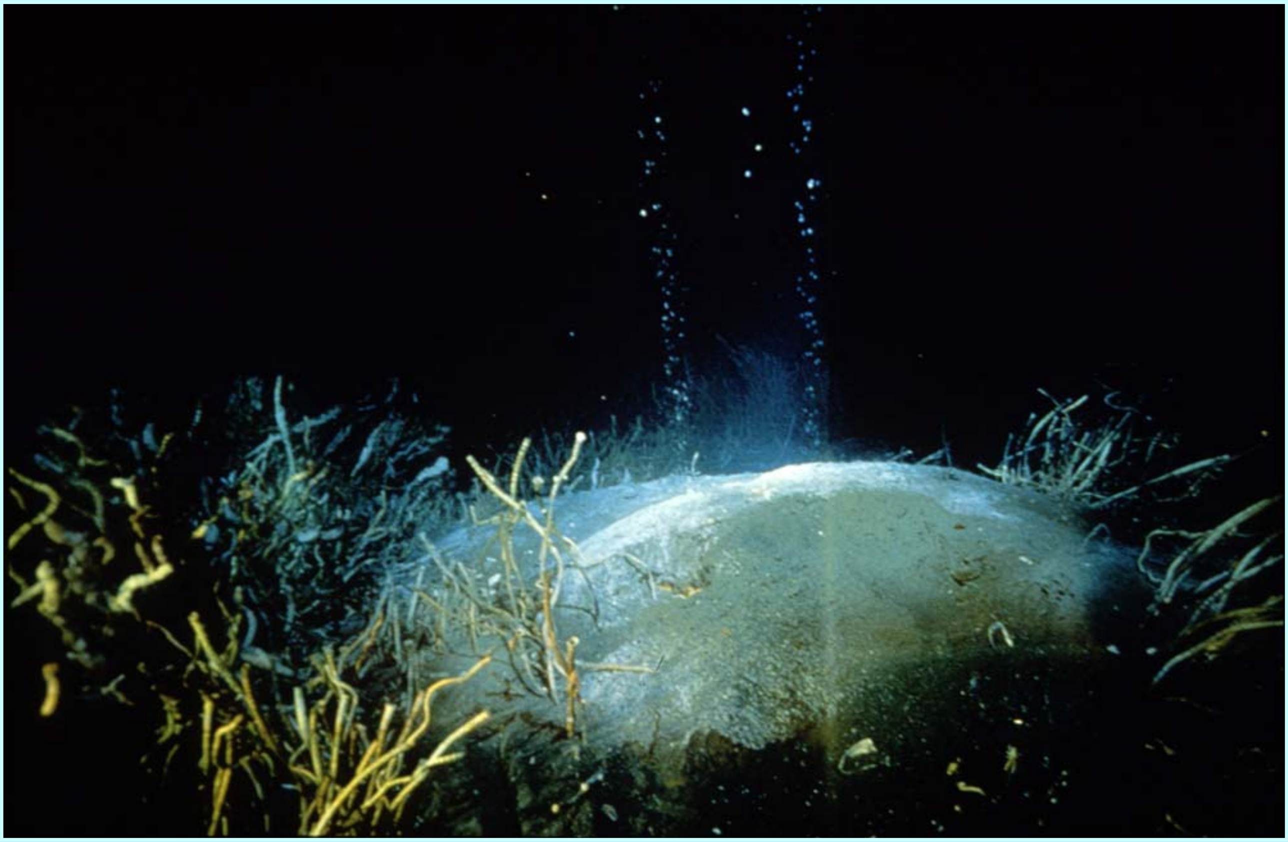
Report of the
Methane Hydrate Advisory Committee
on
Methane Hydrate Issues and Opportunities
Including Assessment of Uncertainty of the Impact of Methane Hydrate on Global Climate Change



December 2002

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Methane Hydrate Issues and Opportunities Including Assessment of Uncertainty of the Impact of Methane Hydrate on Global Climate Change

The Methane Hydrate Advisory Committee was established by the Secretary of Energy in November 2000 in compliance with the requirements of the Methane Hydrate Research and Development Act of 2000, Public Law 106-193. The Advisory Committee advises the Secretary on potential applications of methane hydrate and assists in developing recommendations and priorities for the methane hydrate research program. Consistent with the legislation, one of the tasks assumed by the Committee was the preparation of a report assessing the potential impact on global climate change from methane hydrate formation, methane hydrate degassing, and consumption of natural gas produced from methane hydrates.

As noted in this report, the possible impact on global climate is one of several key issues related to methane hydrate currently being studied. Other issues include the emerging resource potential of methane hydrates, and the implications of methane hydrate on the safety of offshore facilities and on seafloor stability.

Funding by the government and private sectors has accelerated the progress made in these areas in recent years, however continued Federal investment is recommended to maintain the momentum in making production of methane from hydrate commercially viable. This is an active global effort in which the United States should sustain its preeminent role.

What is Methane Hydrate?

Methane hydrate is an ice-like crystalline substance that is essentially frozen methane. It forms when water and methane gas combine under conditions of relatively high pressure and low temperature (Figure 1). While the most common gas hydrate on earth is methane hydrate, other gases also form hydrates. These include hydrocarbon gases such as ethane and propane as well as non-hydrocarbon gases such as CO_2 and H_2S (Figure 2). Methane hydrate occurs naturally in sediments associated with deep permafrost in Arctic environments and is widespread in the uppermost few hundred meters of slope and rise sediments in continental margins where the appropriate conditions of temperature and pressure exist (Figures 3 and 4).

Methane hydrate forms at appropriate pressure and temperature conditions and where sufficient gas is present. These conditions are common at water depths greater than 500 meters (1600 feet) at mid to low latitudes and greater than 150–200 meters (500–650 feet) at high latitudes. At these water depths, hydrate can occur within a stability zone that extends into the marine sediments to depths of tens to hundreds of meters beneath the seafloor. The thickness of the hydrate stability zone varies with temperature, pressure, composition of the hydrate-forming gas, underlying geologic conditions, water depth, and other factors.

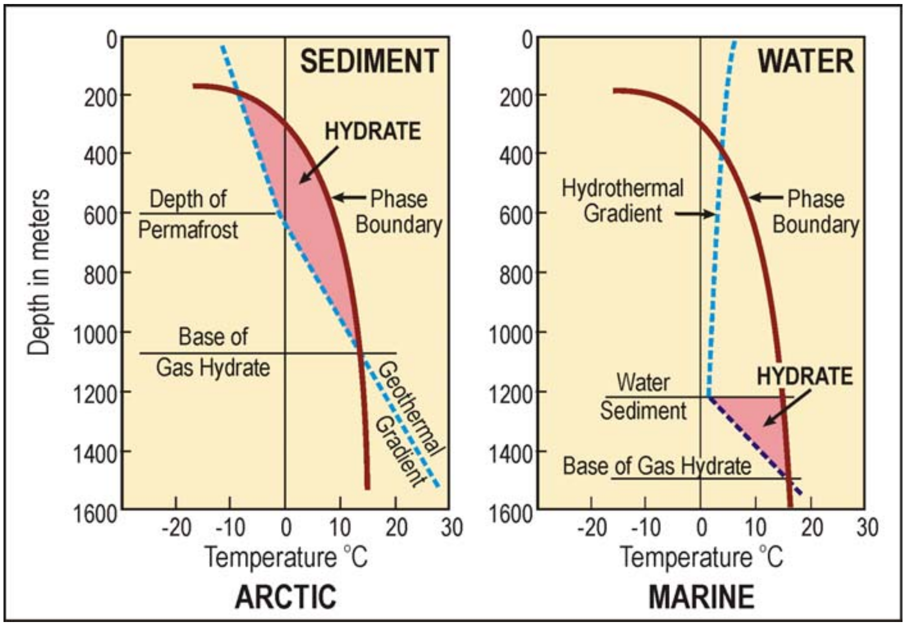

Figure 1. Phase diagrams for methane hydrate in both Arctic permafrost and marine continental margin settings.

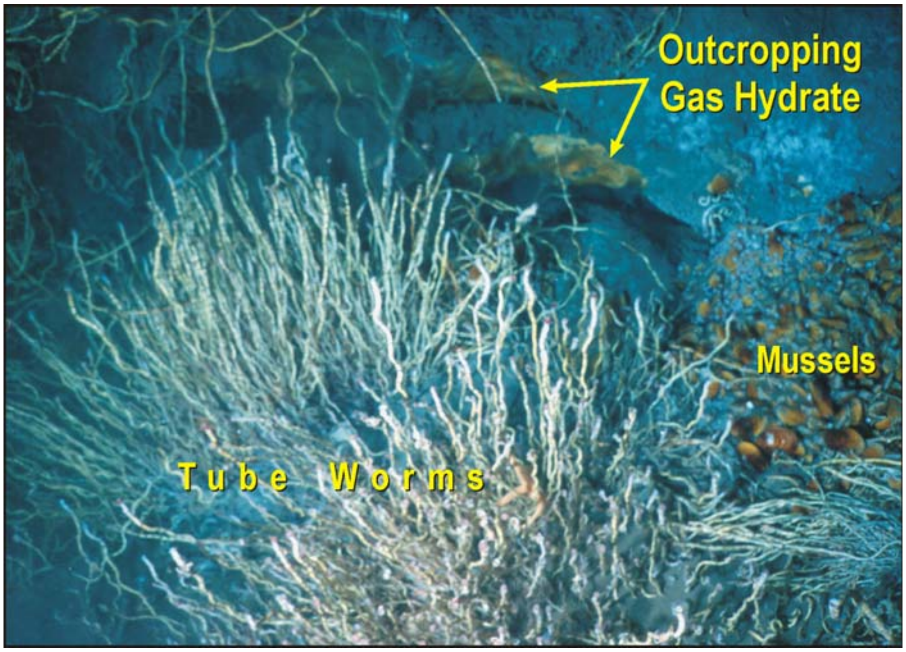

Figure 2. Outcropping exposures of gas hydrate and unique associated chemosynthetic organisms (tube worms and mussels) on the Gulf of Mexico continental slope (water depth 575 m).

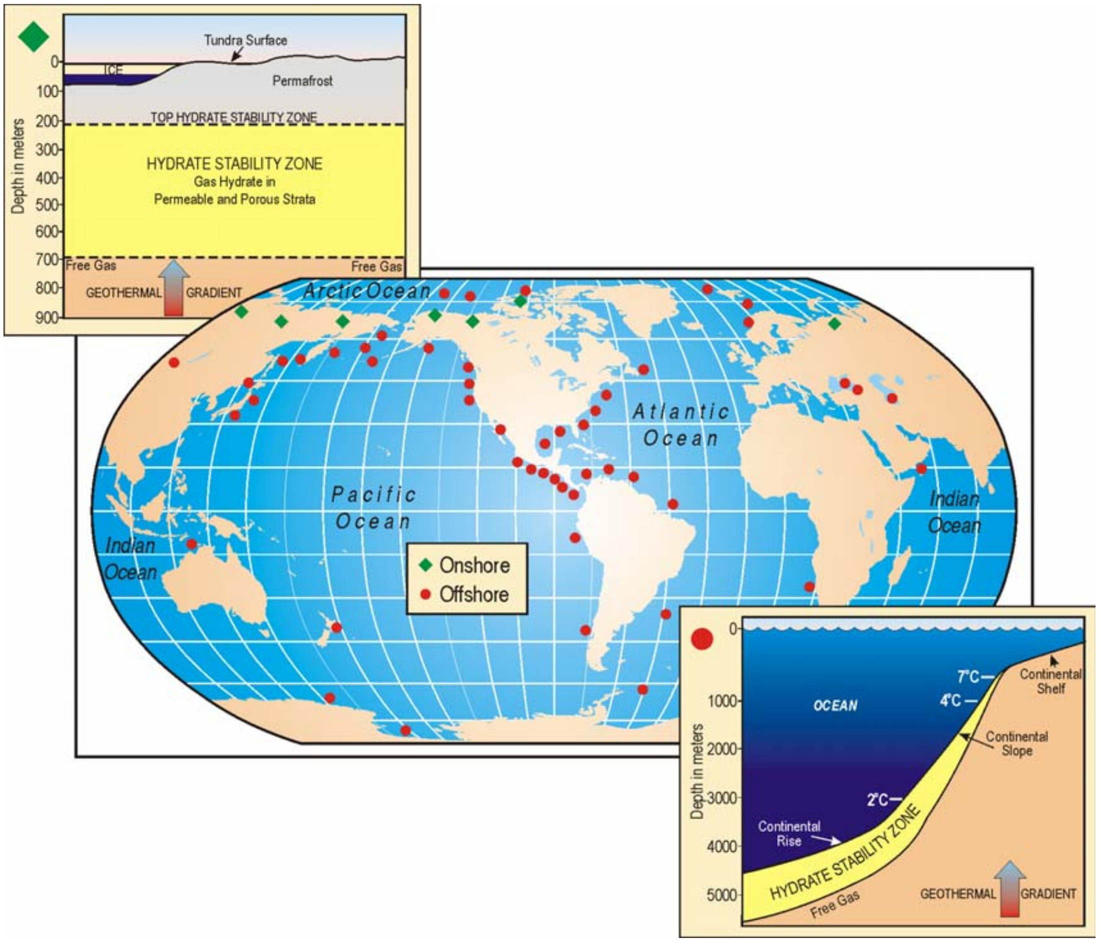

Figure 3. Worldwide locations where gas hydrate has been sampled or inferred from seismic records. These areas cover both occurrences in continental margins and permafrost regions.

There is now scientific evidence that much of the methane that forms methane hydrate is “biogenic,” meaning that it is generated from biological activity in sediments. Geological processes deeper within the earth also produce methane and other hydrocarbon gases. These “thermogenic” gases form hydrates that are often associated with underlying conventional oil and gas fields.

If methane hydrate is either warmed or depressurized so that it is no longer within the zone of hydrate stability, it will revert back to water and gas, a process termed “dissociation.” Methane is concentrated in the hydrate structure, with the dissociation of a cubic meter of methane hydrate yielding 0.8 cubic meters of water and approximately 170 cubic meters of methane gas.

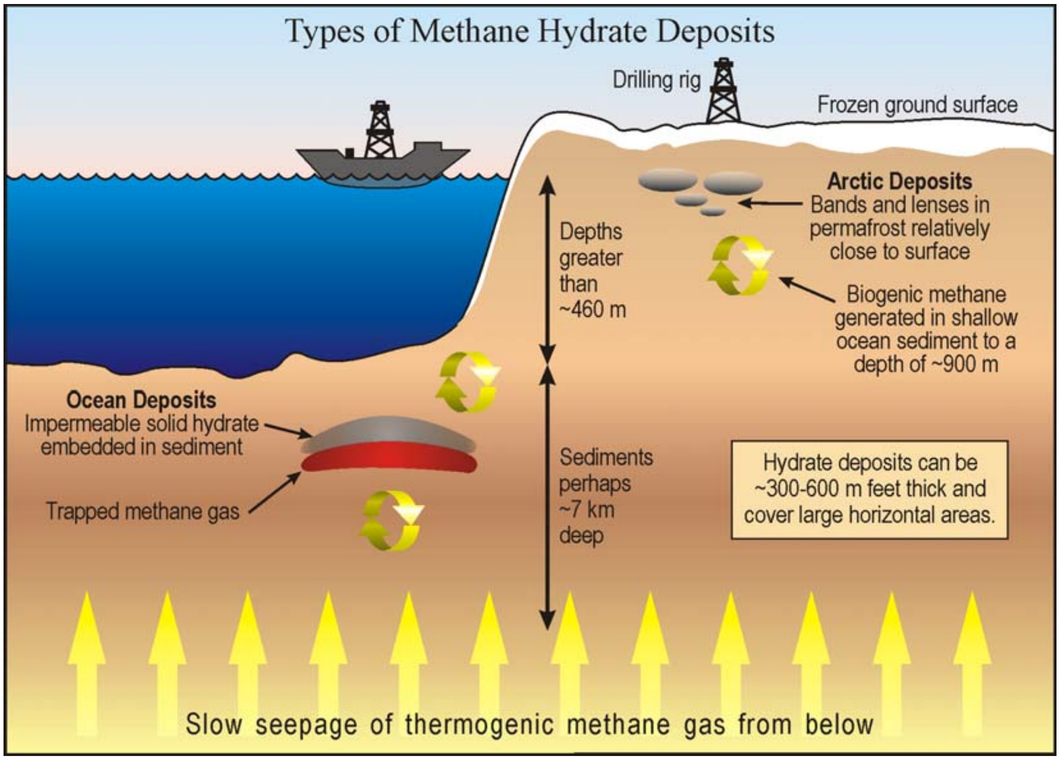

Figure 4. Types of methane hydrate deposits.

Why Methane Hydrate Matters for the United States?

While global estimates vary considerably, the volume of methane occurring in hydrate form is truly immense, almost certainly exceeding the combined volume of all other known hydrocarbon sources (Figure 5). Known methane hydrate deposits occurring within U.S. territory appear to be quite substantial. If developed successfully and safely this great abundance of methane in the subsurface could enhance energy security for the United States in coming decades.

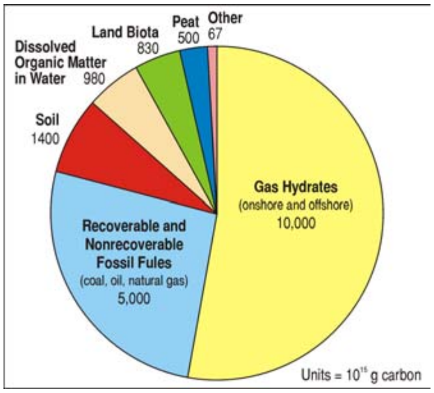

Figure 5. Worldwide distribution of organic carbon. Methane hydrates contain more organic carbon than all known fossil fuels by a factor of 2.

Methane hydrate research in the U.S. is currently being conducted by government agencies, universities and private industry. The Federal agencies involved include the Department of Energy, the U.S. Geological Survey, the Minerals Management Service, the National Oceanographic and Atmospheric Administration, the

National Science Foundation, and the Naval Research Laboratory, with coordination through an Interagency Coordinating Committee. Recently, this led to the generation of two U.S. DOE documents entitled “A Strategy for Methane Hydrate Research and Development (1998)” and “National Methane Hydrate Multi-Year R&D Program Plan (1999).” The key subtopics identified in these reports are discussed below under respective operational headings.

These are:

- Resource Potential,
- Safety and Seafloor Stability, and
- Global Climate.

Furthermore, the Methane Hydrate Advisory Committee has identified an additional objective which is:

- Protecting Marine Ecosystems if Commercialization of Hydrates Proceeds.

Resource Potential of Methane Hydrate

So far, methane hydrates have been identified under Arctic regions and continental margins in many locations in the United States and throughout the world. Active research and evaluation programs are being carried out by over a dozen nations, most prominently Japan, Canada, India, and the United States. These programs have confirmed the resource potential of methane hydrates.

Figure 6. Resource potential of methane in methane hydrate associated with the continental United States.

The volume of methane in hydrates beneath the North Slope of Alaska and within the U.S. Exclusive Economic Zone (EEZ) offshore is estimated to be between 3,200 and 19,000 trillion cubic meters (tcm) (110,000–670,000 trillion cubic feet (tcf)), with a mean value of 9,000 tcm (320,000 tcf) (Figure 6). By comparison, current domestic consumption of methane is 0.6 tcm (22 tcf) per year and is expected to grow to 1.0 tcm (35 tcf) per year by the year 2020. Domestic demand for natural gas could grow even faster if regulations are enacted to reduce greenhouse gas emissions. Yet, conventional gas resources are expected to decline at some point during the next two decades. While most methane hydrate occurs as dispersed particles, significant concentrations of methane hydrate have been discovered in some areas and are viewed by many scientists to be a potential emerging energy source for the United States.

Most of the methane hydrate research to date has focused on detection and characterization of hydrate deposits. Extraction methods that are commercially viable and environmentally acceptable are still at an early stage but are progressing rapidly and initial hydrate production is likely in the Arctic in less than 10 years. The production methods currently favored involve dissociation of the methane hydrate *in situ*, either by heating the hydrate or decreasing the pressure of the hydrate-bearing reservoir. Developing a safe and cost effective method of dissociating methane hydrate remains a significant technical and economic challenge for the development of hydrate deposits.

Implications of Methane Hydrate on Safety and Seafloor Stability

The presence of methane hydrate in sediments near the seafloor and in the shallow subsurface of the Arctic raises several safety concerns. First, the hydrate-bearing sediment often overlies sediments containing free methane. Worldwide, many large, ancient submarine landslides appear to be related to hydrate dissociation, although the mechanisms involved are not fully understood (Figure 7). Second, dissociation of methane hydrate during drilling and production in

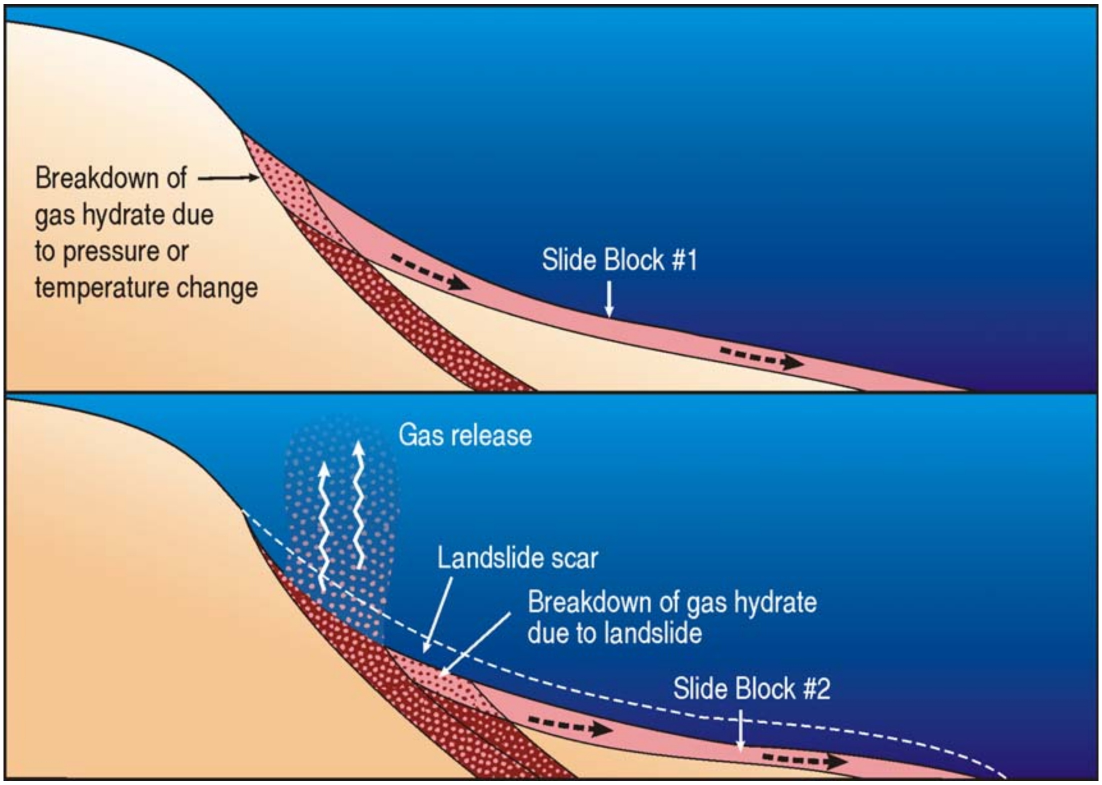

Figure 7. Schematic representation of a possible mechanism for initiating submarine landslides by methane hydrate dissociation due to an increase in temperature, or decrease in hydrostatic pressure, or a combination of the two.

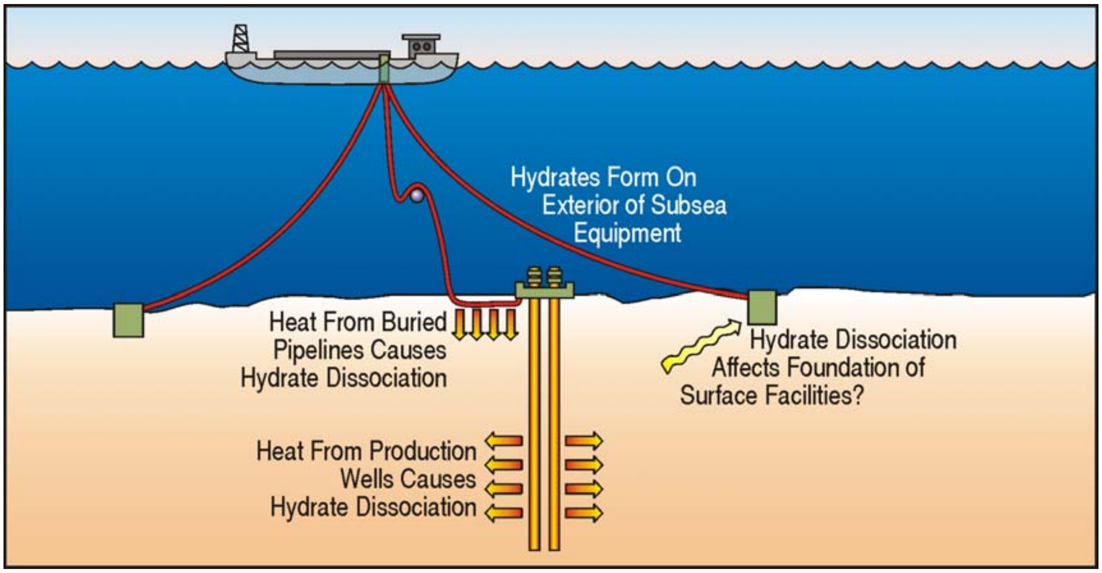

Figure 8. Potential impact of marine methane hydrate on offshore oil and gas production facilities.

deepwater environments could result in casing failure and loss of well control. These problems have been encountered in Arctic drilling and protocols have been established that have mitigated the problem. Third, methane hydrate formations on or near the seafloor may vary in extent over a span of months causing shifts in seafloor sediment. Such movement could damage facilities, including production platforms, subsea wellheads, and pipelines (Figure 8).

A number of exploratory wells have been safely drilled through hydrate deposits in both the Arctic and the oceans. While our knowledge base is growing, no hydrate production has yet occurred on a commercial basis. Thus the potential impact of methane hydrate production on seafloor stability is not yet known.

Implications of Methane Hydrate on Global Climate Change

The current concentrations of CO_2 and methane in the atmosphere are 370 parts per million (ppm) and 1.8 ppm, respectively. One of the concerns regarding methane hydrate is the potential for large releases of methane gas into the earth's atmosphere. Underlying this concern is that methane is far more potent as a greenhouse gas than CO_2.

Methane enters the atmosphere from a number of sources, both natural and anthropogenic (those related to human activities) (Figure 9). The most significant natural sources are microbial reduction of organic matter, largely in wetlands, and natural hydrocarbon vents. Anthropogenic sources include agricultural activities, waste disposal, coal mining, and petroleum production and transportation. During the past 200 years, atmospheric concentrations of methane have approximately doubled.

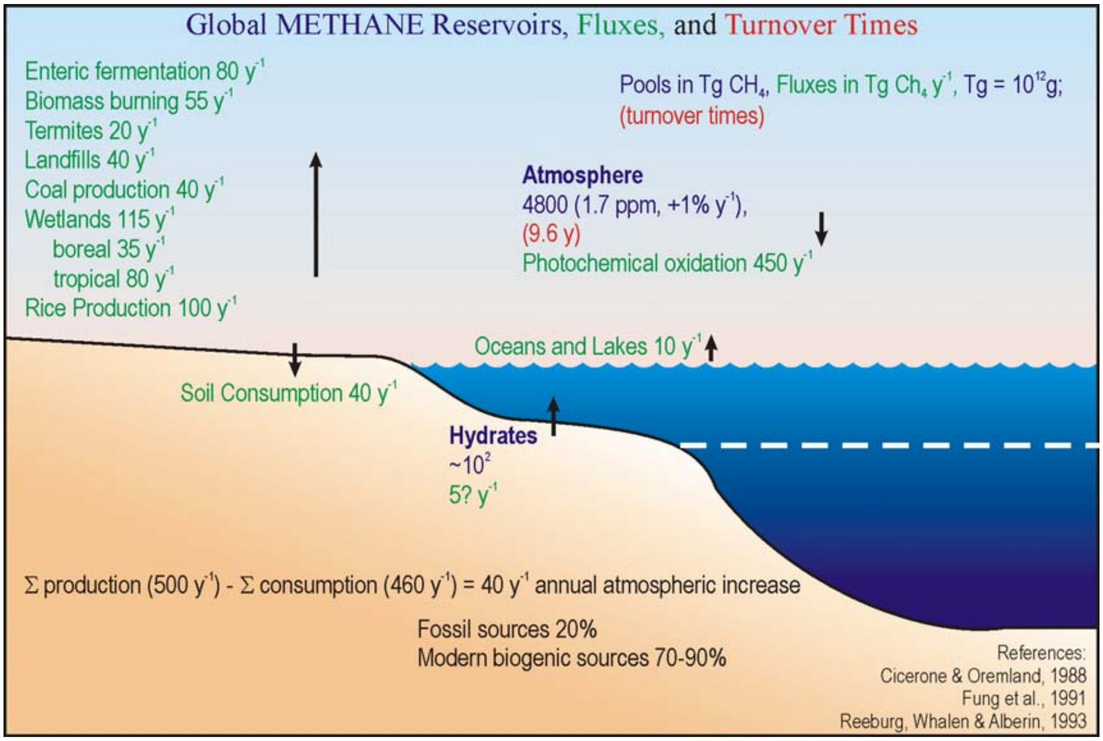

Figure 9. The methane cycle: global reservoirs, fluxes, and turnover times.

The Impact on Global Climate Change from Methane Hydrate Formation and Dissociation

The formation of methane hydrate in the subsurface environment sequesters methane and temporarily prevents it from entering the ocean or atmosphere. Methane hydrates that are buried beneath the seafloor or permafrost may sequester methane for centuries or longer. Those that form on the seafloor or in the shallow subsurface are often seasonal, with methane being released into the ocean/atmosphere system after less than one year. Where the release is gradual, most of the methane will be bacterially oxidized and/or dissolved in seawater and often does not reach the atmosphere. Therefore, the natural formation and dissociation of methane hydrate may buffer the volume of methane entering the atmosphere. A massive release of hydrate could result in significant amounts of methane entering the atmosphere. The magnitude and likelihood of a major methane release event from hydrate production are not yet known, nor is the mitigating effect of seawater that would prevent released methane from reaching the atmosphere. The global geologic record appears to indicate that very substantial releases of methane have resulted from past destabilization of the hydrate zone. The triggering mechanisms for such a massive release are not yet well understood. The appendix to this report illuminates the challenges posed by earth's history.

The Impact on Global Climate Change from the Consumption of Natural Gas Produced from Methane Hydrates

The methane gas derived from methane hydrate is indistinguishable from the methane gas currently produced from gas wells. While the combustion of methane yields CO_2 (a greenhouse gas), methane yields less CO_2 per BTU of energy than does the combustion of coal or oil. Thus the use of methane hydrate as a fuel will have a net benefit relative to coal and oil.

Possible Link Between Methane Hydrate and Past Climate Change

Concerns over the impact of large methane releases on global climate are tied to analyses of past climate changes. Throughout earth's history, global climate has continually changed. These changes have often been gradual but have at times been extremely rapid. An example of rapid change occurred at the end of the last Ice Age, approximately 15,000 years ago, with the global temperature rising by as much as 17°C (30°F). By comparison, the temperature increase for the entire 20th Century has been between 0.3 and 0.6°C (0.5 and 1.0°F).

Rapid climate change has been difficult to explain. Fortunately, additional data collected in recent years suggest possible answers to the rapid warming. The most significant are ice cores from Greenland and Antarctica that preserve trapped air from the ancient atmosphere. The ice cores show that methane concentration in the atmosphere increased dramatically in conjunction with rapid temperature increases. Marine sediment cores also reveal chemical and microfossil distribution variations that imply a rapid increase in methane. Whether the increase in methane caused the temperature increase or was the result of it has not been resolved. The increased methane may have come from new wetlands that developed as the temperature increased. However, there is also the possibility that the abrupt dissociation of methane hydrate resulted in the release of large quantities of methane into the ocean and atmosphere, leading to rapid global warming episodes. More research will be required to determine the cause of rapid temperature changes in the past.

Future Directions

Addressing the future energy needs of the United States, while addressing potential climate and safety issues, is at the heart of this report. Rapid progress is being made in all areas of methane hydrate research. Planned research work, framed through discussions among the Federal agencies involved and in consultation with advisory panels from industry and academia, will pursue the following objectives:

- Better characterize the chemical and physical properties of methane hydrates;
- Provide needed technology for a more complete survey of methane hydrate distribution;
- Describe and devise means to mitigate the hazards that hydrates pose to ongoing deepwater oil and gas drilling and production;
- Improve our understanding of how hydrates interact with the natural environment, including any links to issues of seafloor stability and global climate;
- Visit, sample, characterize, and protect the unique biological communities dependent on methane hydrate occurrences;
- Develop tools to improve the investigation of hydrates in both the laboratory and the field; and
- Appraise technologies for the safe and commercial production of methane from hydrates so that hydrates can be part of the solution for the Nation's long-term energy security.

Report by Dr. James P. Kennett

The possible interaction between methane hydrate and global climate is a rapidly emerging topic in the scientific literature. The Committee therefore sought the advice of a leading expert in this area. Dr. Kennett has provided a report that is the most recent scientific summary of the proposed link between hydrates and global climate. This is an area of ongoing study and a wide range of experiments (outlined in the report) are required to test the hypothesis. However, Dr. Kennett's report is a valuable addition to the global climate discussion. The report is attached as Appendix B.

Suggested Additional Reading

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This draft report is available online at: http://www.igbp.kva.se/obe/background.html.

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This report is available online at: http://joides.rsmas.miami.edu/journal/index.html.

Appendix A

The Methane Hydrate Advisory Committee

Methane Hydrate Advisory Committee was established in November, 2000 in accordance with Public Law 106-193, which authorized the Secretary of Energy to establish an advisory panel consisting of experts from industrial enterprises, institutions of higher education, and Federal agencies. The members of the committee are:

Peter Brewer
Monterey Bay Aquarium Research Institute

Richard Charter
Environmental Defense

Gerald Holder
University of Pittsburgh

Stephen Holditch
Schlumberger Technology Corp.

Arthur Johnson, Chair
Hydrate Energy International

Miriam Kastner
Scripps Institution of Oceanography
University of California, San Diego

Devinder Mahajan
Brookhaven National Laboratory

William Parrish
ConocoPhillips

Harry Roberts
Louisiana State University

Carolyn Ruppel
Georgia Institute of Technology

Sabrina Watkins
ConocoPhillips

Mike Smith, Assistant Secretary for Fossil Energy
Designated Federal Official
U.S. Department of Energy

Appendix B

ROLE OF METHANE HYDRATES IN GLOBAL CLIMATE CHANGE?

James P. Kennett
Department of Geological Sciences and Marine Science Institute
University of California Santa Barbara

August 2002

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BRIEF SUMMARY

This report addresses the overarching question whether methane degassing from the methane hydrate (clathrate) reservoir is an important agent in climate change. The hydrate reservoir in marine sediments is now known to contain a very large volume of exchangeable carbon stored as solid methane hydrate. This reservoir has been shown to be potentially unstable in response to changing intermediate water temperature and sea level (pressure). Recently, support has grown from geochemical and other evidence for past episodes of massive methane release. The best documented of these exhibit clear association with episodes also marked by abrupt global warming. Yet, most studies of mechanisms of past climate change, especially those of the Quaternary, do not consider methane hydrates as an integral part of the global climate system. Abrupt increases in atmospheric methane recorded in polar ice cores are widely believed to have resulted not from methane hydrate degassing but instead from continental wetland activation, a hypothesis thus far unsupported by geological data. Furthermore, as part of this *Wetland Methane Hypothesis* the abrupt methane increases are often considered to be in response to climatic warming rather than in any way driving or contributing to it. Nevertheless, an alternative view (formulated as the *Clathrate Gun Hypothesis*) is that the speed, magnitude and timing of abrupt climate change in the recent geologic past are consistent with the process of massive degassing of methane hydrates. Since this is the interval during which humans have developed highly complex societies it is especially important to determine if the methane hydrate reservoir is or is not an agent in abrupt climate change. Given this, a wide range of experiments outlined in the report are required to test this hypothesis.

SUMMARY

The earth science community is both intrigued and amazed by recent discoveries from ice-core and marine sediments that global climate and the ocean/atmosphere system can abruptly switch from glacial to near-interglacial temperatures within decades, one single human life span! Remarkably, these climatic swings occurred many times during and at the end of the last glacial episode only several thousand years ago, causing enormous disruptions in the global biosphere. Such discoveries are double-edged, however. Along with the excitement of discovery of these rapid climate shifts comes a grand challenge: their explanation. What factors can possibly drive the climate so far and so fast? Where does the energy come from? Understanding of such phenomena becomes paramount in a world with increasing concern about the role humans play in global climate change.

The discovery of the abruptness of climatic jumps on millennial time scales has, during the last decade, forced serious reevaluation of processes that might drive such remarkable change, because no obvious external forcing such as changes in the Earth’s orbit around the sun exists at these time scales. In spite of much research, there is no consensus about the origin of these events. A recent National Research Council (2002) review of the character, causes, and consequences of abrupt climate change concluded that this climate behavior still remains elusive. So far, no proposed hypothesis has successfully explained a wide range of climate changes that have occurred on decadal through millennial time scales of obvious interest to human society.

Within the context of this climatic problem, there has been growing interest in the hypothesis that methane hydrates have played an important, even critical role in abrupt climate changes of the past. One hypothesis, although unconventional, is that each of the numerous abrupt warmings during the last ice age was accompanied by, and in part driven by, massive releases of methane (CH_4) into the ocean and atmosphere system by dissociation of "frozen" methane hydrates stored in marine sediments on continental margins. Sudden, massive releases of methane into the global atmosphere likely contributed to global warming and destabilized climate. Methane is a potent greenhouse gas that is 23 times more effective at warming than an equivalent volume of CO_2 over a 100-yr time frame, and an astonishingly 62 times more powerful greenhouse gas over a shorter, 20-yr time span. The presence of 1.5 parts per million of atmospheric methane would cause globally averaged surface temperature to be 1.3°C higher than without methane. If rapid, such a rise would be significant for global warming because of the promotion of positive climatic feedbacks.

Methane hydrates or clathrates, the ice-like solid form of methane, form under conditions of low temperature, high pressure, and sufficient gas concentrations, conditions that occur widely in marine sediments on the continental margins. Wide acceptance now exists that the global methane hydrate reservoir is very large (consensus value is ~10 Eg; 1 Eg = 10^{18} g). Such a volume represents ~3000 times the amount of methane in the modern atmosphere and is the largest fossil fuel reservoir. This large reservoir of exchangeable carbon is stored as solid methane hydrate, with possibly equivalent or greater volumes of free methane gas trapped below the hydrate zone. In all, and despite significantly different estimates of methane carbon stored as methane hydrate and associated free gas, it is clear that this reservoir contains sufficiently large volumes of methane to potentially play an important role in global climate change. This appreciation of the extent of the methane hydrate reservoir as a major carbon reservoir and its possible role in climate change has become especially relevant within context of two other key discoveries: 1) the extreme sensitivity of the Earth's environmental system to change during the Quaternary, especially the last ice age; and 2) the abruptness and near global extent of major climate and environmental change that occurred over decades during the last glacial episode. The possibility has thus arisen that all three factors are linked in explaining abrupt climate change; that unstable methane hydrates represent a critical component of the climate system in providing crucially needed energy to force and accelerate abrupt climate change at a time of particular sensitivity of the Earth System.

The methane hydrate reservoir appears to have the capability of both storing and suddenly releasing free methane into the ocean and atmosphere when environmental conditions are suitable. The ability to form and dissociate methane hydrates results from the interaction of large changes in sea level (pressure) and fluctuating character of intermediate water (temperature) impinging on upper continental slopes (~400 to 1000 m water depth); the zone of potential methane hydrate instability. Methane hydrates become unstable under conditions of increased temperature and decreased pressure. But what evidence exists in support of major methane emissions from methane hydrates into the ocean/atmosphere in the geologic past? During the last few years there is growing acceptance that geochemical and other evidence supports the existence of massive methane releases from hydrates at specific intervals in the geologic past prior to the Quaternary (the geologically recent ice age period). As for the Quaternary, in spite of growing evidence, no consensus currently exists and few earth scientists seriously consider that methane hydrates are related in any way to the climate system. This seems surprising since the Earth during the late Quaternary has almost certainly been subjected to the largest ocean temperature and sea level oscillations for at least the last 15 million years and probably longer; conditions highly conducive to methane hydrate instability.

Yet evidence is beginning to grow that inferred methane emissions may have been closely linked with abrupt climate changes during the Quaternary. What is this evidence that the methane hydrate reservoir has experienced significant instability during the Quaternary and that resulting inferred methane emissions to the atmosphere have played a role in abrupt climate change? Since this is the interval during which humans have developed highly complex societies, it is especially important that this be resolved.

Air trapped in ice cores provides the most direct evidence for past changes in the atmospheric trace gases methane, CO_2, and N_2O. These records are of great significance for understanding late Quaternary climate dynamics because of the intimate relationship that exists between methane and temperature records in ice cores. Antarctic ice core records show that methane and CO_2 exhibit remarkable similarities with Antarctic air temperatures throughout the late Quaternary. The regularity of the methane and CO_2 variations through several 100-kyr climate cycles suggests a well-ordered set of dominant mechanisms that are highly sensitized to change during the late Quaternary. These records indicate that atmospheric methane levels doubled several times during the Quaternary and that these increases occurred as jumps lasting no more than decades to hundreds of years. Furthermore, the records reveal an intimate relationship between methane (and CO_2) and temperature oscillations in the pre-Holocene. Changes in methane and temperature appear almost in lockstep, suggesting a common origin and a fundamental relation between methane and temperature change. Some workers have therefore suggested that greenhouse gases (CH_4 and CO_2) are important amplifiers of the initial orbital forcing of late Quaternary climate change and have significantly contributed to the glacial-interglacial oscillations. Others suggest little or no causal role for methane in warming based on their calculation of phasing between methane and temperature in Greenland ice cores. What produced the rapid, large atmospheric methane increases during the late Quaternary? A general consensus exists that they were the result of increased methane emissions from continental wetlands when climate became warmer. However, a recent, extensive compilation of geological evidence suggests a near-absence of major wetland systems at these critical times. This synthesis indicates that the growth of wetlands cannot account for the observed changes in atmospheric methane. A more likely source for the methane appears to be from methane hydrates. These conflicting interpretations require resolution.

Two other lines of evidence have recently emerged supporting Quaternary instability of methane hydrates and associated major emissions of methane into the ocean/atmosphere system. First, episodes of major methane release from hydrates appear to have been recorded in late Quaternary sediment sequences on different continental margins by very negative carbon isotopic excursions recorded in microfossils. Methane's carbon is isotopically very negative and this imparts a distinctive geochemical fingerprint in the marine record. Methane emission events have also been identified using distinctive organic biomarkers that are uniquely related to methane. Since the initial discovery of carbon isotopic excursions only a few years ago, these events have been identified in several other sediment records. No other reasonable hypothesis exists for their origin other than by methane emissions from methane hydrates.

Other evidence for methane hydrate instability is derived from the timing of marine slumps and sediment transport on continental slopes. The distribution of methane hydrates on upper continental slopes appears closely associated with evidence of mass sediment movement, pockmarks, and other features such as collapse structures resulting from mass sediment disturbance. Based on this relationship, it is possible to indirectly infer timing of gas hydrate instability by determining the age of mass sediment disturbance. Mass sediment disturbance caused by methane hydrate instability is likely to be episodic, rather than continuous because of the different rates of change of sea level and bottom-water temperature related to climate oscillations of the late Quaternary. Major slumps on the upper continental slope likely transferred large volumes of methane from the methane hydrate reservoir to the ocean/atmosphere system. Large slumps can potentially release enormous volumes of methane (~1 Pg=10^{15} g) into the ocean/atmosphere system.

Marine geological evidence suggests that large slumps activated by dissociating methane hydrate appear to be widespread, implicating hydrate instability as an important process in climate change. Furthermore, the timing of slumps and downslope mass sediment transport suggests that slumping episodes activated by methane hydrate instability occurred at times of relatively low sea level and increased bottom-water temperatures. The last such major episode was during the last glacial to interglacial transition, an especially vulnerable time for methane hydrate instability.

A large and diverse suite of data has recently been employed to establish a coherent and testable hypothesis that links relations between methane hydrate reservoir instability and abrupt climate change during the Quaternary. This is termed the *Clathrate Gun Hypothesis*. According to this hypothesis, methane hydrates stabilized and accumulated during late Quaternary cool intervals when cold intermediate waters bathed upper continental margins. Coldest intervals occurred when reinforcement of orbital insolation cycles led to largest ice sheets and the greatest accumulation of methane hydrates. Changes in thermohaline circulation that caused warming of upper intermediate waters resulted in methane hydrate instability and catastrophic release of methane into the ocean/atmosphere system associated with sediment disruption on upper continental slopes. Release of methane hydrate-derived methane into the atmosphere initiated a cascade of feedbacks, especially on short time scales: greenhouse warming by atmospheric methane, water vapor and CO_2; warming and expansion of intermediate waters; additional methane hydrate dissociation over broader depths and regions, and so on, all at a time when sea level and confining pressure were lowest. Gradual coolings followed dissociation of most readily accessible methane hydrates, depletion of atmospheric methane, and weakening of associated global warming feedback mechanisms. Re-expansion of methane hydrates into shallow sediment and water depths, the zone of potential methane hydrate instability, only followed sufficient cooling of upper intermediate waters. The implication of this hypothesis, if correct, is that major emissions of methane from gas hydrates have driven abrupt climate warmings many times during the last 60 thousand years, the last of which was centered at 10 to 11 thousand years ago at the end of the last ice age. Since that time, the methane hydrate reservoir has probably been expanding in the absence of major widespread emissions in response to the relative stability of bottom water temperatures and sea level. As a result, the climate during this time has been in relative steady state with respect to the methane hydrate reservoir.

If it is ultimately shown that methane hydrate degassing was a critical component of the climate system in the past associated with abrupt warmings, clearly this indicates that methane hydrates can significantly impact future climate change. Global climate has constantly changed for a number of reasons through geologic time and associated ocean temperature and sea level changes can lead to methane hydrate degassing, contributing to further global warming. Thus, understanding this process has important implications for human society. Recent research has shown that deep ocean waters are currently warming, likely in association with global warming over the last several decades. This warming is at water depths at which methane hydrates are potentially unstable. The Arctic Ocean is also warming at these same critical depths. If methane hydrates were to experience significant degassing causing methane emissions into the atmosphere, this would act as a further positive feedback to global warming. However, this remains quite speculative given the limited research conducted on the potential role of methane hydrates in global climate change.

Nearly all data relevant to this hypothesis has resulted from studies conducted during the last decade or few years. This is a youthful field of enquiry and many of the most fundamental questions remain unresolved. Given this, a wide range of experiments are necessary to test the hypothesis that methane hydrates represent a critical and integral part of the late Quaternary climate system. It is likely that a number of rigorous tests, summarized in this report, will be required to confirm or negate the various elements that make up the hypothesis. Examples of such studies include: 1) Better understanding of relationships between atmospheric history of methane and climate change as recorded in ice cores; 2) Geochemical studies to determine whether the source of the methane during rapid rises in atmospheric levels came from methane hydrates or continental wetlands; 3) Refinement of understanding of continental wetland evolution during the late Quaternary, especially in the tropics, and their associated role in methane production; 4) Determination of spatial and temporal variability of inferred major methane emissions from methane hydrates as recorded in sediments during the late Quaternary and their relation with the ice core methane records; 5) Strengthening of understanding of proxies employed to detect past methane emissions into the water column from methane hydrates; 6) Determination of the spatial and temporal history of mass sediment wasting from continental slopes and in relation to possible methane hydrate instability; 7) Development of better understanding of processes that destabilize the methane hydrate reservoir and transport methane out of marine sediments into the ocean and then into the atmosphere; 8) Development of better understanding of spatial and temporal variability of upper intermediate water thermohaline circulation, especially as it affects bottom water temperature within the depth zone of potential methane hydrate instability (~400 to 1000 m) on continental slopes; 9) Inclusion of methane hydrates as an integral part of a wide range of needed climatic modeling experiments; and, 10) Investigations of climate behavior intervals prior to the late Quaternary to test and better understand the potential role of methane hydrates as a cause of climate variability.

INTRODUCTION

This report summarizes evidence suggesting that instability of the methane hydrate reservoir and resulting changes in atmospheric methane (CH_4) concentrations played a major and critical role in late Quaternary climate change. Methane is the most abundant atmospheric organic compound. Atmospheric methane has been shown to be an exceedingly powerful greenhouse gas [Hanson and Hanson, 1996] - 62 times the Greenhouse Warming Potential of CO_2 [Ehhalt et al., 2001] on the short time scales (decades) of late Quaternary abrupt warmings [Alley and Clark, 1999]. The presence of 1.5 ppmv of atmospheric methane would cause globally averaged surface temperature to be 1.3°C higher than without methane [Donner and Ramanathan, 1980]. Doubling of atmospheric methane is generally considered to cause an average global surface temperature rise of ~1°C [Leggett, 1990]. If rapid, such a rise would be significant for global warming because of the promotion of positive feedbacks [Crowley and North, 1991]: increases in methane directly enhance the trapping of terrestrial infrared radiation, perturb tropospheric chemistry, produce O_3 (another greenhouse gas) in the upper troposphere, reduce OH concentrations, and increase tropospheric water vapor [Hanson and Hanson, 1996]. Methane increases also occur in the stratosphere, increasing stratospheric water vapor, an even more powerful greenhouse gas [Cicerone and Oremland, 1988]. Estimates of climate forcing between the years 1850 and 2000 [Hansen et al., 2000] indicate that methane has had a larger influence on modern global warming (0.7 watts m^{-2}) than has generally been recognized, fully half that of the forcing by CO_2 (1.4 watts m^{-2}).

In essence, this report presents the hypothesis for further testing that methane hydrates have played a critical role in Quaternary climate change including abrupt warmings. This hypothesis remains highly controversial and remains to be seriously tested by the earth science community.

Valuable general reviews about methane hydrates have been presented by Kvenvolden [1988b; 1993], MacDonald [1990a; 1992], Haq [1998b], Buffett [2000], Kastner [2001], and by many authors in Max [2000]. Concern about the possible influence of hydrate-derived methane on global warming led MacDonald [1982] to consider the potential role of methane hydrate instability in climate change. Bell [1982] and Revelle [1983] followed with the first formal analyses of the problem. Nisbet [1990, 1992] introduced the hypothesis that hydrates played a major role in Quaternary climate change, suggesting that methane released from high latitude hydrates at the end of the last glacial episode forced a rapid rise in global temperatures. Under this hypothesis, initial deglacial warming resulted from methane emissions from melting Arctic permafrost, in turn leading to a cascade of methane hydrate release from ocean sediments. This rapidly provided new energy to the climate system, abruptly driving it to a warmer state. Several other workers have implicated methane hydrates in past climate change [MacDonald, 1990a; Kvenvolden, 1993; Paull et al., 1994; Dickens et al., 1995, 1997; Kennett et al., 1996, 2000a, b; Haq, 1998a, b, 2000;]. Early support for methane hydrate instability as a potential mechanism for climate change came from the realization that decreased pressurization of the methane hydrate reservoir by sea-level lowering can destabilize hydrates [Nisbet, 1990; Paull et al., 1995; Haq, 1993]. More recent work suggests that bottom-water temperature changes may play a crucial role in methane hydrate destabilization [Dickens et al., 1995, 1997; Dickens and Quinby-Hunt, 1997; Kennett et al., 2000a; Haq, 2000].

This report results from a major (5-year) synthesis of the subject leading to the publication of a book in 2002 entitled " Methane Hydrates in Quaternary Climate Change: The Clathrate Gun Hypothesis" by J. Kennett, K. Cannariato, I. Hendy and R. Behl. This book has been published by the American Geophysical Union, the largest and most prestigious earth and planetary scientific society in the world. This volume provides a more thorough treatment of this subject.

THE CHALLENGE

Explaining Abrupt Climate Change

Understanding the causes of late Quaternary climate behavior represents one of the major challenges in earth sciences. High-resolution studies of climate change using ice cores [e.g., Dansgaard et al., 1993; Grootes and Stuiver, 1997], and marine and terrestrial sediments [see Kennett et al., 2002 for references] have revealed rapid, large millennial-scale climate oscillations during the last glacial episode (Figure 1(A)). These studies describe a bistable oscillatory behavior of the climate system, with switches between distinctly different states occurring in decades or less [Alley and Clark, 1999]. Even more remarkable is the amplitude of temperature changes associated with these high-frequency climate shifts, at times reaching glacial-interglacial magnitudes (Figure 1(A)). Each of the warm events (interglacials and interstadials) during the late Quaternary required a trigger to initiate the change, strong positive feedbacks for reinforcement, and a process that maintained the new, nearly stable state. Major positive feedbacks were necessary to produce such large, rapid shifts in global climate, but the nature of these feedbacks has remained enigmatic.

Pervasive millennial-scale climate oscillations are now well known to have persisted during the latest Quaternary [Sarnthein et al., 2000], superimposed on Milankovitch-band insolation cycles (including glacial-interglacial episodes; Figure 2). These oscillations are recognized in ice cores, terrestrial lakes and bogs, cave deposits, and marine sediments from the North Atlantic, Pacific and Indian Oceans. Evidence exists for strong involvement of the polar, mid-latitude, and tropical regions in this climate change.

First identified in Greenland ice cores, a series of warm interstadials (200 to 2500-yr durations) (Figure 1(A)) punctuated the otherwise cold conditions of the last glacial episode [Dansgaard et al., 1993; Bond et al., 1993]. These climatic oscillations are often referred to as the Dansgaard-Oeschger (D/O) cycles [Dansgaard et al., 1984; Oeschger et al., 1984]. The air temperature shifts between these changes in climate state were large, likely ~6° to 10°C [Broecker, 2000] and remarkably abrupt, within decades to years. Thus, these climate oscillations essentially

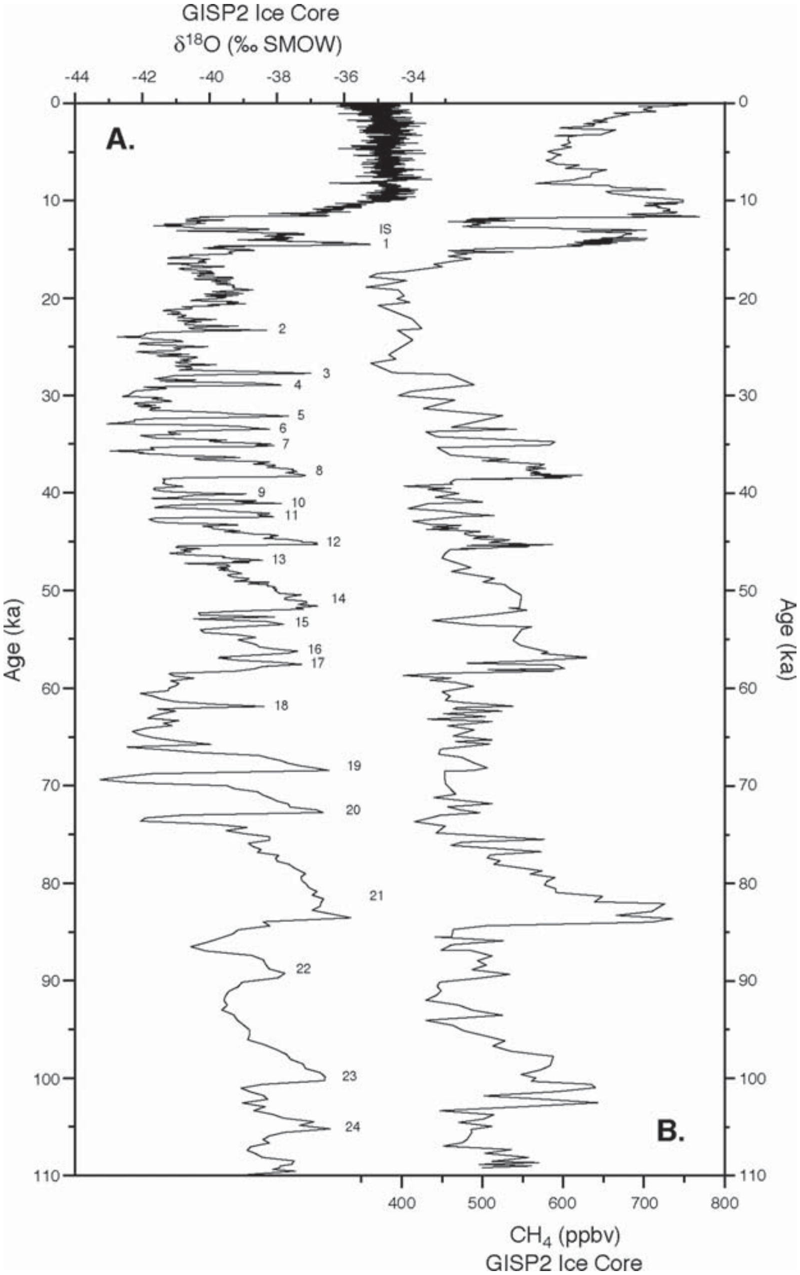

Figure 1. Comparison of (A) GISP2 d18O [Grootes et al., 1993; Stuiver et al., 1995] and (B) CH$_4$ [Brook et al., 2000] records for the last 110 kyr from the Greenland ice core reveal a close correspondence of millennial-scale oscillations in air temperatures over Greenland and atmospheric CH$_4$ concentrations. Interstadials 1 to 24 are present [Dansgaard et al., 1993]. Chronology of d18O record after Meese et al. [1994] and Sowers et al. [1993]. The GISP2 gas-age time scale from Brook et al. [1996].

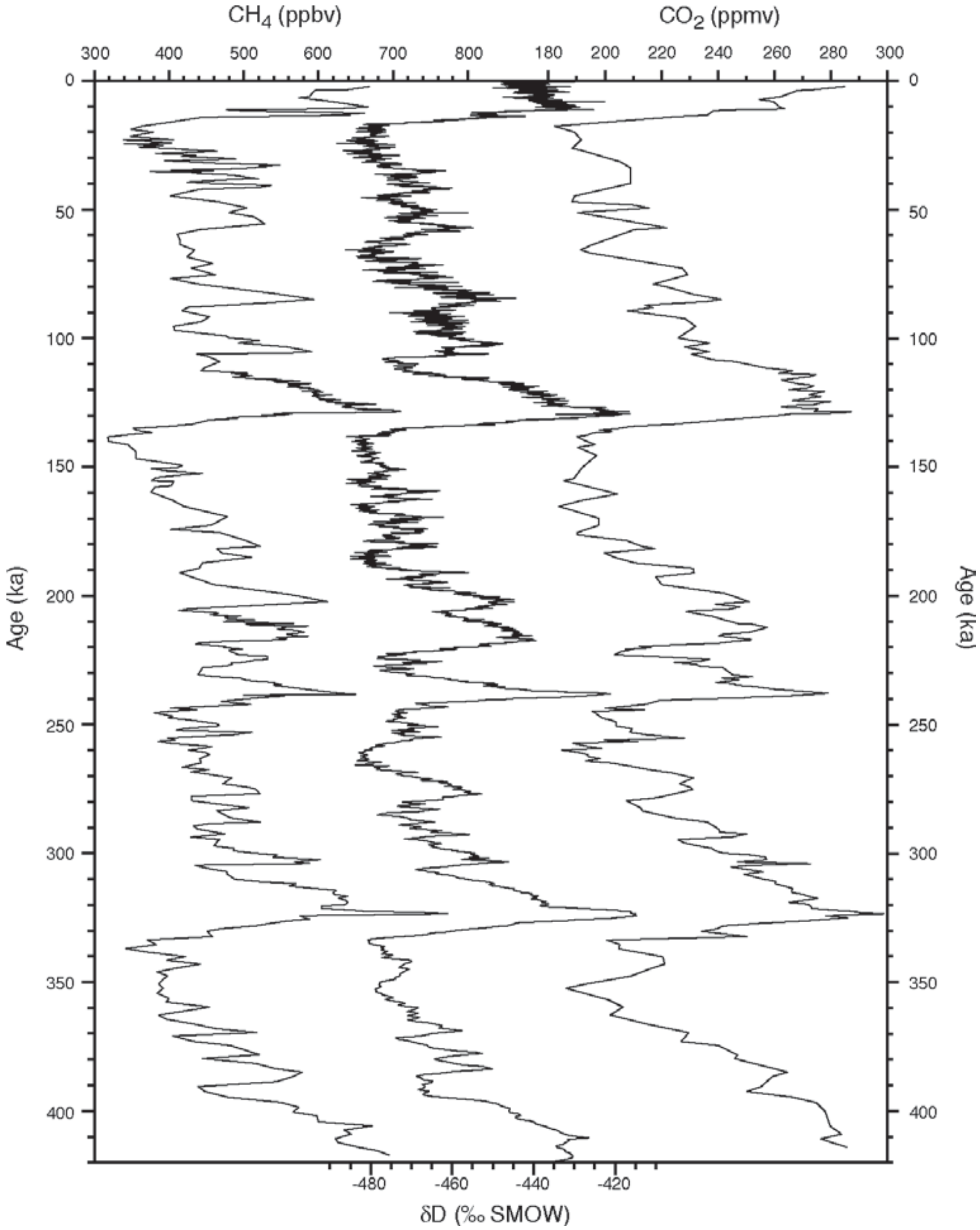

Figure 2. Glacial-interglacial variations of (A) CH4, dD (middle), and (B) CO_2 for the last 4 glacial cycles (423 kyr) recovered from the Vostok ice core, Antarctica (depth 3,310 m in the East Antarctic ice sheet) [Petit et al., 1999]. dD is largely a measure of atmospheric temperature. Mean sample resolution of CO_2 over most of the record is 1500 yr. The resolution of the chronology (Model GT4) is better than ±10 kyr for most of the record and better than ±5 kyr

reflect major, abrupt shifts in the ocean/atmosphere system between cool and warm states associated with changes in greenhouse gas composition and the Earth's reflectivity to solar radiation. These climate events are also associated with significant changes in trace atmospheric gases (CH_4, CO_2, N_2O) (Figures 1(B) and 2) and in the marine and terrestrial biospheres [e.g., Cannariato and Kennett, 1999].

The discovery of millennial climate variability was instrumental in forcing reevaluation of the processes driving the late Quaternary climate system, because no obvious external forcing exists at these frequencies and magnitudes. Although there is currently no consensus for the origin of the abrupt climate changes, their existence suggests that internal feedback mechanisms, including greenhouse gas variations, played a crucial role both in setting the sensitivity of the climate system and creating or amplifying major change at orbital and sub-orbital time scales. Understanding what the amplifiers are and how the feedback mechanisms operate is central to understanding the character of late Quaternary climate change. The two most frequently considered hypotheses are that rapid millennial-scale cycles were triggered by 1) changes in thermohaline circulation associated with North Atlantic Deep Water (NADW) production or 2) changes in tropical heat distribution. Although these processes appear to have played important roles in the climate oscillations, computer models used to test the leading hypotheses suggest that it is unlikely that they could have, by themselves, caused such large and abrupt climate changes as recorded or maintained the warmth of the interstadials. Models have so far failed to fully explain the climate record including the magnitude, speed and extent of the climate changes during the shifts [National Research Council, 2002].

The thermohaline circulation hypothesis links changes in surface-water salinity at high northern latitudes of the Atlantic with abrupt switches in the strength of North Atlantic thermohaline circulation ("The Great Ocean Conveyer" [Broecker, 1999]). This in turn severely affects climate of the North Atlantic [e.g. Broecker et al., 1985; van Kreveld et al., 2000]. During glaciations, the circum-North Atlantic ice sheets provided a ready supply of freshwater to the North Atlantic, and perhaps played a key role in causing large, abrupt climate change through iceberg release, rerouting of continental drainage pathways, and episodic drainage of glacier-dammed lakes [Clark and Mix, 2000; Clark et al., 2001]. In this hypothesis, ice sheet dynamics are central in controlling climate behavior [Bond et al., 1992, 1993]. Although strong evidence supports such a sequence of events [van Kreveld et al., 2000], the hypothesis appears to be insufficient to explain the abruptness, magnitude, and global extent of the warmings. The largest problem with this hypothesis is its limitations in affecting rapid climate change beyond the North Atlantic region [National Research Council, 2002].

The second hypothesis for the driver of millennial-scale climate change relates to changes in tropical heat distribution and consequent modulation of atmospheric water vapor. At present, atmospheric water vapor, the most important greenhouse gas, is dominantly produced in the tropics; its atmospheric abundance depending exponentially on temperature [Oltmans and Hofmann, 1995]. Thus, it can exert strong positive feedback on climate change and has rapid response times [Pierrehumbert, 1999]. Tropical surface ocean temperature changes in phase with higher latitude air and ocean temperature records suggest that the tropics have not passively responded to climate change triggered by other mechanisms such as changes in thermohaline circulation [Bard et al., 1997]. Yet several modeling studies suggested the opposite - that tropical climate and associated heat distribution responded to changes in North Atlantic thermohaline circulation [Fawcett et al., 1997]. Although it is clear that the tropics were strongly involved in global climate change [Cane and Evans, 2000; Peterson et al., 2000], the nature of the forcing agent for tropical change remains undetermined.

Any proposed mechanism for late Quaternary climate change must be consistent in explaining patterns of change in the earth system on orbital, millennial, and decadal time scales (Figures 1 & 2), as well as their global or regional distribution. For example, it is necessary to explain why, during deglaciation, a major reduction in ice volume followed each maximum in ice sheet expansion [Denton et al., 1999; Alley and Clark, 1999]. Understanding the causes of these rapid climate cycles and their interaction with orbital forcing is key to understanding late Quaternary climate variability. The rapidity of the climate changes indicates that the amplifying feedbacks were able to respond within years to decades. Curiously, this climate instability was most pronounced during the last glacial episode, at a time when large ice sheets led to the exposure of continental shelves.

A recent National Research Council [2002] review of the character, causes, and consequences of abrupt climate change concluded that this climate behavior still remains to be explained. Furthermore, climate models have typically underestimated the magnitude, speed, and extent of these abrupt changes. Hypotheses proposed to account for the remarkable late Quaternary climate behavior are numerous and diverse, but usually invoke forcing by greenhouse gases (e.g., CO_2, CH_4, N_2O, H_2O) [Petit et al., 1999] and/or rapid shifts in ocean thermohaline circulation [Broecker, 1997a; Keeling and Stephens, 2001]. Any mechanism proposed to explain late Quaternary climate behavior must explain a diversity of documented changes, including: the character, magnitude, and abruptness of climate change, synchronism and diachronism between different regions and components of the earth system, changes in atmospheric greenhouse gas composition, deep and intermediate-water circulation, ecosystem changes influencing global biogeochemical cycling, and the leads and lags between the different components. So far, no proposed hypothesis has successfully explained the wide range of climate changes that occurred on orbital, millennial, and decadal time scales during the late Quaternary [Paillard, 2001].

THE POTENTIAL ROLE OF METHANE HYDRATES

Methane Hydrates in Climate Change

One potentially important mechanism involved in late Quaternary climate change that is beginning to receive attention by the paleoclimate community is the role of greenhouse forcing by atmospheric methane emissions and associated feedbacks resulting from degassing of the marine sedimentary methane hydrate reservoir. Methane hydrates (clathrates), the ice-like solid form of methane, are formed as methane molecules captured within a cage of water molecules. Methane hydrates [Sloan, 1990, 1998; Kvenvolden, 1993; Henriet and Mienert, 1996, 1998; Kleinberg and Brewer, 2001; Paull and Dillon, 2001] form under conditions of low temperature, high pressure, and sufficient gas concentrations [Kvenvolden and McMenamin, 1980; Sloan, 1990, 1998; Dickens and Quinby-Hunt, 1997] (Figure 3). They are now known to occur extensively in marine sediments on continental margins, especially where high organic carbon content leads to anoxia and methanogenesis. Methane hydrates also occur in some deep fresh water lakes and beneath the permafrost layer in the high northern latitudes. The sensitivity to form and dissociate methane hydrates results from the interaction of large changes in sea level (pressure) and fluctuating character of intermediate water (temperature) impinging on upper continental slopes (~400 to 1000 m water depth); the zone of potential methane hydrate instability (Figure 4). Methane hydrates become unstable under conditions of increased temperature and decreased pressure.

This enormous reservoir of exchangeable carbon is stored as solid methane hydrate, with possibly equivalent or greater volumes of free methane gas trapped below the hydrate zone [Dickens et al., 1997]. Global estimates of the methane content of methane hydrates range from as low as 0.5 Eg (1 Eg = 10^{18} g) to as high as 24 Eg [Kvenvolden and Lorenson, 2001]. An intermediate value of ~10 Eg is considered a consensus value based on independently determined values by Kvenvolden [1988b] and MacDonald [1990a]. Such a volume represents ~3000 times the amount of methane in the modern atmosphere [Buffett, 2000] and is the largest fossil fuel reservoir [Dickens et al., 1997]. In all, and despite significantly different estimates of methane carbon stored as methane hydrate and associated free gas, it is clear that this reservoir contains sufficiently large volumes of methane to potentially play an important role in global climate change. As a result, it has become more widely recognized that methane hydrates represent a large reservoir of carbon that both stores and has the potential of releasing free methane into the ocean and atmosphere when environmental conditions are suitable.

At present, this large methane reservoir is relatively stable, thus playing only a minor role in the modern methane cycle [Cicerone and Oremland, 1988; Judd, 2000]. However, this may not have been the case throughout earth history, as increased evidence suggests that important paleoclimatic events were associated with atmospheric methane emissions from methane hydrates [e.g., Dickens et al., 1995]. During the last few years support has grown from geochemical and other evidence for massive methane releases from hydrates at specific times in the geologic past, but this has been largely limited to intervals before the Quaternary (the geologically recent ice age period of the last ~2 million years). The origin of several brief episodes of global warming has been linked with massive dissociation of hydrates and methane transfer into the atmosphere [Dickens et al., 1995, 1997 and other references shown later]. What evidence exists in support of major methane emissions from methane hydrates into the ocean/ atmosphere in the geologic past? The strongest evidence implicating methane hydrates are records of large, negative carbon isotope excursions affecting carbon reservoirs of the ocean,

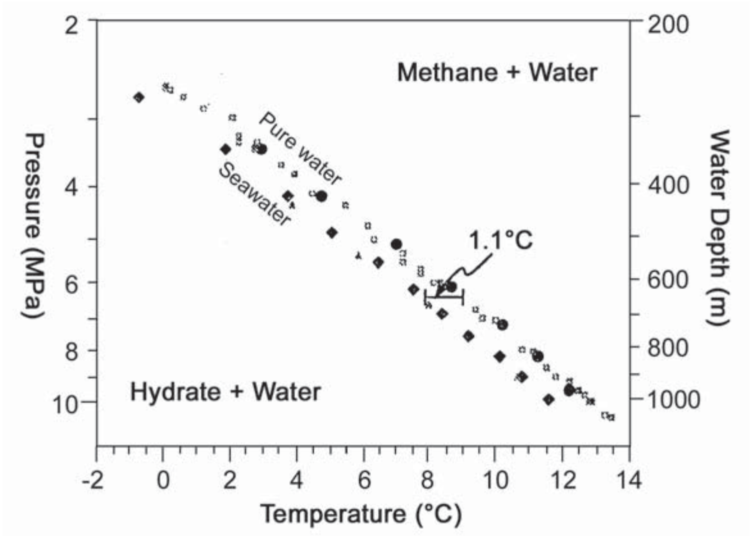

Figure 3. Effect of water depth (pressure) and temperature on phase relationships between methane hydrate and dissolved or gaseous CH_4 [after Dickens and Quinby-Hunt, 1994; see reference for detailed explanation of symbols].

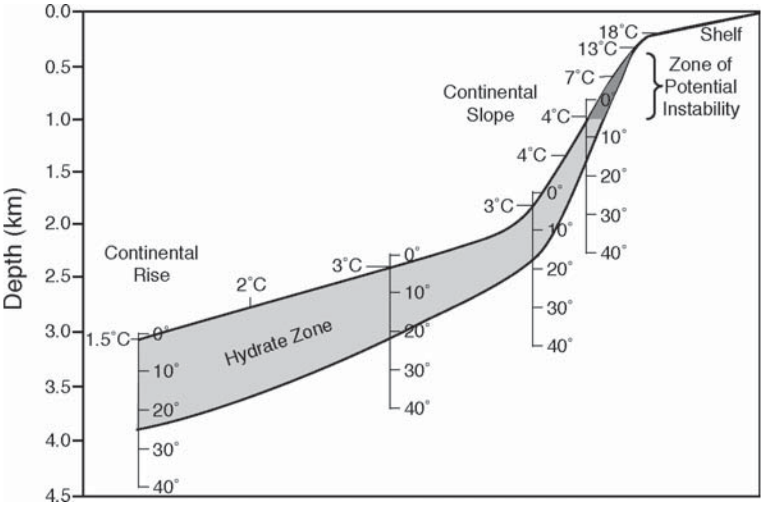

Figure 4. Schematic diagram illustrating potential distribution and thickness of methane hydrate zone in continental margin sediments [after Kvenvolden and McMenamin, 1980]. Stippled zone represents potential areas of methane hydrate formation, where pressure and temperature conditions combine to produce methane hydrate stability, assuming a sufficient supply of CH_4. Thickness of this zone increases with depth (pressure) and lower water temperature. Geothermal gradient is assumed to be 27.3°C/1000 m. Zone of potential instability during the late Quaternary is between ~400 and 1000 m water depth.

biosphere, and atmosphere. Biogenic methane has highly negative carbon isotopic values (~-65‰) and therefore can provide a distinct isotopic fingerprint when present in sufficient environmental concentrations. Methane released from the hydrate reservoir is transferred to the exchangeable carbon reservoir via diffusion into the water column and/or outgassing into the atmosphere during sediment failure [Dickens et al., 1997]. The magnitude of the climate response would have largely depended on how much methane reached the atmosphere.

Despite the potential for large, episodic releases of methane by hydrate dissociation, intense ongoing investigations of late Quaternary climate behavior have not included the methane hydrate reservoir as an integral part of the global climate system. This is surprising given the immense amount of methane estimated to be stored in the modern reservoir [MacDonald, 1990a; Kvenvolden, 1988a, b; 1993]. Paull et al. [1995] stated that "if these natural gas hydrate deposits are dynamic reservoirs, the potential to affect the Earth's climate by releasing methane to the atmosphere has to be considered." Furthermore, the Earth during the late Quaternary has almost certainly been subjected to the largest ocean temperature and sea level oscillations within the last 15 million years and probably longer. It is unlikely that conditions have been as favorable for methane hydrate instability than during the late Quaternary.

Why have methane hydrates been little considered as an important component in late Quaternary climate change? There appear to be several reasons for this: the reservoir is remote and poorly studied; little was known about methane hydrates until recently; and modern hydrates appear relatively stable and show little evidence during the Holocene compared with prior instability evident earlier in the Quaternary. Furthermore, the upper continental margin, containing most of the reservoir, has been considered a relatively stable oceanic environment, uninvolved with Quaternary climate behavior, especially on millennial time scales. For these and other reasons, methane hydrates have been considered "a last resort" hypothesis for climate change [K. Kvenvolden, personal communication]. Nevertheless, Buffett [2000] has suggested that methane hydrates may be the "dark horse" of global climate change.

Interest in the potential role of methane hydrates in late Quaternary climate change has recently intensified for several reasons:

- Recognition of the potential instability of methane hydrates on continental margins because of sea-level and bottom-water temperature changes [Paull et al., 1995; Kennett et al., 1996, 2000a, b].
- Widespread agreement that catastrophic methane release from dissociating hydrates caused a distinct episode of global warming at the end of the Paleocene [e.g., Dickens et al., 1995, 1997; Katz et al., 1999].
- Discovery of large, negative carbon isotopic excursions in late Quaternary marine sediments from the southern California margin [Kennett et al., 2000a], Gulf of California [Keigwin, 2002], East Greenland [Smith et al., 2001], and Amazon Fan [Maslin et al., 1997] attributed to methane release from methane hydrates associated with millennial-scale climate change and deglaciation.

- Recognition of the close association between methane and climate recorded in ice cores, both at orbital [Petit et al., 1999] and millennial time scales [Brook et al., 2000]. The inferred changes in atmospheric methane concentrations have generally been linked to wetland development; potential effects of methane hydrates have been largely ignored.
- The growing recognition of the powerful Greenhouse Warming Potential of methane as reinforced by reactions and feedbacks with other atmospheric gases [Ehhalt et al., 2001].
- Discovery of large, seasonal fluxes of methane released from beneath sea ice in the Sea of Okhotsk, a region with an ocean-floor gas source [Suess et al., 1999]. Methane derived from hydrates is transported to surface waters in gas plumes [Zonenshain et al., 1987]. Kvenvolden et al. [1992] also discovered methane trapped beneath sea ice off Alaska. These observations led Suess et al. [1999] to conclude that methane hydrates may be a significant source of atmospheric methane. Loehle [1993] considered methane to be an important, but cyclic component of the global carbon cycle during the late Quaternary.

Methane has a short atmospheric residence time (~20 yr) [Leggett,1990], being rapidly oxidized to CO_2 and H_2O. Thus, sustained climate warming resulting from increased methane requires a continuous supply. Sustained supplies must be provided by the major potential sources including methane hydrates, continental wetlands and/or permafrost. Positive feedback processes should have played a major role towards sustained methane input into the atmosphere during global warming. The role of increased water vapor is crucial in assessing the impact of atmospheric methane increases. Even if relative humidity remains fairly constant as methane and consequently temperature rise, an absolute increase in the amount of atmospheric water vapor occurs, which in turn causes further temperature amplification of perhaps 50% [Cicerone and Oremland, 1988].

We suggest that significant atmospheric methane increases can force rapid global warming. However, such warming must have been reinforced by several other processes acting as positive feedbacks. These would have included increases in other greenhouse gases. The feedbacks would have occurred rapidly because much of the initial change occurs within the atmosphere and near the ocean surface (including the melting of sea ice at high latitudes). This is supported by a modeling experiment involving major (4000 Tg) methane release to the atmosphere which was alone insufficient to cause radiative forcing of a magnitude to induce the magnitude of the recorded deglacial warming. However, the model was able to simulate deglacial warming when additional feedbacks were included, specifically combinations of methane, CO_2, and heat transport [Thorpe et al., 1998].

Processes That Can Destabilize Methane Hydrates

Nisbet [1990] and MacDonald [1990b] have both argued that major destabilization of methane hydrates is central to the processes that end glacial episodes. Their hypothesis invokes dissociation of methane hydrates because of reduced hydrostatic pressure associated with sea-level fall and possibly warming of bottom waters. In their scenario, a sufficient volume of methane was released into the atmosphere to cause global warming through various feedback processes. The dissociation of methane hydrates was implicated from evidence of massive sediment failure on continental slopes. Hydrostatic changes related to sea level, even on tidal time scales, are known to affect rates of emissions from marine gas fields [Boles et al., 2001].

An ~120-m sea-level lowstand during the LGM would have reduced hydrostatic pressure sufficiently to cause the gas hydrate stability zone to shallow by ~20 m, decreasing its thickness by several percent [Dillon and Paull, 1983]. Gas hydrates at shallow water depths would have been particularly vulnerable to dissociation. This suggested the hypothesis that glacioeustatic sea-level fall and increasingly large CH4 releases into the atmosphere limit the extent of glaciation [Paull et al., 1991]. However, this hypothesis is not supported in detail by the methane record in ice cores [Chappellaz et al., 1990; Lorius et al., 1990], which exhibits increasingly low, stable values of atmospheric methane into the LGM [Eyles, 1993]. On the other hand, large, rapid methane increases at glacial terminations, which represent the largest warmings of the Quaternary, are consistent with the hypothesis of Paull et al. [1991] that major glaciation is limited by greenhouse warming resulting from major methane hydrate dissociation.

Methane hydrate stability at continental margin depths was probably more sensitive to temperature than sea-level changes during the late Quaternary [Buffett, 2000]. A change in temperature of only 1°C is sufficient to offset the effect of a 100 m change in sea level, although the equivalent temperature change has been estimated to be as little as several tenths of a degree by Buffett [2000]. Nevertheless, it should be emphasized that increase in temperature alone does not necessarily lead to significant dissociation of methane hydrate, which like ice, requires sustained input of heat energy and thus prolonged temperature rise. Thermal effects on hydrate stability have not been seriously considered in previous late Quaternary investigations, probably because of the general assumption that bottom-water temperatures on upper continental margins were relatively stable. However, significant bottom-water temperature changes within the zone of potential hydrate stability (~400 to 1000 m) (Figure 20) have recently been discovered [Kennett et al., 2000a; Hendy and Kennett, submitted], refuting this assumption.

EXISTING EVIDENCE

Have Massive Releases of Methane Contributed to Past Global Warming Events?

As outlined above, although there is much potential for significant degassing of methane hydrates into the ocean/atmosphere system when conditions were favorable, if such events occurred, they must have left geological evidence. There seems to be general acceptance of geological evidence for major methane degassing events in the distant geological past well before the Quaternary. This interpretation is relatively uncontroversial and is briefly summarized first. We then summarize evidence in support of methane hydrate degassing during the Quaternary which is considered by most workers to be highly controversial. Nevertheless, evidence continues to grow that inferred methane emissions may have been closely linked with abrupt climate changes during this time. What is this evidence that methane hydrates experienced significant degassing during the Quaternary and that resulting inferred methane emissions to the atmosphere have played a role in abrupt climate change? This question is obviously crucial to resolve conclusively given that we as humans inhabit the earth under these very conditions of potential instability.

Emission Events Before the Quaternary

Documented major inferred methane emission events from hydrates based on large, abrupt negative carbon isotopic anomalies are considered by some to have occurred during the latest Paleocene (55 Ma) [eg. Dickens et al., 1995], early Cretaceous (Aptian; 120 Ma) [Hesselbo et al., 2000], late Jurassic [Padden et al., 2001], and early Jurassic (Early Toarcian; 183 Ma) [Hesselbo et al., 2000]. Major episodes of hydrate dissociation based on negative carbon isotopic anomalies in marine sequences have also been inferred for the Triassic/Jurassic boundary [Pálfy et al., 2001], the Permian/Triassic boundary [Krull et al., 2000] (although other causes have been suggested to explain this anomaly), the early Paleozoic [Quinby-Hunt and Wilde, 1995], and immediately following Neoproterozoic glacial episodes [Kennedy et al., 2001; 2002] (see Hoffman et al. [2002] for alternate views). Many of these events are known to be associated with major global warming episodes likely caused by massive methane releases from hydrates.

The most thoroughly documented event is that which occurred at the end to the Paleocene and associated with a sharp warming considered to be the warmest interval of the last 65 million years (the Late Paleocene Thermal Maximum). This episode, marked by rapid carbon isotopic shifts, began abruptly within 2 kyr, and lasted only ~220 kyr [Röhl et al., 2000]. It is inferred that methane, stored as methane hydrate, was released suddenly, then was gradually depleted from the ocean/atmosphere system, leaving a sawtooth shape to the carbon isotopic record. Dickens [2001c] compares the process to charging, discharging, and recharging an electrical capacitor. The early Jurassic event, estimated to represent one of the largest methane hydrate dissociation episodes of the last 200 myr, occurred mostly within only ~70 kyr [Hesselbo et al., 2000]. Both the late Paleocene and early Jurassic episodes were associated with oceanic warming, including deep waters that have been implicated in methane hydrate dissociation.

Jumps in Atmosphere Methane and Global Temperature Change in Quaternary

Trapped air in ice cores provides the most direct evidence for past changes in the atmospheric trace gases methane, CO_2, and N_2O [Flückiger et al., 1999] (see Raynaud et al. [1993, 2000] for reviews). In particular, these records have revealed remarkable changes in atmospheric methane concentrations during the late Quaternary on orbital, millennial, and decadal time scales (Figures 1(B) & 2). Large, rapid variation in atmospheric methane contrasts with much slower changes in atmospheric CO_2 (Figure 2). These records are of great significance for understanding late Quaternary climate dynamics because of the intimate relationship that exists between methane and temperature records in ice cores. Determining the relationship between methane, CO_2, and climate at decadal resolution is of fundamental importance [Severinghaus and Brook, 1999]. These records pose two key questions: 1) What produced the rapid, large atmospheric methane increases at glacial and stadial terminations? and 2) Were the large atmospheric methane increases instrumental in forcing the rapid climate warming episodes that marked the late Quaternary?

The Antarctic ice core records show that methane and CO_2 exhibit remarkable similarities with Antarctic air temperatures throughout the late Quaternary [Petit et al., 1999] (Figure 2). The regularity of the methane and CO_2 variations through several 100-kyr climate cycles (Figure 2) suggests a well-ordered set of dominant mechanisms [Sigman and Boyle, 2000] that are highly sensitized to change during the late Quaternary. One of the most significant observations made in ice core stratigraphy is of the intimate relationship between methane and temperature oscillations in the pre-Holocene record of the late Quaternary [Jouzel et al., 1993; Brook et al., 1996; Petit et al., 1999]. Changes between the two climate parameters appear almost in lockstep (Figure 2), suggesting a common origin [Brook et al., 2000] and a fundamental relation between methane and temperature change. Petit et al. [1999] and Raynaud et al. [2000] have therefore suggested that greenhouse gases (methane and CO_2) are important amplifiers of the initial orbital forcing of late Quaternary climate change and have significantly contributed to the glacial-interglacial oscillations. On the other hand, Severinghaus et al. [1998] and Brook et al. [1999] suggest little or no causal role for methane in warming based on their calculation of phasing between methane and temperature in Greenland ice cores. Clearly, if climate change was forced in part by methane variations, the changes should be recorded in ice cores as synchronous or with a minor lag. However, as discussed below, determining this relationship in ice cores has been difficult because of the differences in age between the trapped gas and ice, variation in this age difference through time, and because the timing of methane and temperature changes were extremely close.

What produced the rapid, large atmospheric methane increases during the late Quaternary? A general consensus exists that they are the result of increased methane emissions from continental wetlands when climate became warmer. However, geological evidence suggests a near-absence of major wetland systems at these critical times. During the last ice age the earth was a dry planet with limited wetland ecosystems. Sea level was low and thus continental lowlands were well drained by well incised rivers. This strongly limited the extent of flooded areas that could form methane producing wetlands. The geological evidence is strong in suggesting that the growth of wetlands cannot account for the observed changes in atmospheric methane. A more likely source for the methane appears to be from methane hydrates. These conflicting interpretations require resolution. If methane from methane hydrates played a role in the rapid warmings that marked the late Quaternary, increases in atmospheric methane should have been synchronous with or ahead of the rapid warming episodes.

Instability of Methane Hydrates During the Quaternary

We now summarize marine geological evidence that appears to support major degassing of methane hydrates at times during the late Quaternary. This evidence suggests the following: 1) significant instability of methane hydrates on the upper continental margins did occur during the late Quaternary; 2) methane hydrate instability contributed to major sediment failure and mass transport on continental slopes; 3) unroofed methane hydrates contributed to further hydrate instability and methane release to the ocean/atmosphere system; 4) this process did not occur uniformly throughout the late Quaternary, but was focused at specific intervals. It is likely that large processes such as major slumping are essential in delivery of methane to the atmosphere in sufficient volume to affect climate change. It is unlikely that upward advection or diffusion of methane through marine sediments would be effective in transporting significant amounts to the atmosphere because the methane flux from these processes is generally insufficient to overcome oxidation, consumption, or dissolution within the sediment or lower part of the water column. Catastrophic slope failure appears to be necessary to release a sufficiently large quantity of methane rapidly enough to be transported to the atmosphere without significant oxidation or dissolution. Geochemical evidence is beginning to emerge in support of such events which is next summarized.

Geochemical Signatures of Methane Release

Most methane stored on continental margins as methane hydrate and free gas trapped beneath exhibits very negative carbon isotopic values (~-65‰) typical of biogenic methane produced by methanogenesis within anoxic sediments [Kvenvolden, 1995; Cicerone and Oremland, 1988]. Release of sufficient quantities of this methane imparts a very negative carbon isotopic signal to the dissolved inorganic carbon of seawater through oxidation. This process has been described for the modern ocean by Suess et al. [1999].

Large, negative carbon isotope values have been recorded in benthic foraminifera of the last interglacial age from Peruvian margin near-surface sediments [Wefer et al., 1994] and cold methane seeps on the northern California margin [Rathburn et al., 2000]. In both cases, the large, negative values appear to have resulted from environmental methane influence, such as suggested by Borowski et al. [1999], rather than organic matter oxidation from sulfate reduction [McCorkle et al., 1990] or enhanced organic carbon rain rate [Stott et al., 2002]. This interpretation was also made for large, millennial-scale negative carbon isotopic shifts in benthic foraminifera in the late Quaternary Santa Barbara Basin sequence (Figure 5) [Kennett et al., 2000a]. Millennial and orbital-scale oscillations in carbon isotopes varied by up to 5‰, being

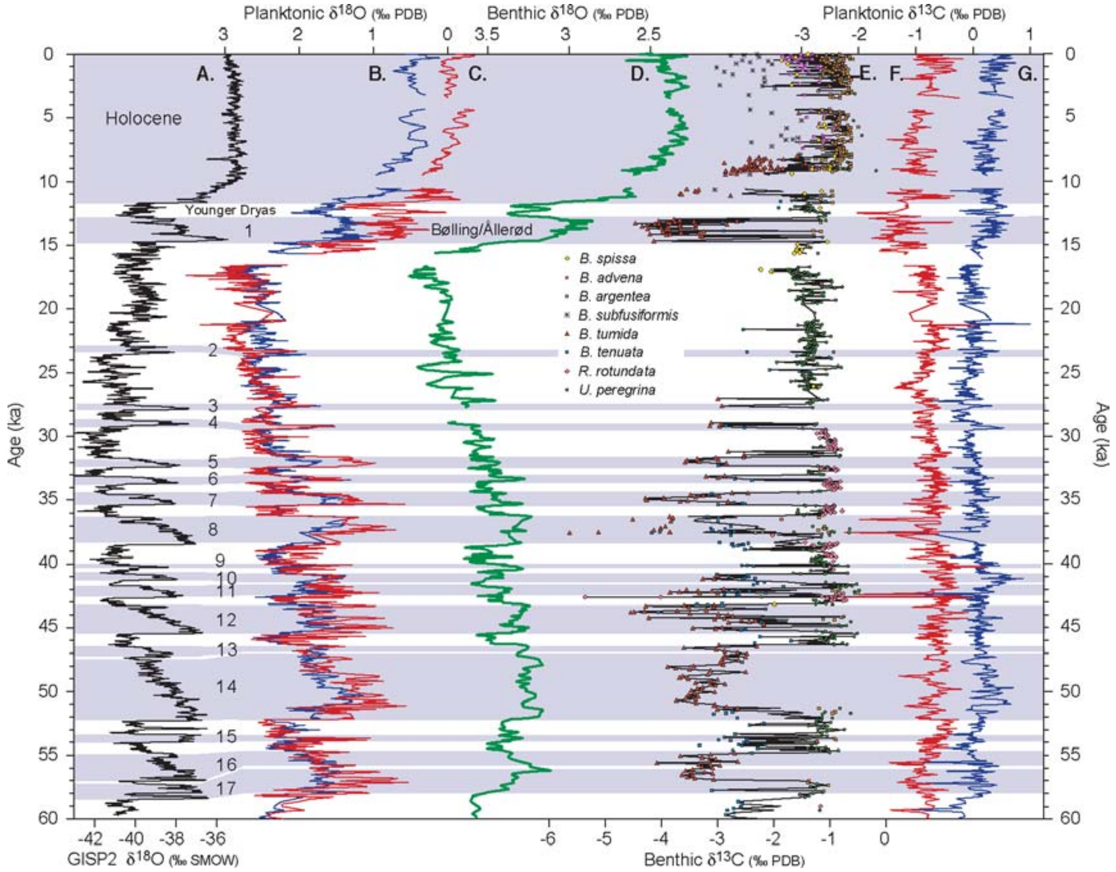

Figure 5. Correlations between (A) GISP2 d18O record [Grootes et al., 1993, Grootes and Stuiver, 1997; Stuiver et al., 1995; Stuiver and Grootes, 2000; chronology of Meese et al., 1994 and Sowers et al., 1993] and (B to G) planktonic and benthic foraminiferal d18O and d13C records from Ocean Drilling Program Site 893, Santa Barbara Basin, California, for past 60 kyr including (B) thermocline-dwelling Neogloboquadrina pachyderma d18O(blue), (C) surface-dwelling Globigerina bulloides d18O (red) [Hendy and Kennett, 1999; Hendy et al., 2002], (D) benthic d18O as a five-channel binomial average (green), (E) benthic d13C record (species shown near center of figure), and planktonic d13C records for (F) G. bulloides (red), and (G) N. pachyderma (blue) [Kennett et al., 2000a]. The warm Dansgaard-Oeschger (DO) interstadials (numbered 1 to 17) [Dansgaard et al., 1993] are clearly shown punctuating the otherwise cold conditions (stadials and glacials) of the last glacial episode. Shading represents intervals of laminated sediments [Behl and Kennett, 1996] associated with warming (interstadials and Holocene). Note benthic d13C oscillations associated with millennial-scale climate change and brief, episodic negative excursions in planktonic and benthic d13C records. ODP Site 893 chronology based on radiocarbon ages and stadial-interstadial transition tie points to GISP2 ice core [Hendy and Kennett, 2000].

very negative (-2 to -6‰) during interstadials and the early Holocene and more positive (~-1‰) during stadials and the LGM. These oscillations were also inferred to reflect widespread shoaling of sedimentary methane gradients and increased outgassing from methane hydrate dissociation during interstadials and the early Holocene [Kennett et al., 2000a].

Past episodes of major methane release from hydrates into the water column were first inferred from carbon isotopic anomalies [Kennett and Stott, 1991] recorded in the latest Paleocene for the entire ocean [Dickens et al., 1995, 1997]. Similar, but local, negative carbon isotopic anomalies have been identified in late Quaternary foraminifera [Maslin et al., 1997; Kennett et al., 2000a; Smith et al., 2001; Keigwin, 2002]. Brief, highly negative carbon isotopic anomalies recorded by latest Quaternary planktonic and benthic foraminifers in East Greenland (68°N) marine sediments have been attributed to methane release into the water column from methane hydrate dissociation [Smith et al., 2001]. These episodes occurred during the glacial terminations at times of deglacial sea-floor depressurization resulting from ice sheet retreat and associated isostatic rebound, and bottom-water warming. Major methane releases are indicated by carbon isotopic excursions in near-surface dwelling planktonic foraminifera living in the open ocean in close proximity to the East Greenland Current. Emerging from these investigations is a record of major but brief episodes of methane releases from methane hydrates into the water column in areas of relatively limited surface water advection. In such restricted areas the geochemical fingerprint of methane emissions is recorded in sediments by microfossils and organic biomarkers. Thus the process of methane hydrate degassing is clearly recorded in sediments of Quaternary age; furthermore, episodes of degassing appears not to be random through time but rather focused at times of significant climate change. The last major episode likely occurred during the last glacial to interglacial transition.

Slope Instability and Mass Sediment Transport

Other evidence for methane hydrate instability is indirectly derived from the timing of marine slumps and sediment transport on continental slopes. The distribution of methane hydrates on upper continental slopes appears closely associated with evidence of mass sediment movement, pockmarks, and other features such as collapse structures resulting from mass sediment disturbance. Based on this relationship it is possible to indirectly infer timing of gas hydrate instability by determining the age of mass sediment disturbance. Mass sediment disturbance caused by methane hydrate instability is likely to be episodic, rather than continuous because of the different rates of change of sea level and bottom-water temperature related to climate oscillations of the late Quaternary. Major slumps on the upper continental slope likely transferred large volumes of methane from the methane hydrate reservoir to the ocean/atmosphere system. Large slumps can potentially release enormous volumes of methane (~1 Pg) into the ocean/atmosphere system. Furthermore, marine geological evidence suggests that large slumps activated by methane hydrate instability appear to be widespread. If correct, this would clearly implicate hydrate instability as an important process in climate change. For example, the Storegga submarine slump off Norway [Bugge et al., 1988] is associated with unstable hydrate fields.

The Storegga slump was enormous, having transported 5600 km3 of sediment 800 km from the upper continental slope into the Norwegian Sea Basin. This slump could have rapidly released between ~1 and 5 Pg of CH4 [Nisbet and Piper, 1998]. Instability of methane hydrates in this region has been exaggerated by post-glacial uplift of the margin [Bugge et al., 1988].

The catastrophic methane releases in Santa Barbara Basin recorded by large, negative benthic and planktonic carbon isotopic excursions (Figure 5) [Kennett et al., 2000a] and may have been associated with submarine slides [Kennett and Sorlien, 1998]. Although these events could be considered relatively small in terms of aerial extent, they have the potential for significant methane release. Conservative calculations accounting for the magnitude and duration of the isotopic excursion suggest 6.4 Tg yr^{-1} was expelled into basin waters, which if transported to the atmosphere, would be equal to ~1.3% of the modern annual flux. At this rate, one brief event may have released ~18% of the average methane increase associated with interstadials [Kennett et al., 2000a]. If methane was efficiently transported to surface waters and the atmosphere, then the total volume of gas released by these events was likely greater than calculated because the amount that escaped into the atmosphere was not recorded by the carbon isotopes of foraminifera.

The high-resolution carbon isotopic records from Santa Barbara Basin (Figure 5) [Kennett et al., 2000a] suggest modulation of methane hydrate instability by millennial-scale oscillations in intermediate-water temperature closely associated with stadial-interstadial cycles. Interstadials were marked by warmer intermediate waters that destabilized basinal hydrates and activated upward methane flux through the sediment (Figure 5). Methane hydrate instability is also inferred to have caused sporadic submarine sliding in the basin that de-roofed methane hydrates and caused massive methane release into the water column and atmosphere (Figure 6). In contrast, cooler stadial waters led to methane hydrate stability, accumulation, and reduced methane flux into the basin (Figure 5). These oscillations were likely widespread along the California margin and elsewhere, affecting methane hydrate instability over broad areas of the margins, and contributing to millennial-scale atmospheric methane oscillations [Kennett et al., 2000a].

Preliminary investigations suggest that there has been a systematic history of major mass sediment deformation on upper continental slopes during the late Quaternary, i.e., slumping episodes activated by methane hydrate instability would have occurred at times of relatively low sea level and increased bottom-water temperatures (Figure 6). The last such major episode was during the last glacial to interglacial transition, an especially vulnerable time for methane hydrate instability. This should have been a time of major sediment instability on the slope. Although the age of most slump activation is poorly constrained, general trends of slump activity are now becoming better known and suggests increased activity during the last glacial termination.

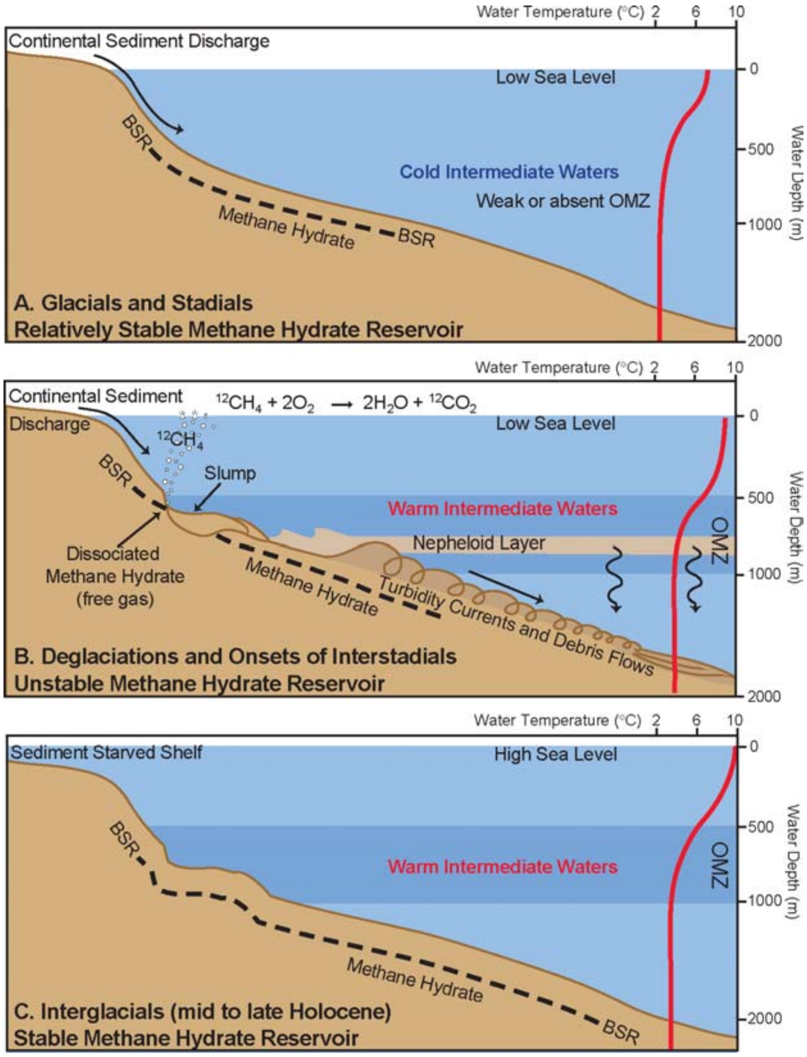

Figure 6. Schematic diagram depicting three different ocean states and associated stability/instability of the upper continental slope methane hydrate reservoir. During glacial and stadial episodes (A), cold intermediate waters led to a relatively stable methane hydrate reservoir, in spite of lower sea levels. Greatest stability of hydrates occurred during the middle to late part of interglacial episodes (C) in response to high sea level and relatively long-term stability of intermediate waters. High instability of hydrates occurred during the intermediate deglacial times and following the onset of interstadials (B). Warming of intermediate waters then caused dissociation of hydrates. This in turn led to major instability of slope sediments, associated mass sediment transport and major release of CH_4 into the ocean/atmosphere system. The presence of methane hydrates on continental slopes is often detected seismically by the presence of a bottom-simulating reflector (BSR) if hydrates are underlain by sufficient free gas. The ocean states are marked by differences in vertical temperature gradient and changing strength of the oxygen-minimum zone (OMZ).

THE CLATHRATE GUN HYPOTHESIS

In response to increasing support that methane hydrates have been an integral part of the climate system and play a role in abrupt climate change a hypothesis has been posited that episodic atmospheric methane emissions resulting from instability of the marine sedimentary methane hydrate (clathrate) reservoir contributed significantly to the distinctive behavior of late Quaternary climate on orbital (Milankovitch) and millennial time scales [Kennett et al. 2002]. Because this model involves punctuated releases of methane from the methane hydrate reservoir, this has been termed the Clathrate Gun Hypothesis. According to this hypothesis, changes in upper intermediate waters intersecting upper continental slopes caused temperature changes of sufficient magnitude to partially destabilize the methane hydrate reservoir (Figure 7). Resulting methane releases to the atmosphere/ocean system provided the amplification to "jump-start" rapid warmings at stadial and glacial terminations that were significantly reinforced by other greenhouse gases, especially water vapor. Collectively, these changes shifted the climate system into an interglacial or interstadial state (Figure 7).

According to this hypothesis, late Quaternary methane hydrate instability occurred even during times of relative sea-level stability because of frequent, rapid upper intermediate-water temperature oscillations over wide areas of the upper continental margins in the depth zone of potential hydrate instability. These temperature oscillations led to successive intervals of methane hydrate instability during the transitions and early portions of warm intervals and stability during cool intervals. It is suggested that the methane hydrate reservoir (clathrate gun) was episodically "loaded" or recharged during cold intervals of the late Quaternary when cold intermediate waters bathed upper continental slopes (Figure 7). The changing temperatures on the upper continental slopes resulted from oscillations in the production of upper intermediate waters in low and high latitudes (Figure 7). Switching to sources of warm intermediate waters at stadial and glacial terminations created instability in the methane hydrate reservoir and catastrophic release of methane into the ocean/atmosphere system as a result of sediment disruption that unroofed hydrates on the upper continental slopes. This led to the well-known rapid warmings of the late Quaternary on different time scales and magnitudes and also produced the sawtooth pattern of late Quaternary climate and atmospheric methane variability exhibited in the 100-kyr cycle and in millennial- scale oscillations (Figures 1 and 2).

The hypothesis predicts extensive instability of upper continental slope sediments during rapid atmospheric methane increases (Figure 7). This instability would have been reflected by widespread development of slumps, debris flows, and pockmarks on continental slopes, and associated downslope mass sediment transport into the ocean basins. The hypothesis predicts that glacial terminations represent intervals of greatest sensitivity of the methane hydrate reservoir because of vertical and lateral expansion of the zone of hydrate-bearing sediment due to prolonged cooling near the end of the glacial cycle combined with especially low sea level (and pressure). Methane emissions would have been greatest during these intervals when methane hydrates were destabilized, a prediction supported by the ice core records. The oscillatory pattern of late Quaternary climate change at millennial to orbital time scales suggests a climate system highly sensitive to feedbacks within the system.

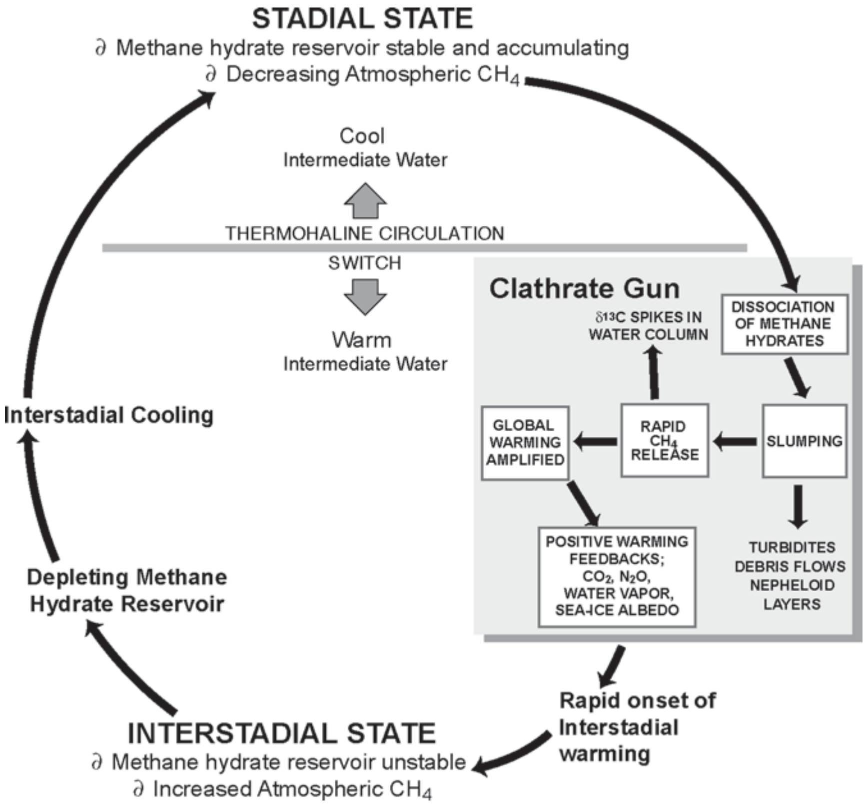

Figure 7. Summary diagram illustrating major elements of the Clathrate Gun Hypothesis. In this hypothesis, climatic feedbacks associated with changing atmospheric CH_4 composition result from changes in the stability of the methane hydrate reservoir associated with changes in bottom-water temperature (shifts in thermohaline circulation). Oscillations occur between stadial (glacial) and interstadial (interglacial) states.

CONSISTENCY OF HYPOTHESIS WITH CLIMATE HISTORY

The speed, magnitude, and timing of the glacial terminations during the late Quaternary ice age are consistent with a process involving major atmospheric methane emission from destabilized methane hydrates. The *Clathrate Gun Hypothesis* predicts that the largest exchange of methane from the hydrate reservoir to the ocean/atmosphere system would occur at glacial terminations for several reasons: 1) low sea levels would have decreased pressure on the hydrate reservoir and increased its potential instability creating a hypercritical state for some hydrates [Buffett & Zatsepina, 1999; Buffett, 2000]; 2) expansion of cold intermediate waters during glacial maxima would have caused growth of hydrates on shallower regions of upper continental slopes; and 3) the several thousand year interval during glacial maxima marked by relatively stable, cold deep-sea waters would have caused growth of hydrates especially in areas where continuous upward diffusion of methane adds to the volume of hydrate [Hyndman et al., 2001]. Such conditions should have occurred at shallow depths within the sediment column. At this stage in the glacial cycle, conditions were most favorable for the largest volume of gas to be released by methane hydrate dissociation upon warming of intermediate waters [Kennett et al., 2000a; Hendy and Kennett, submitted]. Consistent with this explanation is the repeated association of the coldest, most glaciated interval, followed by the warmest with distinct methane overshoots observed at some terminations. Highest methane values tend to occur early in interglacial and interstadial episodes which is consistent with this hypothesis.

A critical component of the *Clathrate Gun Hypothesis* is the effect of bottom-water temperature increases at the depths of potential methane hydrate instability (~400 to 1000 m) (Figure 4). Changes in sea level alone were not sufficient or rapid enough to cause major instability. Pressure decrease related to a 100 m drop in sea level is equal to only about one degree or less of bottom-water warming in the zone of potential methane hydrate instability (Figure 4). Yet, strong evidence exists for significant temperature increase (~3°C) of upper intermediate waters on continental margins during deglaciation, probably sufficient to destabilize methane hydrates.

The remarkable millennial-scale climate variability during the latest Quaternary, including abrupt global warmings, was driven by processes yet unexplained. The behavior of these short-duration events gives insight into the processes involved in the larger orbital-scale deglaciations. Any hypothesis proposed to explain this climate history must be consistent in explaining the record at all time scales through the late Quaternary. The following major characteristics of millennial-scale climate behavior during the last glacial cycle appear consistent with the *Clathrate Gun Hypothesis*:

- Remarkably rapid warmings at the onset of interstadials.
- Significant climate instability during these warmings [Sachs and Lehman, 1999].

- Close association and similar relative magnitude of temperature and atmospheric methane variation.
- Largest climate variability during MIS 3 when the methane hydrate reservoir was particularly unstable because of low sea-level and intermediate-water temperature oscillations.
- Strong tropical involvement in stadial-interstadial cycles including large changes in temperature and continental precipitation.
- Largest warmings at the onset of interstadials when methane hydrate dissociation and hence atmospheric methane emission would have been greatest.
- Brief, conspicuous temperature overshoots at the onset of many interstadials recorded in polar ice cores and marine sediment suggestive of dynamic temperature increases.
- Brief, conspicuous methane overshoots at the onset of several interstadials suggesting dynamic methane release from methane hydrates.
- Sawtooth pattern of temperature and methane during interstadials because of rapid increases and slower decreases.
- Clustering of stadial-interstadial cycles into groups (Bond Cycles) that initiate with the warmest interstadial and subsequently decrease in magnitude. Bond Cycle terminations are marked by the most extended cool episode (Heinrich Event) that immediately precedes the next major warming marking the onset of the next Bond Cycle. Thus, the coldest episodes are juxtaposed with the warmest, much like that of the 100-kyr cycle. The resulting sawtooth pattern is thus consistent with cycles that begin with major hydrate dissociation following extended cool periods followed by interstadial episodes of decreasing magnitude. This pattern is consistent with initial dissociation of the most accessible, near surface methane hydrates followed by the gradual accumulation of methane hydrates as colder intermediate waters become progressively more dominant and warm intermediate waters during interstadials become weaker and less extensive. The magnitude and duration of interstadials are also likely modulated by orbital forcing (tilt and precession), that affects the extent, temperature and duration of thermohaline circulation changes in a non-linear relationship. Thus MIS 5 and early MIS 3 warm episodes were of longer duration and generally warmer than those of MIS 4 and later MIS 3.
- Synchronous millennial-scale climate change between the high northern latitudes, middle latitudes, and tropics and between terrestrial and marine systems. This is consistent with a greenhouse forcing mechanism and teleconnections via the atmosphere.
- Rapid (decades to centuries) interstadial terminations. These intervals are matched in Santa Barbara Basin by sudden, rapid bottom-water cooling, reflecting a sudden switching to cool intermediate waters. This evidence is consistent with a sudden decrease in

methane emissions because of the methane hydrate reservoir stabilization. The brevity of interstadials (500 to 2000 yr) is thus linked to the duration of warm intermediate-water episodes that largely control methane hydrate reservoir stability. Initial warming of upper intermediate waters is amplified into abrupt, major warming marking the onset of interstadial and interglacial episodes by release of methane from dissociating methane hydrates. This forcing of temperature change in upper intermediate waters operates at a more rapid pace than orbital cycles. The nature of this suborbital pacemaker remains largely unknown and represents one of the most vexing problems in earth sciences.

THE FUTURE

Can Changes in Methane Hydrates Significantly Impact Future Climate Change?

The methane hydrate reservoir is known to contain sufficiently large volumes of methane to potentially play an important role in global climate change. This is the largest fossil fuel reservoir and has been estimated at containing ~3000 times the amount of methane in the modern atmosphere. Thus even some instability of the methane hydrate reservoir could have significant climatic consequences given the potency of methane as a greenhouse gas. However, in spite of the potential for climate change and evidence of some instability of the reservoir in the recent geologic past, it remains unclear if methane hydrates experienced degassing episodes of sufficient magnitude to affect global climate warming during the late Quaternary. The initial challenge is to conclusively determine if major degassing events did occur during the late Quaternary and if the abrupt increases in atmospheric methane recorded in ice cores are related to hydrate instability. A further challenge is to determine if these degassing events were important agents in climate change. If so, it is clear that such events can be expected in the future. A primary question is the relative sensitivity of the modern methane hydrate reservoir to dissociation and instability in response to possible future increases in temperature of intermediate waters. It is possible that the geologic evidence may indicate no major effects of methane hydrate degassing on abrupt climate change, in which case future concerns are markedly decreased. Nevertheless, it can be expected that during the last 10 thousand years, methane hydrates have been relatively stable in response to high sea levels (higher pressure) and relative stability of intermediate water temperatures. This is supported by marine geological evidence. If this is the case, in the absence of major degassing it follows that the methane hydrate reservoir likely has increased in volume. This potentially increases vulnerability to any future temperature increases in bottom waters.

The possible future consumption of hydrate methane as a fuel will clearly contribute to atmospheric CO_2 with potential climatic effects. On the other hand, methane as a fuel has the advantage of being a relatively clean and more efficiently burning fuel than other fossil fuels. Furthermore, technological developments may enable methane to be employed as a hydrogen fuel source with significant societal benefits.

RESEARCH NEEDS

In this report, we have briefly summarized a wide range of data from ice cores and marine and continental sedimentary and paleontological records that, collectively formulated as the *Clathrate Gun Hypothesis*, appear to make a compelling explanation of many aspects of late Quaternary climate behavior. Nearly all data relevant to this hypothesis has resulted from studies conducted during the last decade or few years. This is a youthful field of enquiry and many of the most fundamental questions remain unresolved. Given this, a wide range of experiments are required to test the hypothesis that methane hydrates represent a critical and integral and part of the late Quaternary climate system. It is likely that a number of rigorous tests, summarized in this report, will be required to confirm or negate the various elements that make up the hypothesis. Some of these are suggested below, arranged by the component tested.

Atmospheric Methane Record of Ice Cores

- Refine models and tests of the effects of gas diffusion, gravitational separation and the gas-age/ice-age difference on the phasing and rate-of-change of methane relative to temperature in ice cores during abrupt warmings. Simply stated, if methane was a primary mechanism driving abrupt climate warming events, the rises in methane could not have lagged the abrupt climate changes.
- Investigate the influence of post-incorporation microbial and chemical processes on preserving or modifying atmospheric gas concentrations in the ice, especially that of methane.
- Determine validity and frequency of brief methane “overshoots” associated with rapid methane increases in ice cores through high temporal resolution investigations.

Source of Atmospheric Methane

- Determine the stable isotopic composition of C and H from methane in ice cores as an indication of its source-methane hydrate or terrestrial wetlands.
- Determine ^{14}C activity of methane in ice cores from samples of known age to differentiate contemporaneous wetland sources from predicted older methane derived from methane hydrates.

Wetland History

- Refine timing of wetland initiation and evolution in several critical areas including the large modern ecosystems in southeast Asia.
- Determine wetland extent and variability during the millennial-scale climate oscillations of the last glacial episode.

Marine Methane Hydrate Stability

- Determine spatial and temporal variability of inferred major methane emissions from methane hydrates during the late Quaternary and compare them with the ice core methane records.
- Develop better understanding of processes that destabilize the methane hydrate reservoir and transport methane out of marine sediments into the ocean and then into the atmosphere. What are the processes that modify methane as it migrates through the oceans?
- Strengthen understanding of proxies for past methane emissions to the water column from methane hydrates including carbon isotopes, organic biomarkers, and faunal assemblages.
- Better determine the spatial and temporal history of mass sediment wasting from continental slopes for comparison with predicted intervals of methane hydrate instability during the late Quaternary.
- Determine if evidence exists, such as pockmark fields, for widespread methane hydrate distribution at or near the ocean floor during predicted intervals of methane hydrate instability during the late Quaternary.

Paleoceanography/Paleoclimatology

- Improve global coverage of records of rapid, millennial-scale climate oscillations during the late Quaternary to determine potential inter-hemispheric climate synchroneity that would have resulted from greenhouse gas forcing.
- Better understand spatial and temporal variability of upper intermediate water thermohaline circulation especially as it affects bottom water temperature within the depth zone of potential methane hydrate instability (~400 to 1000 m) on continental slopes.
- Determine whether anomalous ^{14}C reservoir ages documented for the deglacial episode and other times during the late Quaternary were affected by release of ^{14}C-depleted methane from methane hydrates rather than by changes in ocean circulation.
- Investigate earlier episodes of climate behavior like that of the late Quaternary (“100-kyr world”) to test the potential role of methane hydrates as a cause of this climate variability.

Modeling

- Expand models of methane atmospheric chemistry to accommodate the full range of variation in fluxes, sources, and sinks likely encountered during the late Quaternary, especially with respect to changes in atmospheric methane residence time related to inferred rapid, major releases from methane hydrates.

- Evaluate if estimated increases in atmospheric methane levels were sufficient to activate global warming episodes. Refine climate models by incorporating additional feedbacks associated with rapid atmospheric methane increases.
- Refine models of late Quaternary changes in the inter-polar methane gradient to incorporate the potential contributions of methane hydrates as globally distributed at various times on the continental margins.
- Model the variation in size and distribution of the methane hydrate reservoir through the late Quaternary as constrained by changes in intermediate water temperature, sea level, and ice coverage.

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