gas hydrate zone within the sediment column can potentially extend from the seafloor down to 1100 m sub-bottom. However, the vertical distribution of the clathrate within this zone is more likely to be patchy and discontinuous. In the high latitudes of the Arctic (and also presumably around the Antarctic, although such data are lacking), where bottom water temperatures are sufficiently low, hydrates may form in marine sediments at shallower depths. On land at these latitudes significant quantities of clathrates occur a few cm below the surface of the permafrost. At present permafrost is distributed over as much as 20% of the land area in the northern Hemisphere.

Relatively high gas content is required to form hydrates. Rapidly deposited sediments with high biogenic content are more amenable to the production of large quantities of methane by bacterial alteration of the contained organic matter. Thus, another important limiting factor for gas hydrate occurrence may be the generation of large enough quantities of gas in marine sediment to stabilize the clathrate structure (Kvenvolden and Barnard, 1983). A molar ratio of methane to water of 1: 6 is required in an ideally saturated methane hydrate, which translates to a volumetric ratio of about 164:1 (Kvenvolden, 1988).

DETECTION OF GAS HYDRATES AND THEIR QUANTITATIVE ESTIMATES

On continental margins gas hydrates can be detected through the presence of the so called bottom simulating reflectors (BSR's) on seismic reflection profiles, which delineate the base of the clathrate concentration zone (fig. 2). However, such seismic reflection indicators may not always be observable in the presence of gas hydrates. The BSR's represent diagenetic boundaries and often cut across local depositional surfaces. The acoustic velocity change marking the BSR represents the transition between hydrate-cemented sediments above and water-filled uncemented or gas-charged sediments below (Dillon and Paull, 1983). Although the BSR's have been observed in sediments of many continental margins around the world, clathrates have only been sampled rarely, and the estimates of methane trapped within gas hydrate zones, or the free gas below them, remain speculative. Several important questions about BSR's remain unanswered: Do all BSR's mark the transition between clathrate and free gas? How often does the gas hydrate zone above the BSR extend (as is often assumed) to the seafloor? Is the distribution of solid hydrates within this zone continuous or patchy? How large are the quantities of free gas trapped below BSR's (in large reservoirs gas hydrates could function as stratigraphic seal for the trapped natural gas)? These and other questions need to be answered before BSR' s can provide a direct and meaningful indication of the size of methane reservoir in gas hydrates.

The lack of direct observations and sampling makes it difficult to estimate total methane trapped in gas hydrates with any degree of accuracy. The estimates of methane in hydrates range widely from 1.7 10^3 to 41.1 10^4 Gt (1 Gigaton $= 10^{15}$ grams). Kvenvolden (1988) cites widely differing estimates of total methane carbon in gas hydrates (between 2 10^3 to 4 10^6 Gt), but favors a

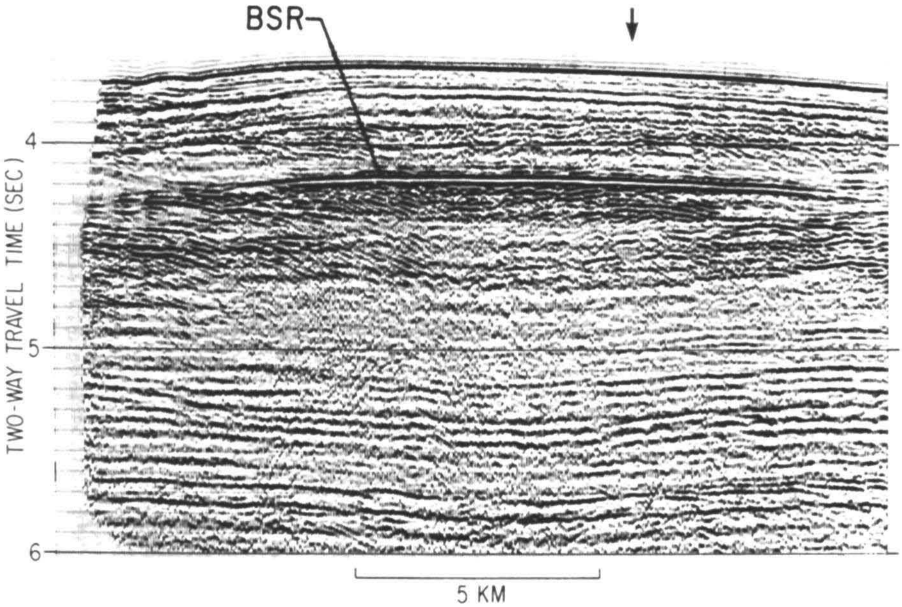

Fig. 2. A bottom simulating reflector (BSR), boundary between solid clathrate above and free gas below, from the axis of Blake Ridge (after Dillon and Paull, 1983).

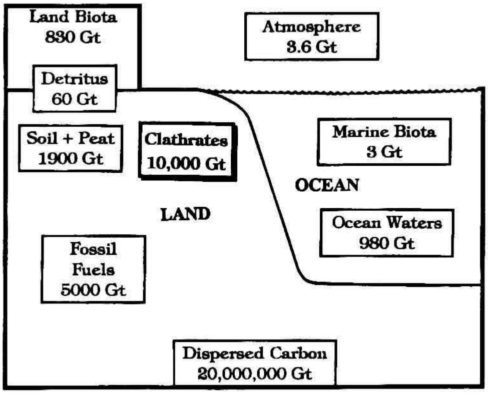

Fig. 3. The Bolin estimates of global organic carbon tied up in various sources in gigatons (1 Gt $= 10^{15}$ g) (after Kvenvolden, 1988).

somewhat conservative estimate of $1 - 10^4$ Gt of carbon sequestered in methane hydrates on continental margins (fig. 3). This estimate of gas-hydrate carbon exceeds estimates of organic carbon from all other sources (ca. 0.9 10^4 Gt) and is double the estimate of carbon from fossil fuel sources. The carbon tied up in gas hydrates therefore represents a significant portion of total carbon within the shallow geosphere, second only to the total pool of widely dispersed organic carbon in sedimentary rocks (ca. 2 10^7 Gt). And yet, the gas-hydrate source of carbon has so far largely been ignored in considerations of the global carbon cycle (Kvenvolden, 1988).

GAS HYDRATE INSTABILITY AS A FORCING MECHANISM FOR ABRUPT CLIMATE CHANGE

The special low temperature-high pressure relationship necessary for the stability of gas hydrates (see fig. 1) implies that any major change in either of these parameters will tend to alter the zone of hydrate stability. For example, a significant drop in eustatic sea level will reduce the hydrostatic pressure on the continental shelf, slope and rise, altering the temperature-pressure regime, leading to destabilization of the gas hydrates. Paull et al. (1991) have offered a model of gas hydrate instability caused by sea-level fall associated with the Pleistocene glaciation that may have led to major slumping on the continental margins. A sea level drop of ca. 120 m during the Pleistocene reduced the hydrostatic pressure sufficiently to raise the lower boundary of gas hydrates by an estimated 20 m (Dillon and Paull, 1983). The ensuing destabilization created a zone of weakness where solid clathrate was replaced by a slushy mixture of free gas and water that was more susceptible to sedimentary failure, leading to major slumps along the continental margins worldwide. They ascribe the occurrence of common Pleistocene slumps on the seafloor to this mechanism. McIver (1977, 1982) was the first to recognize the possible causal relationship between gas hydrates and submarine slumps. Since then such slumps have been identified in young sediments of widely separated margins of the world (Kvenvolden, 1993).

Submarine slumping could be accompanied by liberation of large volumes of methane trapped below the levels of the slumps, injecting significant amount of this greenhouse gas into the atmosphere as well defined peaks on the curve. These spikes would tend to become larger and more frequent and would be associated with increased frequency of slumps as glaciation progresses. This would eventually trigger a negative feedback to glaciation, leading to the termination of the glacial cycle. Paull et al. (1991) attributed the abrupt nature of Pleistocene glacial terminations to this process.

The glacially-forced sea-level lowering leading to slumping and release of methane providing negative feedback to glaciation can at first function effectively only in tropical to temperate latitudes. At higher latitudes glacially-induced freezing would tend to delay the negative feedback effect, but once deglaciation begins, even a relatively small (a few degrees) increase in atmospheric temperature of the higher latitudes could cause release of methane from near-surface sources, providing a positive feedback to warming. Nisbet (1990) suggested that a small triggering event and liberation of one or more Arctic gas pools could initiate massive release of methane from the permafrost. The strong positive feedback would provide increased emissions of methane and accelerated warming. Nisbet ascribed the abrupt nature of the younger Dryas termination (some 10 Ka. ago, see fig. 3) to such an event and suggested that gas hydrates may play a dominant role, more important than ocean degassing, in recharging the biosphere with CO_2 at the end of the glaciation.

THE NEGATIVE-POSITIVE FEEDBACK LOOP

The paleoclimatic record of the recent past, e.g. ice-core record of the past 200 k.yrs., clearly shows gradual decrease in CO_2 and methane at the onset of glaciations (fig. 4). Deglaciations, on the other hand, tend to be relatively abrupt and are associated with rapid increases in methane and CO_2 While Milankovitch orbital forcing can explain the broad variations in glacial cycles, it fails to account for the relatively abrupt terminations. Oceanic degassing of CO_2 alone cannot explain the relatively rapid switch from glacials to interglacials (Nisbet, 1990). To explain the combined effect of glacially-induced sea-level lowering leading to gas hydrate instability, and low-latitude warming leading to higher latitude release of methane, Haq (1993) extended these notions into a 'negative-positive feedback' model (fig. 5). A similar feedback mechanism was also suggested by Kvenvolden (1993).

The initially delayed effect of sea-level fall in the high versus low latitudes constitutes a negative and then positive feedback loop that could be an effective mechanism for terminating ice ages. It may be that a combined effect of low seastand induced slumping and methane emissions in low latitudes triggers a negative feedback to glaciation as sugges ted by Paull et al. (1991), and the en-

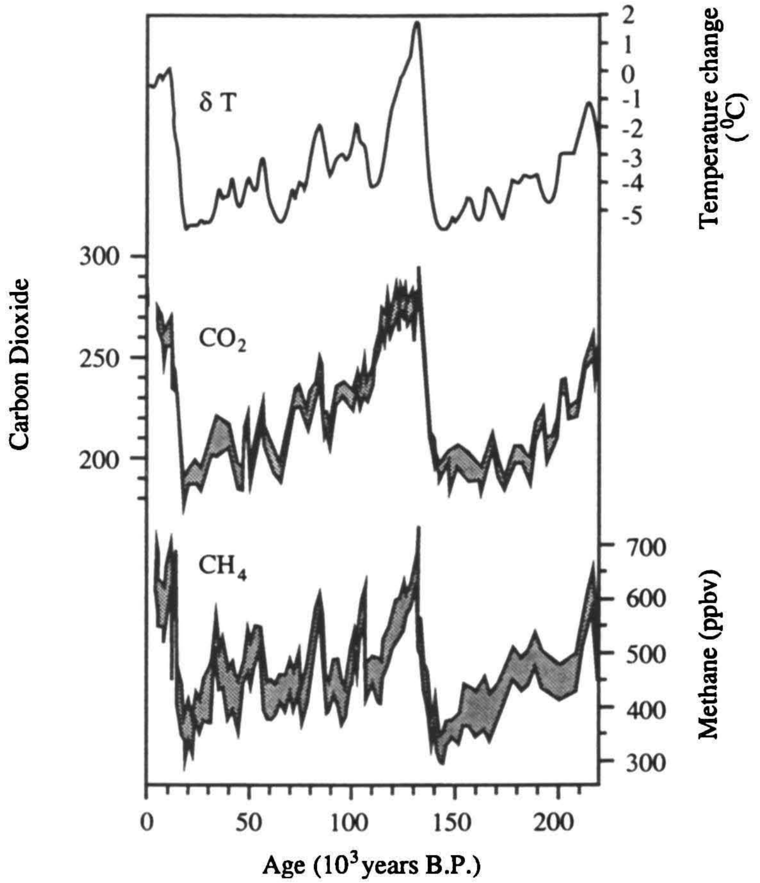

Fig. 4. Ice-core record of from Antarctic Vostock ice core showing simultaneous temperature, carbon dioxide and methane variations over the past 200 k.yrs. (modified after Jouzel et al., 1993).

suing positive feedback from ocean CO_2 degassing and warming in higher latitudes leads to further release of methane from near-surface sources of the permafrost as envisioned by Nisbet (1990). These mechanisms would reinforce a relatively rapid termination of the glacial cycle. The present day estimate of methane in the atmosphere is 3.6 Gt of carbon (Kvenvolden, 1988). Thus, even a small amount of methane release from the vast gas hydrate reservoir could conceivably double the atmospheric methane content and cause increased greenhouse warming lasting a decade or more.

Although methane is nearly ten times as effective as CO_2 (by weight) as a greenhouse gas, its residence time in the atmosphere is only on the order of a decade and a half (Lashof and Ahuja, 1990). During this time it reacts with the hydroxyl radical and oxidizes to CO_2 and water. The atmospheric retention of CO_2 is somewhat more complex because it is readily transferred to other reservoirs, such as oceans and the biota, from which it can reenter the atmosphere. Lashof and Ahuja (1990) estimate an effective average residence time of

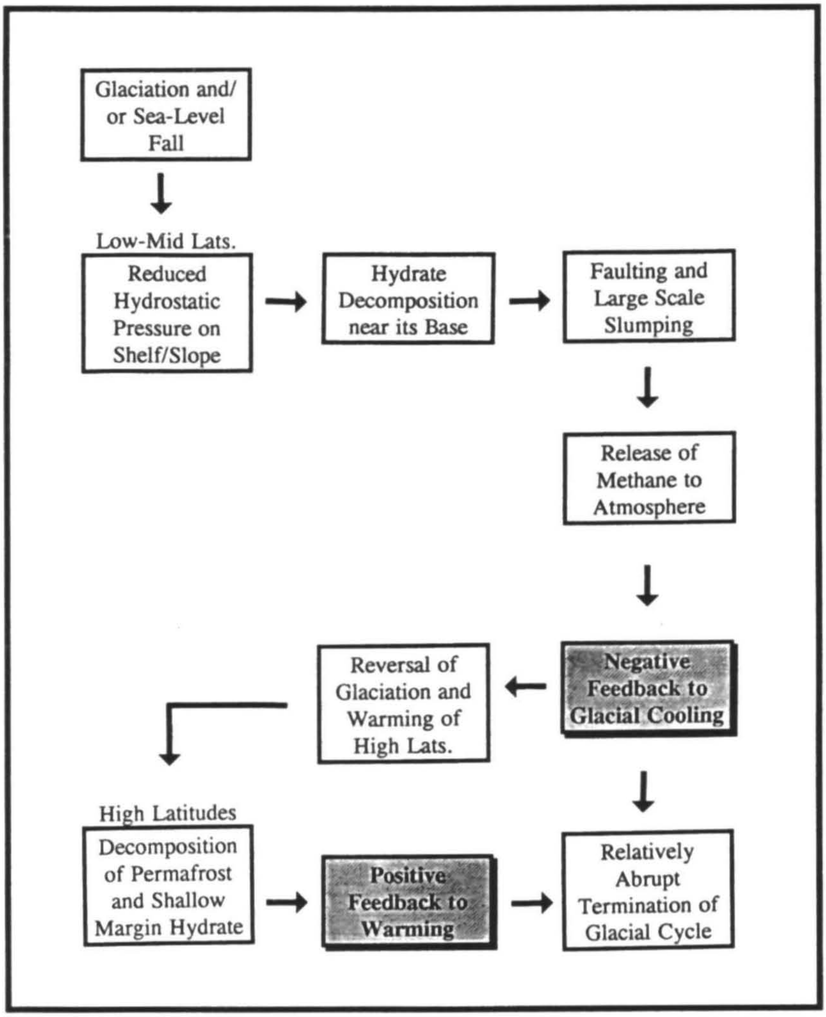

Fig. 5. The negative-positive feedback loop of sea-level rise and fall, gas-hydrate growth and decay, and climate change through methane release (after Haq, 1993).

ca. 230 years for CO_2. This gas accounts for up to 80% of the contribution to greenhouse warming in the atmosphere.

The relatively short residence time of methane in the atmosphere means that for the optimal functioning of the negative-positive feedback model, methane would have to be continuously replenished during the switchover from new and larger sources. Once significant quantities of methane are released into the atmosphere and the greenhouse effect is enhanced, further release of methane could become self-sustaining (Nisbet, 1990). These short retention times mean that in order for the cumulative impact of methane and CO_2 to be effective both methane and CO_2 must continuously enter the system through the feedback process: methane from continental margin and permafrost clathrate sources, and CO_2 from the degassing of the ocean water, until that threshold is reached where the sea level is high enough that it can once again affect gas-hydrate genesis and stabilization.

GAS HYDRATE INSTABILITY AND DESTRUCTIVE PROCESSES ON CONTINENTAL MARGINS

The above observations open an intriguing possibility that past sea-level lowerings, especially major eustatic falls, may have been accompanied by massive slumping and mass wasting along the margins. Slumping need not be forced by gravity-driven slope failure alone, but may also be due to development of zones of weakness within the sedimentary column related to the breakdown of gas hydrates.

In a simply stated scenario, the breakdown of gas hydrate in lower latitudes occurs in response to drastic reduction in hydrostatic pressure on the shelf/slope and rise following a major drop in sea level. This causes the base of the hydrate zone to migrate upward by an amount that depends on the overall change in the temperature-pressure regime that determines the clathrate stability. The base of the gas hydrate is first to destabilize because it is at the limit of stability, below which geothermal gradient increases more rapidly. Where the solid clathrate turns into slushy mixture of free gas and water it generates a zone of greatly decreased sediment strength which can act as a lubricated horizon that is more prone to faulting and block slumping. Weakening of mechanical strength of sediments leading to megaslumps may be an important first-order mechanism for tectonic activity on continental margins. This may be evidenced in the Carolina Trough area, off the East Coast of the United States, by the association of slump features and numerous faults that sole out at or above the BSR levels (Paull et al., 1989).

TIMING OF THE DEVELOPMENT OF GAS-HYDRATE

When did the gas hydrates first develop in the geological past? The special low temperature-high pressure requirement for the stability of gas hydrates suggests that they have existed at least since the latest Eocene, the timing of the first development of the oceanic psychrosphere and cold bottom waters. Prior to that, bottom waters in the world ocean are inferred to have been relatively warm even in the higher latitudes. This raises questions about the presence of hydrates in pre-psychrospheric times. Does this imply that gas hydrates are a relatively recent, largely post-Eocene, phenomenon? Or could hydrostatic pressure alone have maintained the clathrate stability? According to gas-hydrate stability window (Kvenvolden and Barnard, 1983) it seems apparent that bottom water temperature need not be very low, but instead the geothermal gradient within the sediments and the hydrostatic pressure above would be more critical for clathrate stability. Clathrates could exist on the continental slope and rise where the bottom-water temperatures reach those estimated for Late Cretaceous and Paleogene (ca. 7° – 10° C), though they would tend to occur deeper within the sedimentary column and would be of relatively smaller thickness.

In the pre-Oligocene there were no large ice caps, and the mechanism for short-term sea-level changes also remains uncertain. And yet, the Mesozoic-early Cenozoic eustatic history is replete with major sea-level falls in the range of 50 to 130 m that are comparable in magnitude, if not in frequency, to glacially-induced eustatic changes (see Haq et al., 1988). If gas hydrates existed in the pre-Oligocene, major sea-level falls would imply that hydrate destabilization may have contributed significantly to shallow-seated tectonics along continental margins.

Is there geological evidence of increased frequency of slumping associated with major eustatic falls in the pre-Oligocene which could be ascribed to gas-hydrate breakdown? As a test case one could look for such evidence on seismic data for erosion and slumps along continental margins that can be tied to sea-level falls (e.g., Mountain, 1987). Various studies along ocean margins have made it clear that sediment accumulation and preservation patterns result from a complex interaction of sea-level changes, fluctuating sediment supply rates and seafloor subsidence, and along-margin and abyssal current flow. But perhaps destabilization and movement of sediment wedges caused by gas-hydrate breakdown during lowstand times have also played a significant, but largely unrecognized, role.

In a seismic study of the New Jersey margin of the US. East Coast, Mountain (1987) documented buried canyons, massive erosion and slumps within the sediment wedges. One upper Cretaceous and four Paleogene periods of slope failure, slumping and infilling along the continental slope were mapped. The Paleogene events occurred near the Cretaceous-Tertiary boundary, at the Paleocene-Eocene boundary, at the top of Lower Eocene, and in the Middle Eocene. In addition, Mountain and Tucholke (1985) have shown a widespread unconformity near the Eocene/Oligocene boundary which wiped out much of the Oligocene stratigraphic record. Another major unconformity with slump sediments on top is dated as mid Miocene (see fig. 6). These unconformities represent hiatuses of one to several million years and have little or no shallow water debris resting on them. Channeling on the lower slope seems to be coincident with the hiatuses and channels are often partly filled by slump debris. Mountain and Tucholke (1985) and Mountain (1987) proposed that these unconformities were related to slope failure following episodic collapse of the underlying Mesozoic carhonate margin. The presence of coeval onlapping units at the foot of the slope associated with the unconformities also suggested shelf erosion and transportation of sediment during the low seastand times.

All of the events documented by Mountain and Tucholke (1985) and Mountain (1987) occur close to major sea-level lowstands (see Haq et al., 1987). In particular, the events near the Paleocene-Eocene boundary, at the top of Lower Eocene and in the middle Miocene are associated with major slumps. The latter two are associated with a clear evidence of a megaslumps, which are compositionally similar to enclosing sediments and apparently traveled some distance

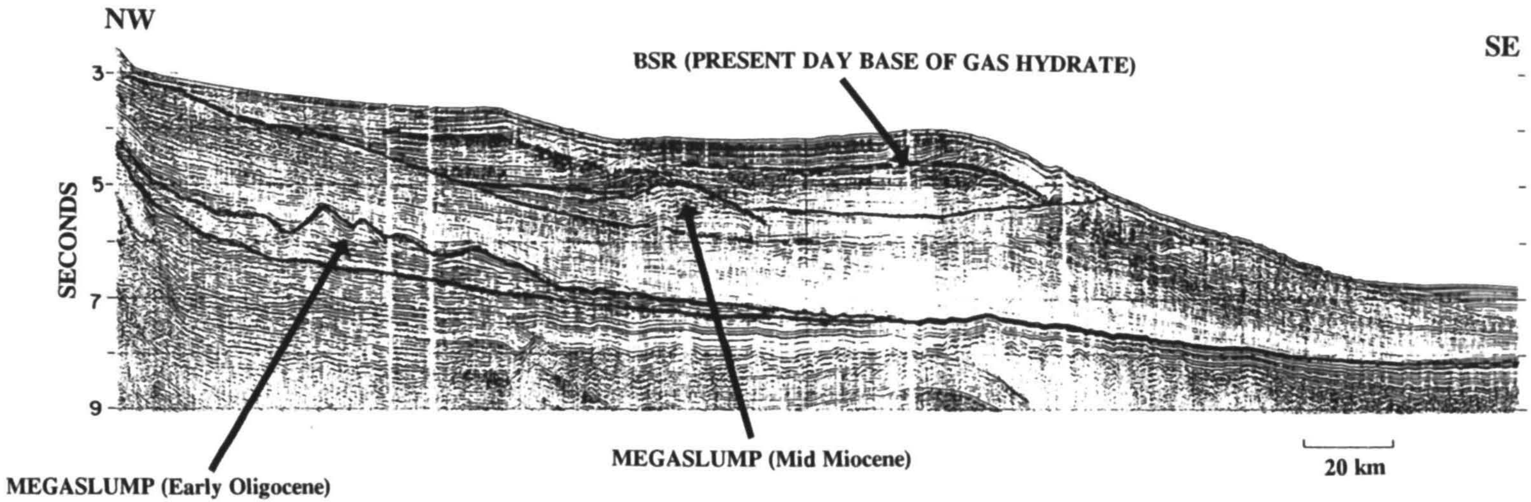

Fig. 6. Seismic line off the coast of North Carolina, US. Atlantic margin, showing the present-day BSR, and two large slump features sitting on top of late Eocene/Early Oligocene and mid Miocene unconformities (slightly modified after Mountain and Tucholke, 1985).

downslope to their present positions (fig. 6). Mountain (1987) ascribed the slope detachment and slumping to diagenesis and/or local faulting. However, these downward movements of sediment wedges, with some of the original bedding still intact, are more readily explained by gas-hydrate destabilization following lowered sea level and reduced hydrostatic pressure on the shelf and slope. Mountain (1987) wondered what process could be responsible for unconformities that appear to develop simultaneously on shelf and rise. Slump scar unconformities caused by downslope movement of large sediment blocks over lubricated horizons of destabilized gas hydrates would produce just such an effect (see fig. 6).

Another example of slope scour and associated seafloor unconformity that could be attributed to gas hydrate destabilization is provided by Angstadt et al. (1983) in their study of the seismic data from the southeastern Gulf of Mexico. Two deep-sea drill sites in the area provide a precise age for the missing section and it is clear that this prominent unconformity is centered on a global sea-level lowering event near the Middle/Late Eocene boundary at 39.5 Ma (Haq et al., 1987). The rough surface of the unconformity was also interpreted as due to channelized flow. Angstadt et al. (1983) ascribed the event to slope instability and mass wasting. They argued that bottom effects of surface currents in the region would not be intense enough to erode at water depths of 2 to 3 km. However, intensified currents due to climatic cooling, and retreat of shoreline due to sea-level lowering may have combined to affect the event. They go on to speculate that perhaps a meteoritic impact (postulated for the Late Eocene) may have been partially responsible, causing rapid, high-magnitude, sea-level changes and intensified currents that would have triggered gravity flows and seafloor erosion.

Once again, the decomposition of gas hydrates on the slope of the Florida Escarpment caused by a major sea-level drop at 39.5 Ma (Haq et al., 1987) and the ensuing mass wasting provide a simpler and more probable scenario for this and similar events on margins elsewhere, especially if a connection with eustatic lowering can be established.

When we consider the non-glacial world, the eustatic fall-related methane release as an agent of global climate change can be effective over a long term (on the time scales of million years) only if methane is replenished continuously over a long period. This implies that the total duration of lowstand would be an important factor in determining the long-term effect on climatic change – long, sustained lowstands would cause continued and increasingly frequent slumps and release of methane, leading to longer lasting climatic change.

In this context, we could examine two case studies of the Paleogene sea-level falls. A major sea-level drop of estimated 110–130 m occurred near the termination of Early Eocene (49.5 Ma event of Haq et al., 1987) but was relatively short lived, lasting ca. 0.5 m.y. In contrast, the major sea-level fall in the mid Oligocene (30 Ma event of Haq et al., 1987) is estimated to be ca 150–180 m. This was followed by minor fluctuation of the baseline for several million years. The overall sea level during this hme remained lower than that in the Early

Ohgocene, returmng to a sustained highstand only in the Aquitanian. The first event has already been shown to be associated with megaslump features on the New Jersey margin (the top of Lower Eocene event of Mountain, 1987). The mid-Oligocene event should be associated with significant number of slumps along ancient continental margins and should have had a more lasting effect on the climate. However, the effect of a long-term overall sea-level retreat also means that there are lesser chances of finding this record intact due to extensive erosion accompanying each successive sea-level fall. This may be the reason for the general worldwide dearth of shallow marine strata of Oligocene age (and particularly upper part of the Epoch). These ideas need to be tested.

CONCLUDING REMARKS

It is very likely that fluctuations in the gas hydrate stability has been an important factor in reshaping continental margin stratigraphy. As agents of periodic slumping and block sliding they may have played a significant role in modifying stratigraphic patterns, particularly during the lowstand phases of the eustatic cycles.

The role of gas-hydrate breakdown in the rearrangement of sediment wedges is obviously a complex issue. Some of the ideas concerning this role have been touched upon here, but many major questions about gas hydrates remain unanswered. Notwithstanding the importance of clathrates in sedimentary geology and global paleoclimate, surprizingly little research has been attempted on this topic. A better understanding of the mechanics of gas hydrates growth, decay and distribution patterns is critically needed to evaluate their considerable role in controlling continental margin stratigraphy and tectonics, as well as in global climatic change, and by implication, their potential as agents of biotic evolution. A systematic search for evidence of major slumping amd normal amd growth faulang assoriated with gas. Hydrate destabilization needs to be carried out using existing seismic and stratigraphic data along continental margins. A much greater research effort is warranted to unravel the enigma of gas hydrates. Clathrates may also prove to be an important untapped resource of energy for the future, both as a direct source of natural gas and as potential stratigraphic seals for the large pools of free gas below.

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REFERENCES

Angstadt, D.M., J.A. Austin Jr. and R.T. Buffler – Deep-sea erosional unconformity in the southeastern Gulf of Mexico. Geology 11, 215–218 (1983).

Dillon, W.P. and C.K. Paull – Marine gas hydrates II: Geophysical evidence. In: L.L. Cox (ed.), Natural gas hydrates, properties, occurrence, recovery. Butterworth, Woburn, Massachusetts. Pp. 73–90 (1983).
Haq, B.U. – Deep sea response to eustatic change and the significance of gas hydrates for continental margin stratigraphy. Spec. Publ. Int. Ass. Sediment. **18**, 93–106 (1993).
Haq, B.U., J. Hardenbol and P.R. Vail – Chronology of fluctuating sea levels since the Triassic. Science **235**, 1156–1167 (1987).
Haq, B.U., J. Hardenbol and P.R. Vail – Mesozoic and Cenozoic Chronostratigraphy and eustatic cycles. Soc. Econom. Paleont. Mineral., Special Publ. **42**, 71–108 (1988).
Jouzel, J. et al. – Extending the Vostock ice-core record of paleoclimate to the penultimate glacial period. Nature **364**, 407–412 (1993).
Kvenvolden, K.A. – Methane hydrates - A major reservoir of carbon in shallow geosphere. Chem. Geol. **71**, 41–51 (1988).
Kvenvolden, K.A. – Gas hydrates - Geological perspective and global change. Reviews of Geophysc. **31** (2), 173–187 (1993).
Kvenvolden, K.A. and L.A. Barnard – Hydrates of natural gas in continental margins. Am. Ass. Petroleum Geol., Mem. **34**, 631–640 (1983).
Lashof, D.A. and D.R. Ahuja – Relative contribution of greenhouse gas emissions to global warming. Nature **344**, 529–531 (1990).
McIver, R.D. – Hydrates of natural gas - Important agent in geological pcesses. Geol. Soc. Am. Abstr. Progams **9**, 1989–90 (1977).
McIver, R.D. – Role of naturally occurring gas hydrates in sediment transport. Am. Assoc. petrol. Geol. Bull. **66**, 789–792 (1982).
Mountain, G.S. – Cenozoic margin construction and destruction offshore New Jersey. Cushman Found. Foraminiferal Research, Special Publ. **24**, 57–83 (1987).
Mountain, G.S. and B.E. Tucholke – Mesozoic and Cenozoic geology of the US. Atlantic continental slope and rise. In: W.C. Poag, (ed.), Geologic Evolution of the United States Atlantic Margin. Van Nostrand Reinhold, New York. pp. 293–341 (1985).
Nisbet, E.G. – The end of ice age. Canadian J. Earth Sci. **27**, 148–157 (1990).
Paull, C.K., E.A. Schmuck, J. Chanton, F.T. Mannheim and T.J. Bralower – Carolina Trough diapirs: Salt or shale? EOS, Trans. Am. Geophys. U. (Abstracts) **70**, 370 (1989).
Paull, C.K., W. Ussler and W.P. Dillon – Is the extent of glaciation limited by marine gas hydrates. Am. Geophy. Un., 4 32–434 (1991).