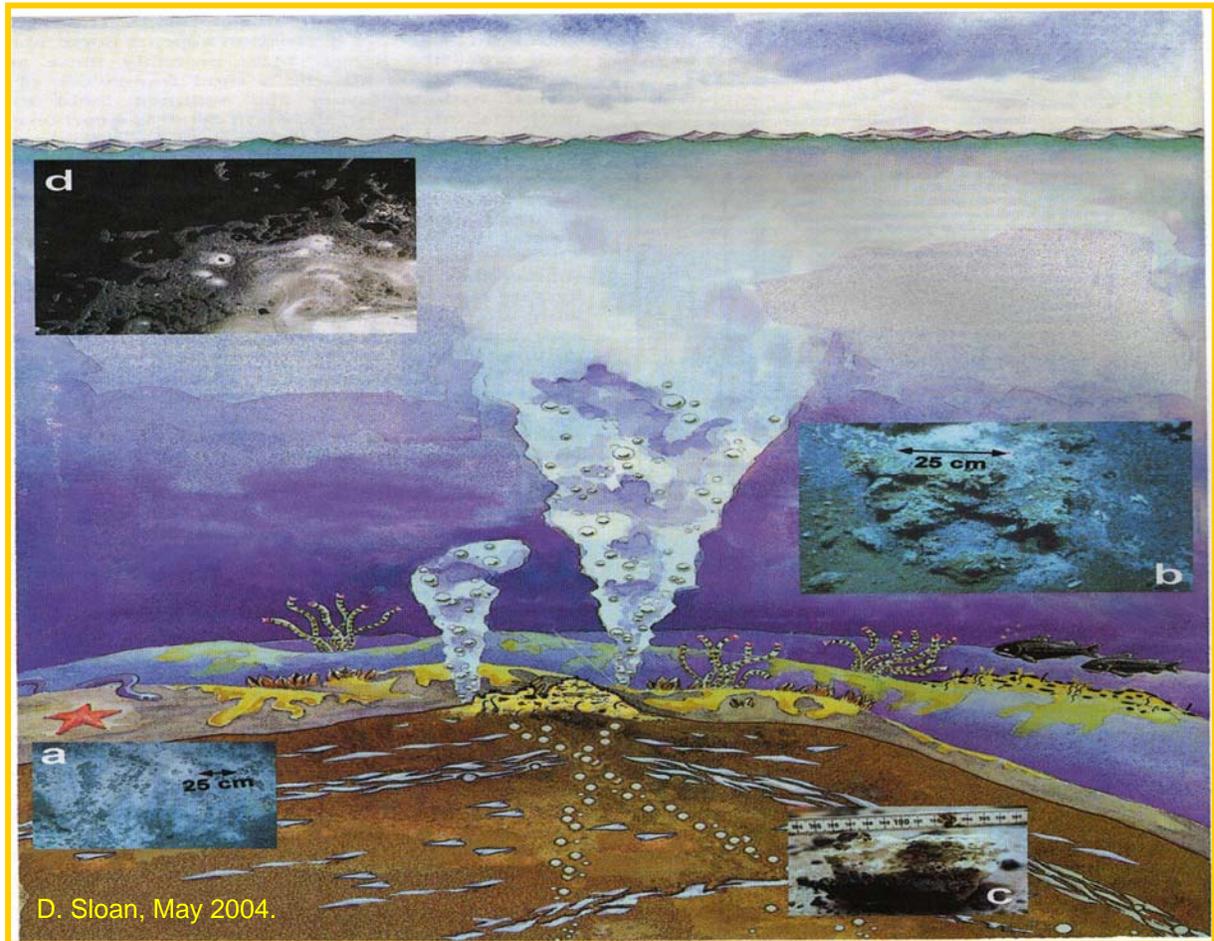


Role of Ocean Methane and Gas Hydrates in Global Climate Change Workshop



May 13-14, 2004
NOAA Climate Monitoring and Diagnostics Lab (CMDL)
Boulder, CO

FINAL REPORT
February 2005

Role of Ocean Methane and Gas Hydrates in Global Climate Change

Report from Workshop, May 13-14, 2004, NOAA Climate Monitoring and Diagnostics Lab (CMDL), Boulder, CO

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- Dr. Jean Whelan, Woods Hole Oceanographic Institute (lead)
- Andrew Shepard, University of North Carolina at Wilmington (coordinator)
- Dr. Lori Bruhwiler, CMDL (host)
- Dr. Ed Dlugokencky, CMDL (co-host)
- Barbara Moore, NOAA Undersea Research Program (NURP)
- Tom McGee, University of Mississippi

Sponsors:

- Department of Energy: National Energy Technology Laboratory
- Department of Commerce-- NOAA: CMDL; NURP—headquarters, and regional centers (National Institute of Undersea Science and Technology at University of Mississippi; West Coast and Polar Region at University of Alaska; Southeast and Gulf of Mexico at the University of North Carolina at Wilmington; Mid-Atlantic Bight at Rutgers University; North Atlantic and Great Lakes Center at University of Connecticut)
- Department of Interior: Minerals Management Service; U.S. Geological Survey
- Deep Ocean Exploration Institute, Woods Hole Oceanographic Institution

Acknowledgements:

This workshop was the first ever to bring NOAA carbon and climate modelers and measurers together with methane hydrate and oceanic methane gas experts. It was the result of growing recognition by the undersea research community of the ubiquitous nature of hydrate deposits in the continental margins and a curiosity about this omission from current thinking within the climate modeling community. Arranging this collaboration required that the organizing committee receive help from many people especially Rita Rosson, CMDL, Yvette Jefferson, NURP, and Ann Thorne, CMDL. Special thanks to David Hofmann, CMDL director, for his vision and belief in the project and to Andrew Shepard whose energy and persistence was responsible for the execution of the workshop and overall preparation of the report. We are grateful to the workshop participants who came from across the globe to provide their scientific opinions on a controversial topic:

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EXECUTIVE SUMMARY

Workshop Purpose:

Models used to predict the impact of atmospheric concentrations of radiatively active (greenhouse) gases, including carbon dioxide and methane, and their impact on climate change and sea-level rise, require accurate estimates of gas sources and fluxes (IPCC 1997). According to widely held atmospheric methane budgets (IPCC 2001; Cicerone and Oremland, 1988), the oceans and seafloor annually contribute relatively small amounts of methane, on the order of 3-10 teragrams (Tg) CH₄ yr⁻¹ out of the total 600 Tg. However, evidence presented in recent papers suggests that a variety of poorly constrained geological sources might annually supply 16-60 Tg CH₄ yr⁻¹ to the atmosphere (Judd 2003; Etiope, 2004; Kvenvolden and Rogers, in press). Anecdotal observations suggest the amount may be significantly higher. The types and pathways from ocean sources are especially poorly described and understood, particularly for the deep sea where most ocean hydrates occur. Given that the current total atmospheric methane budget is well-constrained, other methane sources (including anthropogenic) may be overestimated.

Recent reviews also implicate hydrate release events in past, abrupt shifts of global temperature of up to 5-7° C (Dickens et al. 1997), and millennial-scale fluctuations of atmospheric methane over the past 60,000 years (Kennett et al. 2000). As suggested by Kennett (2003), research is needed to “*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*” (Kennett, 2003).

In May 2004, the National Oceanic and Atmospheric Administration (NOAA), the hydrate consortium agency member most concerned with global climate change, coordinated a workshop to address the role that seafloor methane hydrates may play in global climate change—past, present and future. In May 2004, NOAA’s Climate Monitoring and Diagnostics Lab (CMDL), Boulder, CO, hosted the workshop and motivated participation of the climate modeling and measurement community. To our knowledge, this was the first such meeting dedicated to bringing climate/carbon modelers and measurers together with the hydrate research community. Specific workshop objectives included:

- To inform the NOAA carbon and climate community about the status of knowledge and issues related to seafloor gas hydrates;
- To inform the gas hydrates science community about how the carbon/climate community currently perceives the role of gas hydrates in climate change;
- To introduce and form new partnerships between NOAA carbon/climate modelers and measurers and gas hydrate researchers; and
- To propose a pilot experimental program designed to assess flux of methane from seafloor hydrates to the atmosphere.

Findings:

Through plenary presentations, breakout working groups, informal discussions, and post-meeting feedback, the international group of over forty participants arrived at many findings and recommendations, including the following highlights:

- Ocean hydrates are an important part of the bigger ocean methane picture—priority research should consider hydrates as one sink/source and process in the ocean carbon cycle and the methane cycle in particular;
- Total global methane budget is well-constrained, but sources and sinks are less certain;
- Paradigm that oceans are an insignificant methane source is based on small, poorly constrained database;
- Current global atmospheric methane budget does not accurately account for naturally occurring, geologically-sourced, fossil methane emissions;
- Research and modeling efforts are needed to establish the relation (cause/effect) of past spikes in atmospheric methane to episodes of climate change, particularly in Pleistocene, and role of ocean sources;
- Relations between methane spikes, climate changes/global warming, sea level, hydrate destruction, slope failures, and seafloor release events are not understood, and the “Clathrate gun” hypothesis is a theory that needs to be tested.

A pilot experimental program is recommended that will: assess the role of ocean methane and hydrates in global climate; help identify and address priority research questions; develop required approaches and technologies; and involve new expertise and partners. Key objectives should include:

- Map gas deposits at and under the seafloor;
- Determine pathways and fluxes of methane gas from ocean sub-bottom to the atmosphere;
- Describe controlling processes and rates of formation and degradation of ocean methane;
- Determine short and long-term stability of gas hydrates; and
- Determine potential triggers of hydrate dissociation and extreme gas release events, and impacts of events on seafloor stability.

In the final plenary session, participants endorsed development of a position statement regarding the need for future hydrates and climate-related research, for submission to various planning and funding programs (e.g., DoE and International research consortia, NAS Ocean Studies Board, Hydrate Program review panel), and support for the re-authorization of the Methane Hydrate Research Act:

“Ocean floor sediments host enormous quantities of methane as dissolved gas, gas hydrate, and free gas bubbles. This global reservoir leaks into the sea through a variety of poorly described and understood mechanisms and pathways, ranging from rapid emissions from volcano-like vents to slow seepages over wide-area deep ocean bottom seeps.

Current ocean carbon models assume that most methane escaping from the seafloor does not reach the atmosphere, because of intense biological oxidation in the water column and sediments. However, methane does reach the atmosphere in localized zones of intense seafloor seepage where methane is rapidly ejected as bubble streams, mud volcanoes, or gas hydrate pieces—forms that may reach the atmosphere before biodegradation depletes methane. These localized areas of “focused methane flow” are continuing to be discovered in the ocean floor, particularly along continental shelves and margins. There is evidence that occasionally in earth’s history, massive releases of methane from hydrates may overwhelm the biological methane oxidation process, thus introducing vast amounts of methane over short period of geologic time—enough to significantly increase methane in the atmosphere and change global climate

We must improve understanding: 1) of types, fluxes, and fates of methane emissions from the seafloor, 2) of the role of methane in global and localized oceanic carbon cycles, and 3) of the geologic record of past methane release associated with abrupt climate changes and the potential role that seafloor methane may have played.

Major destructive events, such as the recent tsunami generated by a major sub-sea earthquake in the Indian Ocean, highlight the grave need for better monitoring and understanding of seafloor stability and related forcing factors. Gas hydrates have been implicated in past similar events.

The new Department of Energy strategic plan for methane hydrate studies over the next ten years (2005-2010) includes climate-related research as a funding priority. These efforts should be included in the upcoming re-authorization of the Methane Hydrate Research Act, and NOAA and DoE together should partner to develop the research plan and appropriate funding for these studies, beginning immediately.”

This Executive Summary is intentionally limited in its coverage of the broad range of information and key recommendations included in the report and accompanying CD. The latter includes the complete report, plus copies of the plenary presentations and can be obtained from the NOAA Undersea Research Program, 1315 East West Hwy, Silver Spring, MD 20910.

GLOSSARY OF ACRONYMS

CMDL	Climate Monitoring and Diagnostics Laboratory (http://www.cmdl.noaa.gov)
CODATA	Committee on Data for Science and Technology (http://www.codata.org)
DOE	Department of Energy (http://www.doe.gov)
ICHR	International Consortium for Hydrate Research
IODP	Integrated Ocean Drilling Program (http://www.iodp.org)
IOOS	Integrated Ocean Observing System (http://www.ocean.us)
IPCC	Intergovernmental Panel on Climate Change (http://www.ipcc.ch/)
MMS	Minerals Management Service (http://www.mms.gov)
NETL	National Environmental Technology Laboratory (http://www.netl.doe.gov)
NOAA	National Oceanic and Atmospheric Administration (http://www.noaa.gov)
NURP	NOAA Undersea Research Program (http://www.nurp.noaa.gov)
OOI	Ocean Observatories Initiative (http://www.nsf.gov/pubs/2003/nsf03576/nsf03576.htm)
ORION	Ocean Research Interactive Observatory Networks (http://www.orionprogram.org)
USGS	U.S. Geological Survey (http://www.usgs.gov)

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1.0 BACKGROUND

1.1 METHANE HYDRATE ACT AND INTERAGENCY CONSORTIUM

The Methane Hydrates Act of 2000 (<http://www.netl.doe.gov/scng/hydrate/rdprogram/hydratesact2000.htm>) defined key issues surrounding naturally-occurring gas hydrates in the seas, including:

- hydrates as geohazards to fossil fuel development;
- hydrates as a fuel source;
- hydrates as an ecosystem; and
- **hydrates' role in the global carbon cycle and climate change.**

Since the Act was passed, DoE's National Energy Technology Lab (NETL) has led an inter-agency consortium, and hosted annual meetings and workshops to determine research needs and present results of on-going research programs. Their efforts have mostly targeted issues and objectives of primary relevance to oil and gas development. However, NETL's "2003 Report of the Methane Hydrate Advisory Committee," also includes a special report by Dr. James Kennett, UC-Santa Barbara that implicates hydrates as a major forcing factor in climate change and calls for development of a related international research plan.

1.2 METHANE, CARBON CYCLE, AND CLIMATE

Models used to predict reservoir concentrations of radiatively active (greenhouse) gases, including carbon dioxide and methane, and their impact on climate change and sea-level rise, require identification of methane sources and estimates of fluxes. Current global methane budgets estimate that about 600 Tg CH₄ enters the atmosphere each year (IPCC, 2001). The largest estimated annual contributors include: tropical and boreal wetlands [~100 teragrams (Tg) CH₄], fossil fuel exploitation (about 80-100 Tg CH₄), and ruminant animals (about 80 Tg CH₄). At present, gas hydrates are assumed to be relatively small sources, on the order of 3-10 Tg CH₄ yr⁻¹ (IPCC 2001; Cicerone and Oremland, 1988; Judd et al. 2002; Kvenvolden and Rogers, in press). However, published values for total geological methane emissions from all land and seafloor sources to the atmosphere range from 16-60 Tg CH₄ yr⁻¹ (Judd et al. 2002; Etiope and Milkov, 2003; Etiope, 2004; Kvenvolden and Rogers, in press). The types and pathways from ocean sources are especially poorly described and understood, and particularly for the deep sea where most ocean hydrates occur. Given that the current methane budget is well-constrained based on "top down" observations of global atmospheric methane, if ocean emissions are under-estimated and form a significant portion of the total geological emissions (<60 Tg CH₄ y⁻¹), then "bottom-up" estimates of emissions from other sources would have to decrease to maintain the "top-down" global total.

The IPCC Third Assessment Report (IPCC, 2001) stated that there was no evidence for rapid large-scale increases in atmospheric CH₄ from decomposition of hydrates in ocean sediments. This finding is contradicted, however, by other recent literature that indicate hydrates have caused or contributed to past, rapid shifts of global temperature of up to 5-7° C, enough to melt the polar ice caps, raise sea-level by a meter, and cause massive species extinctions (Dickens et al. 1997; Hesselbo et al. 2000). Further, millennial scale fluctuations of atmospheric methane over the past 60,000 years have been attributed to hydrate instability (Kennett et al. 2000). As suggested by Dr. Kennett in his NETL report, also presented as testimonial to Congress, research is needed to "*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” (Kennett, 2003).

1.3 2004 WORKSHOP—GAS HYDRATES ROLE IN CLIMATE CHANGE

In May 2004, the National Oceanic and Atmospheric Administration (NOAA), the hydrate consortium agency member most concerned with global climate change, coordinated a workshop to address the role that seafloor methane hydrates may play in global climate change—past, present and future. NOAA’s Climate Monitoring and Diagnostics Lab (CMDL), Boulder, CO, hosted the workshop and motivated participation of the climate modeling and measurement community. NOAA’s Undersea Research Program (NURP) coordinated the event, led by Jean Whelan, Woods Hole Oceanographic Institution, and Andrew Shepard, NURP Southeast Regional Center at the University of North Carolina at Wilmington. The organizing committee also included: Barbara Moore, NOAA Undersea Research Program; Tom McGee, University of Mississippi; Ed Dlugokencky, CMDL; and Lori Bruhwiler, CMDL. Sponsors included:

- Department of Energy: National Energy Technology Lab
- Department of Commerce-- NOAA: CMDL; NURP—headquarters, and regional centers (National Institute of Undersea Science and Technology at Univ. of Mississippi; West Coast and Polar Region at Univ. of Alaska; Southeast and Gulf of Mexico at the University of North Carolina at Wilmington; Mid-Atlantic Bight at Rutgers Univ.; North Atlantic and Great Lakes Center at Univ. of Connecticut)
- Department of Interior: Minerals Management Service; U.S. Geological Survey
- Deep Ocean Exploration Institute, Woods Hole Oceanographic Institution.

Special thanks to Edie Allison and Brad Tomer at DoE for their continued leadership of the U.S. hydrate program and this workshop.

2.0 GOALS AND OUTCOMES

Workshop goals included:

- To inform the NOAA carbon and climate community about the status of knowledge and issues related to seafloor gas hydrates;
- To inform the gas hydrates science community about how the carbon/climate community currently perceives the role of gas hydrates in climate change;
- To introduce and form new partnerships between NOAA carbon/climate modelers and measurers and gas hydrate researchers; and
- To propose a pilot experimental program designed to assess flux of methane from seafloor hydrates to the atmosphere.

The most prominent and immediate issue regarding ocean methane for NOAA's carbon/climate measuring and modeling community is the disparity between how much methane may theoretically reach the atmosphere from seafloor sources on an annual basis, compared to current estimates of sources from land-based sampling stations. Thus, the primary outcome of the workshop is an analysis of this issue and design of a measuring program that may resolve related questions.

3.0 WORKSHOP PROCESS

3.1 PARTICIPANTS AND AGENDA

Forty-four workshop participants included experts in a wide array of disciplines and areas of expertise (Appendix A). The agenda (Appendix B) included: 1) plenary presentations by a dozen experts in ocean carbon, climate, and methane hydrate research and modeling (Table 1); and 2) breakout sessions by working groups (Appendix C1-C3).

3.2 BREAKOUT WORKING GROUPS

The primary workshop product is an outline for a national, inter-disciplinary proposal that will address the key question identified in the original invitation:

“Regarding methane hydrates, the most prominent and immediate issue for NOAA’s measuring and modeling community is the disparity between how much methane may theoretically reach the atmosphere from seafloor sources on an annual basis, compared to current estimates of sources from land-based sampling stations.”

Prior to the meeting, several of the participants submitted what they considered to be the most pressing research questions, and related objectives and approaches (table of all these responses is included on the meeting CD, but not with this report). The organizing committee reviewed these questions and subdivided them into **three main themes**:

1. What are dissociation rates, formation rates and controls on hydrate formation and destruction in sediments? [**Seafloor processes**]
2. What are the types and causes of extreme methane gas release events from the seafloor? [**Extreme events**]
3. How much and how fast is methane transferred from the ocean bottom to the atmosphere? [**ocean/atmosphere processes**].

Working groups then broke out into two sessions:

SESSION I (Day 1; participants assigned to 3 groups based on mix of disciplines and institutional representation): Review, reword and identify **priority questions** within each of the **three themes**. Led by facilitator and recorder, participants edited and revised the list of priority questions that was submitted before the meeting.

Following Session I, the organizing committee took the working group’s lists and pared them down to 4-5 questions per theme.

SESSION II (Day 2; participants chose working group/theme they wished to attend): Three groups, one for each theme, first reviewed and refined the priority questions, then developed **approaches** needed to address priority questions, and identified **partners and funding** opportunities for each proposed approach.

The final plenary on day 2 also focused on: 1) possible products that could result from the meeting; and 2) critical messages the group wanted to see included in the report.

4.0 RESULTS

4.1 PLENARY PRESENTATIONS

Oral presentations on the first morning familiarized workshop participants with the breadth of oceanic and climatic processes potentially impacted by hydrates, and how these processes may intertwine with efforts to explore for and produce these hydrate-associated resources commercially (Table 1). Introductory talks gave workshop background and objectives (**Hofmann, Moore, Tomer**). Scientific talks began with a summary of state of knowledge of gas hydrates in terms of laboratory studies, where they are located, and how and where they might be produced (**Sloan**). Two talks described the potential role that methane hydrates may have on triggering global climate changes (**Kennett, Dickens**). Two talks then summarized recent advances and future possibilities for observing methane hydrates on and under the seafloor (**MacDonald, Peltzer**). Three talks provided a primer on current state of knowledge of methane’s relationship to climate change and the ocean carbon cycle (**Feely, Bruhwiler, Matthews**). Finally, an overview of international gas hydrate programs was given (**Judd**). Powerpoint versions of these talks are included on the meeting CD.

Table 1. Oral presentations: Powerpoint versions on meeting CD.

Speaker	Affiliation	Title
Hofmann, Dave	NOAA/CMDL	<i>Workshop Welcome</i>
Moore, Barbara	NOAA/NURP	<i>Workshop Objectives</i>
Tomer, Brad	DoE/NETL	<i>DOE Research into Naturally-Occurring Methane Hydrates</i>
Sloan, Dendy	Colorado School of Mines	<i>Hydrates: What and Where are They and How do They Behave in the Ocean?</i>
Kennett, James	Univ. of California at Santa Barbara	<i>Methane Hydrates in Late Quaternary Climate Change: Compelling Evidence and Debate for an Outrageous Geological Hypothesis</i>
Dickens, Gerald	Rice University	<i>Why the Global Carbon Cycle Needs Seafloor Methane</i>
MacDonald, Ian	Texas A&M at Corpus Christi	<i>Transfer of Hydrate Methane to Ocean and Atmosphere: Three Stability Models from Gulf of Mexico</i>
Peltzer, Edward	Monterey Bay Aquarium & Research Institute	<i>Recent Advances in ROV In situ Observations of Gas Vents and Methane Clathrate Hydrates</i>
Feely, Richard	NOAA Pacific Marine & Environmental Lab	<i>Gas Hydrates, Carbon Cycle, and Climate: Workshop to Identify Research Issues and Needs—Ocean Carbon Cycle</i>
Bruhwiler, Lori	NOAA/CMDL	<i>Potential Influence of Hydrates on the Budget of Atmospheric CH₄: Modeling Perspectives</i>
Matthews, Elaine	NASA Goddard Space Flight Center	<i>Using Time Series of Methane Emission to Constrain the Global Methane Budget</i>
Judd, Alan	University of Newcastle	<i>Current Hydrate Research in Europe</i>

4.2 WORKING GROUPS’ FINDINGS

4.2.1 Background Issues

Complete notes from the breakout sessions are included in Appendices D1, D2 and D3. Following are highlighted background issues identified by the working groups or post-meeting position papers:

- Methane is a powerful greenhouse gas. Thus, accurate climate models depend on an accurate global methane budget, particularly for the ocean where current measurements of total methane leaking into the water column from continental shelves and slopes worldwide could be off by as much as an order of magnitude.

- Hydrates likely contain twice the amount of methane as all other fossil fuels combined—a pool with significant potential to contribute to past, current, and future climate changes. However, methane hydrate importance cannot be separated from the larger issue of methane from the sea. Future efforts must focus on ocean methane in general, with gas hydrates as one component.
- Although the total methane budget is well-constrained, the sources and sinks are uncertain. The current global atmospheric methane budget does not account for naturally occurring, geologically-sourced, fossil methane emissions. The current paradigm that oceans are an insignificant methane source is based on a very small and poorly constrained database. Poorly known geologic sources of methane from the seafloor to the atmosphere include natural gas seeps, particularly those in coastal areas and on continental shelves (which are likely most active during storm events), and mud volcanoes that may be larger contributors than gas hydrates. In fact, current estimates of oil and gas industry contributions are probably too high and the likely missing term involves geologic sources on land and under the ocean.
- The atmosphere now contains about 4850 Tg CH₄, resulting in an average atmospheric surface abundance of 1745 ppb (IPCC, 2001). The total amount of methane entering the atmosphere each year is 600 Tg, of which an estimated 95% is destroyed by oxidation. Assuming the current atmospheric budget is correct, postulated additional methane emissions must be accommodated within this total.
- Over 80% of the annual methane flux is estimated to be from microbial processes (methanogenesis). Although oceans are now considered to be a small methane contributor (~5-10 Tg y⁻¹) to this flux, oceanic methanogenesis produces much more than this estimate (70 Tg y⁻¹ in ocean sediments and waters). Clearly, changes over time, small errors in estimated fluxes, or in the amount of methane annually produced or oxidized, would have significant impacts on the current atmospheric budget calculations.
- Etiope (2004) and Kvenvolden (Appendix D) conservatively estimate that 40-60 Tg CH₄ y⁻¹ reaches the atmosphere from geological sources. Because this methane is isotopically heavy in terms of ¹³C and devoid of ¹⁴C, it can only be accommodated in the global atmospheric methane budget within the 110 Tg y⁻¹ currently assigned by IPCC (2001) to fossil fuel usage. Therefore, the amount of methane emission attributed to fossil fuel usage should be reduced by 45 Tg y⁻¹, leaving only 65 Tg y⁻¹ to be attributed to the anthropogenic exploitation of fossil fuels and partitioned between coal mining and petroleum (natural gas) production.
- Although the current on-going methane emissions from ocean sources are not likely enough to significantly affect climate, massive releases of gas-hydrate methane may significantly impact the atmospheric burden by adding large amounts of mainly microbially sourced (¹³C-depleted) methane to the ocean/atmosphere system. Such massive injections of methane from gas hydrate may have affected global climates in the past and could influence climates in the future. Given the current global warming trend, there is great need to understand the relation of past spikes in atmospheric methane to episodes of climate change, particularly in the Pleistocene. What are the relations between past climate changes, global warming, hydrate destruction, slope failure and methane spikes in the atmosphere? The "clathrate gun" hypothesis is a theory that remains to be tested. Time constraints in the geologic record on linkages between any of these processes are poorly understood.

4.2.2 Priority questions:

Day 1 sessions resulted in a list of priority research questions divided by the three main themes (Table 2). Highlighted comments and recommendations from these deliberations follow, subdivided by the

three major themes and priority questions shown in Table 2 (Seafloor Processes, Extreme Events, Ocean/Atmosphere Processes).

Table 2. Priority research questions by themes, identified by working groups (see Appendices D1-D3 for discussion).

Seafloor processes:
Q1) What is the true global distribution and abundance of ocean methane and in what form does it occur? [Including: phases (bubbles, hydrates, dissolved, and liquid); and sources (thermogenic, biogenic, and abiogenic forms)]
Q2) What are the controlling processes and rates of formation and degradation of methane in the marine environment? [Including: biological processes; sediments and water column; shallow, mid-, and deep water]
Q3) How have 1 and 2 changed over geologic time?
Q4) What factors affect methane and hydrate placements, vulnerability and sensitivity to change? [Including: regional tectonics, geologic setting, depth (e.g. Gulf of Mexico close to the deep ocean floor versus sea-level), plumbing, latitudinal position, and human activities in some settings]
Extreme Events:
Q1) Do ocean methane emissions cause climate change, or do climate fluctuations cause changes in methane emissions?
Q2) What are the mechanisms and magnitude of extreme gas release events that can impact climate?
Q3) How does the proposed relation between stability of hydrate-bearing sedimentary strata beneath continental margins and the release of methane into the ocean and atmosphere actually work?
Q4) Were methane hydrates an important contributor to atmospheric methane concentrations in the geologic record?
Ocean/Atmosphere Processes:
Q1) What are the water column processes, pathways, and interactions that affect methane during its transit from the sea floor to the atmosphere? [Including: Bubble types (e.g., dirty/oily, clathrate-armed); dissolution processes; oxidation rate measurements]
Q2) How large a methane release from the seafloor is needed to transit the 'oxidizing gauntlet' and to measurably affect the global atmospheric budget?
Q3) What is the evidence for major seafloor releases of methane to the ocean surface?
Q4) Are intermediate waters, which reside at the depth of the methane hydrate reservoir, unstable enough over broad areas to influence the methane hydrate reservoir?

4.2.2.1 Seafloor Processes

Q1) What is the true global distribution and abundance of methane and in what form does it occur? Phases: bubbles, hydrates, dissolved, and liquid. Sources: Thermogenic, biogenic, and abiogenic forms.

- More data are needed on hydrate distribution by type, including latitude, longitude, depth distribution in sediments, geomorphology (dispersed versus solid beds), and hydrate species (types I, II or H).
- There is a fundamental knowledge gap in the transfer processes that link hydrates in the sediment and methane in the atmosphere. A fundamental problem is detection of seafloor seep sites. Known sites need more detailed carbon and methane budgets, however, there are many more potential unexplored sites. More information and geophysical data are needed about the plumbing system that brings methane to the seafloor. Knowing whether methane is biogenic or thermogenic determines the depth range of the source, hydrate type (which controls phase diagram P/T

conditions), and flow rate in sediments. Thermogenic hydrates are often associated with high-flux rate hydrocarbon seeps and vents. Critical points in the system are at the interfaces; experiments are needed to measure the quantity of methane in sediment pore waters, and in ocean water just above seafloor at *in situ* pressures and temperatures. How much methane in the sediment is consumed by microbial activity? How is hydrate distributed around the seep site? How much hydrate is beneath the sea floor? Outcrops occur in a few specific places, but is this the whole or representative story?

- Two very different hypotheses currently exist for the origin of free and seeping gas associated with hydrates: 1) Gas comes from a deeper source, either thermogenic or biogenic, and forms a hydrate deposit whenever high enough pressures and low enough temperatures are present for hydrate formation. In this scenario, the hydrate is viewed as a capacitor in a dynamic methane flow system; 2) Methane to form hydrates is derived from local *in-situ* sediment sources of biogenic methane produced by anaerobic methanogenic bacteria and archaea, so that hydrate amounts and life-times of the methane hydrate deposit can be estimated from *in situ* pore water profiles of methane and sulfate. In scenario 2, the hydrate and associated seeping gas are primarily a function of the relative rates of hydrate replenishment via upward methane diffusion from the sediments below, and hydrate decomposition due to interactions with warmer water column temperatures above. These two scenarios of methane hydrate formation and maintenance are very different and knowing which applies may significantly impact the amount of methane potentially available to drive global climate change and seafloor stability, as well as the amount and concentration of methane ultimately recoverable as a resource from any particular ocean hydrate deposit. The key data needed to distinguish these two hypotheses are methane flux measurements, or the amount of methane per unit time flowing through and equilibrating with a particular gas hydrate deposit: How much, how fast, and where is methane venting from bottom seeps into the water column?
- A weakness with past seafloor hydrate programs, with respect to discerning resource potential, has been the implicit assumption that seafloor hydrates will behave like conventional oil and gas reservoir deposits. This assumption has not been demonstrated and is probably wrong. Most seafloor hydrate deposits contain biogenic gases that have generation and migration histories very different from those of normal "petroleum" resources in almost every respect. The basic knowledge required to find and produce large deposits of biogenic gas and associated gas hydrate deposits in and under the seafloor is almost totally lacking. Gaining the fundamental knowledge needed to make this evaluation would also go a long way toward enabling other more neglected parts of the national hydrate initiative regarding seafloor stability and global climate change.

Q2) What are the controlling processes and rates of formation and degradation of methane in the marine environment? [Including: biological processes; sediments and water column; shallow, mid-, and deep water].

- The mechanism of heat transfer in sediments and hydrate-sediment mixtures is poorly understood; is it molecular diffusion through porous medium or does mechanical alteration of the medium through disassociation of hydrates increase the diffusivity, and what is the role of extensional fracture porosity?
- How certain are the phase diagrams for various types of hydrates within natural oceanic waters and sediments? Are Pressure/Temperature (P/T) conditions for hydrates in the ocean the same as those for hydrates in the laboratory? How are kinetics of hydrate formation and destruction altered in natural oceanic water?

Q3) How have 1 and 2 changed over geologic time?

Q4) What factors affect methane and hydrate placements, vulnerability and sensitivity to change? [Including: Regional tectonics, Geologic setting, Depth (e.g. Gulf of Mexico close to the deep ocean floor versus sea-level), Plumbing, Latitudinal position, Human activities in some settings]

- Areas of focused fluid flow in and from the seafloor, e.g., faults, gas chimneys, and mud volcanoes, deliver relatively large amounts of methane to the ocean and atmosphere from geological sources. The fate of most of this gas is currently unknown, including the exact distributions and amounts sequestered by gas hydrates where high methane concentrations, high pressures, and low temperatures are encountered.
- Seafloor gas hydrates are commonly associated with gas flows. Theories as to sources and importance of gas flows create considerable disagreement within the scientific community at present. Is the gas source from hydrate dissociation or from a deeper gas source feeding steady state hydrate formation/destruction?

4.2.2.2 Extreme Events

Q1) Do ocean methane emissions cause climate change, or do climate fluctuations cause changes in methane emissions?

- If the timescale of release of hydrates from the seafloor is set by thermal molecular diffusion of heat through the sediments, then release of methane hydrates is too slow to lead to a positive feedback. Alternatively, if there is a mechanism for releasing all hydrates within a zone destabilized by observed warming over the timescale of a century, then a positive warming feedback may sustain additional, continuing release from most marine hydrates. While observations of methane cycling over the last century do not support such recent catastrophic releases, little is known to constrain the potential for such releases in the future. The central missing ingredients are the global 3-D distribution of CH₄ hydrates, amount and form of CH₄ hydrates, understanding of the process of heat transfer within sediments and within CH₄ hydrates, and fraction of hydrate CH₄ that reaches the atmosphere once released from the ocean floor.

Q2) What are the mechanisms and magnitude of extreme gas release events that can impact climate?

- Are there globally significant catastrophic processes (such as meteorite strikes, earthquakes, slumping or tsunamis) that may trigger massive methane releases from hydrates?

Q3) How does the proposed relation between stability of hydrate-bearing sedimentary strata beneath continental margins and the release of methane into the ocean and atmosphere actually work?

Q4) Were methane hydrates an important contributor to atmospheric methane concentrations in the geologic record?

- What is the relation of the isotopic signature of the hydrate reservoir to oceanic ¹³C₂?
- What is the relation of seafloor failure to past episodes of global warming? Is there a relation between methane and carbon dioxide gas release as recorded in the geologic record and the style, extent, and timing of sea-floor failure features (pockmarks, collapse structures, rotational slumping, gravitational gliding, and mud volcanoes)?

4.2.2.3 Ocean Atmosphere Processes

Q1) What are the water column processes, pathways, and interactions that affect methane during its transit from the sea floor to the atmosphere? [Including: bubble types (e.g., dirty/oily, clathrate-armed), dissolution processes; and oxidation rate measurements]

- How much methane is released to the atmosphere directly by bubbles? What is the role and interaction of related processes, for example: initial bubble size distribution, which determines vertical velocity; increase in bubble size with decreasing pressure; dissolution of methane, N₂, O₂, and CO₂ gas exchange within bubble; impediments to gas transfer by oil films; and, impediments to gas transfer by hydrate film formation.
- Rapid localized methane venting from the ocean floor (producing bubble streams, ejection of chunks of hydrate from the ocean floor, or mud volcanoes) has the greatest chance of delivering large amounts of methane directly from the ocean floor to the atmosphere. The heterogeneity of these rapidly venting systems present significant obstacles to understanding basic questions about their operation, such as: Where is rapid gas venting occurring and how widespread is it? Is the venting episodic? How fast is the methane moving and what is its rate of venting? How fast is the methane from rapidly venting sites being biodegraded both within sediments and in the water column? What is the relative importance of rapid versus slower methane venting? Is methane venting very localized or pervasive over a wide area?
- The transfer of methane from hydrates to the atmosphere involves a system that includes the ocean sediments, the water column and the atmosphere. What are the quantities of methane in the storage component of the system (the sediments and hydrates)? What are the transfer mechanisms and the transfer rates of methane from the storage reservoir to the water? What is the evolution of the methane in the water? What are the vertical and horizontal distributions of methane in the water? What are the transfer amounts and rates of methane from the water to the air at the sea surface?

Q2) How large a methane release from the seafloor is needed to transit the 'oxidizing gauntlet' and to measurably affect the global atmospheric budget?

- How certain are we that most of the CH₄ dissolved in the ocean is biologically oxidized rapidly enough within the water column to avoid reaching the atmosphere?
- Bubbles from the ocean floor may allow methane to reach the air-sea interface rapidly enough to escape biodegradation in the ocean. The dynamics of methane bubbles in the ocean are currently very poorly understood, yet extremely important for understanding the relation between methane and global climate change.

Q3) What is the evidence for major sea floor releases of methane to the ocean surface?

- Need to determine the style, extent, and timing of sea-floor failure features (e.g., pockmarks, collapse structures, rotational slumping, gravitational gliding, and mud volcanoes) that release gas into the ocean (methane, carbon dioxide).

Q4) Are intermediate waters, which reside at the depth of the methane hydrate reservoir, unstable enough over broad areas to influence the methane hydrate reservoir?

- Need to measure factors that may affect the flow of methane and the dissociation of hydrates, such as temperature, salinity and biological activity in water, sediment, and hydrate itself over long periods of time.
- The “clathrate gun” hypothesis suggests that warming of intermediate bottom waters at the onset of deglaciation is a possible mechanism for warming sediments, which in turn leads to dissociation of methane hydrate and massive release of methane to the atmosphere-- a positive feedback for climate warming. An experiment should be devised to test this hypothesis and monitor the history of intermediate bottom water temperatures in a region where hydrates and water column temperature variations are known to occur, such as offshore Peru, for a multi-year experiment that includes El Nino Southern Oscillation (ENSO) events.

4.2.3 Approaches and Partners:

In addition to specific approaches and partnerships related to the priority research questions, as presented in the Appendices (Tables D1-1, D2-1, D3-1), general recommendations included:

- Priority hydrate study areas are places where they are most in jeopardy for dissociation in today’s geosphere, including polar margins and pockmark evolutions.
- Industry has resources useful for study of climate change and may embrace a project seeking to quantify ocean methane venting. Potential joint projects should be aimed at industrial priority items, such as understanding of hydrocarbon migration through the shallow subsurface (mitigation of geohazards) and include efforts to mitigate the perception that the oil industry is a "bad guy" on the climate issue. Partner to use established industry infrastructure (e.g., platforms, ships) and data sources (e.g., seismic profiles, cores).
- Test an “assessment” approach to rapidly acquiring quantitative estimates of global geological release of methane from the geosphere, and the amount that may reach the atmosphere. This methodology utilizes geological models, and other economic and technological information, to estimate in-place resources, recoverable resources, and economically developable resources. Government and industry routinely carry out such energy assessments. The advantage of this approach is that it gives numerical estimates of uncertainties and ranges of possible values within a few years, as opposed to many years with the alternate approach-- comprehensive mapping efforts (which should still be pursued).
- Current hydrate research programs suffer from lack of a coherent plan to make the quantitative *in situ* observational measurements on seafloor hydrates, which are badly needed to underpin all parts of the current national hydrate initiative including resource assessment, climate change, and seafloor stability. Seafloor hydrate research, wherever possible, should interface with the NSF’s evolving Ocean Observatories Initiative (OOI) and ORION (Ocean Research Interactive Observatory Networks), as well as the Canadian Neptune and Venus programs and similar international efforts.
- Calibration and testing of existing and future climate models requires near real-time monitoring of sources of methane and carbon dioxide to the water and atmosphere. Development and deployment of reliable *in situ* methane and carbon dioxide sensors should be made a priority as part of the evolving OOI.
- Any program devised by the U.S. should integrate and build on international partnerships.

4.2.4 Pilot Experimental Program

The intended primary outcome of the workshop was to define “an experiment” that would result in a more accurate assessment of the methane contribution that oceans may make to the atmosphere. In an attempt to distill out this global experiment from the workshop discussions, following are related priority **objectives and required approaches** (and related workshop themes, **T1-Sea floor processes, T2-Extreme events, T3-Ocean/atmosphere processes**); they represent a global, multi-disciplinary, long-term series of investigations, including:

Map gas deposits at and under the seafloor [T1, T2, T3]:

Objectives:

- Conduct new and better surveys and exploration of likely reservoir areas of the continental margin
- Develop better methods for rapidly finding and characterizing new seafloor gas seep/hydrate areas.
- Conduct theoretical mapping study using “energy assessment approach,” which combines existing resource assessments, geological models, and mathematical uncertainties to estimate in-place resources, similar to statistical approach currently used by both energy exploration and climate communities.

Approaches:

- Homogenize world-wide data bases for inter-comparison (an immediate need for climate community); work with CODATA HQ in Paris, which currently has no funding, to finish mapping world's hydrates.
- Conduct new mapping efforts in target areas using best available acoustic techniques, and gain access to existing survey data through partnerships with industry, NOAA, USGS, and MMS.
- Target sites include: seeps, mud volcanoes (vents), exposed hydrate beds, and carbonate structures (records of present and past gas venting); including shallow water (gas only), intermediate (gas and gas hydrates) and deep water (gas and gas hydrate) areas.
- Develop tools to survey and identify flux sites, e.g., AUVs and ROVs, sonar equipment (water column emission profilers), and *in situ* gas sensing technologies (e.g., Raman spectrometer).

Determine pathways and fluxes of methane from ocean bottom to atmosphere [T2, T3]:

Objectives:

- Measure where and at what rate methane is being oxidized within ocean sediments and waters. A spectrum of different types of basins and petroleum, as well as biogenic gas systems, need to be studied.
- Determine processes of gas and gas hydrate formation and destruction in top 300 m of the sediment column.
- Determine rates and characteristics of both biogenic and thermogenic methane production and accumulation. Biogenic parts of the system, particularly in deeper sediments, are especially poorly known.
- Determine which hydrate areas are self-sealing and which continue to leak hydrocarbons.
- Assess gas fluxes (methane and CO₂) across the air-sea interface, a first priority need for oceanic and climate modeling, including during storm events and turbulent mixing.

- Collect long-term, *in situ* methane and CO₂ measurements to determine if oceans are a net source or sink of methane to the atmosphere. The net loss term of oceanic methane to the atmosphere is currently not being considered. Experiments are required involving placement of sensors (methane, CO₂, temperature, and possibly others) in the same place at the time-- it is difficult to correlate data from sensors if data is not obtained simultaneously.
- Partner with industry whenever possible to use existing infrastructure and data sources.

Approaches:

- Develop tools to measure rates, particularly on fast time scales, from seafloor to atmosphere.
- Long-term, continuous measurements of methane, CO₂, other carbon species, temperature, and salinity.
- *In situ* sensors and observing systems (e.g., sonar, cameras) in sediments and water column to monitor hydrate responses and off-gassing.

Determine controlling processes and rates of formation and degradation of ocean methane [T1, T3]:

Objectives:

- Studies should include biological processes, sediment and water column, shallow, mid-, and deep water.
- Determine how much gas and gas hydrate exists and how fast it moves between sediment-water-air boxes:
 - Prepare series for “stereotypical” areas and extrapolate to rest of world (e.g. active thermogenic gas area, and active biogenic gas area, where active implies fairly rapid gas movement between boxes); relate to other similar areas worldwide.
 - Assess air/sea fluxes in various regions.
- Develop “prototype” budgets of carbon, methane, and temperature at model seepage type areas.
- Determine influence of oceanic methanotrophic (methane-consuming) and methanogenic (methane-producing) processes on atmospheric methane.

Approaches:

- Fine-scale sampling and measurements at interfaces/boundary layers (seafloor, water mass boundaries such as O₂ minima layers and thermoclines, sea surface).
- Methane sensors and profilers in locations with *in situ* CO₂ monitors, starting at shoreline and moving to deeper water
- Assess air/sea fluxes using synoptic satellite and *in situ* water column measurements.
- Equip existing oceanic long term CO₂ measuring equipment with other sensors, e.g., methane.
- Develop budgets at target places with more than normal amounts of methane (e.g., Gulf of Mexico, Green Canyon 184; Cascadia); apply systematic approaches for application elsewhere.
- Measure ¹⁴C of methane in ocean waters and sediments; indicator of how long methane has been out of contact with cosmic rays and biological carbon sources delivered from surface ocean.

Determine stability of gas hydrates on short-term and long term time scales [T1, T2:]

Objectives:

- Determine if intermediate waters, which reside at the depth of the methane hydrate reservoir, are unstable enough over broad areas to influence the methane hydrate reservoir.

- Classify different hydrate types in each area (e.g., massive versus dispersed, type I, II or H) and determine "typical" stabilities of each (P/T conditions)

Approaches:

- Long term temperature measurements in critical areas, bottom waters and in sediments, particularly on ocean margins (work with IOOS).
- Target study areas where shallow or exposed hydrates are at or near their stability limit and most vulnerable to dissociation, including Arctic margins, polar areas where recent rapid melting of glaciers has occurred, continental margins exposed to bottom water temperature fluctuations, and pockmark evolutions.
- *In-situ* hydrate-related measurements and samples from exposed beds, and from shallow and deeper sediments (work with IODP to instrument boreholes).

Determine potential triggers of hydrate dissociation and extreme gas release events, and impacts of events on seafloor stability [T2]:

Objectives:

- Correlate rising sea levels and warming of permafrost with increased methane emissions; need evidence for this correlation in the geologic record:
 - Step back 100 Kya (Stage 1a-1b transition) for insight as to how climate might be changing now.
 - Millennial time series measurements are needed of, for example, temperature and geochemical proxies in sediments and carbonate substrata.
- Develop accurate time scale of the late Cenozoic through the late Holocene to aid understanding of the geologic record and possible control mechanisms on extreme release events.
- Determine the style, extent, and timing of sea-floor failure features (pockmarks, collapse structures, rotational slumping, gravitational gliding, and mud volcanoes) that release gas, and relation of potential gas release to climate change.

Approaches:

- High resolution surface sediment and rock cores, and ice cores. More high resolution core work on continental margins.
- Use existing cores first; develop inventory of all available and relevant repositories and analyses to date. Review and integrate with NSF Polar Programs ten year ice core plan.
- Examine river deltas that are consistently charged with both biogenic and thermogenic methane, which is commonly discharged into the ocean as gas seepage, mud volcanoes, and gas hydrates. When sea level is lowered, these may be zones of rapid methane release.
- Map sea-floor failures and associated gas flux indicators in selected areas of gas hydrates representative of major tectonic settings, including active and passive continental margins (e.g., Hydrate Ridge on the Oregon margin, and Hudson Canyon region), sediment drift (e.g., Blake Ridge), and salt basin (e.g., Gulf of Mexico).

5.0 CONCLUSION

5.1 OUTCOMES

During the final plenary, useful workshop products identified included:

- Methane Hydrates Act is up for renewal in 2005-- this group should provide input;
- Ocean Commission report includes several related issues, such as gas hydrate as a potential fuel, but not climate factor—this group should issue related statement to the Commission;
- Provide similar input to the new International Consortium for Hydrate Research (ICHR) and the National Academy of Sciences, Ocean Studies Board, as they review “Activities Authorized under the Methane Hydrate Research and Development”;
- In addition to the meeting CD, which will be submitted to all participants and sponsors, Web site should be developed to include meeting results;
- Organizing committee should distill a meeting report for publication in an appropriate outlet, such as AGU’s *EOS*, which is popular with both ocean and atmospheric research communities.

5.2 KEY ISSUES AND VISION STATEMENT

Several outstanding unsolved oceanic methane/hydrate-related problems were identified that require improved *in situ* oceanic methane measurements, including:

- Methane hydrates constitute a temporary long or short term storage site for methane in deeper sections of the ocean floor. The dynamics of methane hydrate and methane gas must be studied together when considering the potential impacts of seafloor hydrates on climate.
- The ocean is most probably a source of methane to the atmosphere (Cicerone & Oremland, 1988; Dickens, 2003; Reeburgh, 2004). However, this conclusion is based on the computed difference between two very large numbers, so that this conclusion is not certain (Reeburgh, 2004). The net venting or uptake of methane in the ocean is probably highly variable between locations.
- The most important oceanic areas venting methane to the atmosphere could be coastal areas and mud volcanoes where hydrates are not involved (Judd 2003).
- Current evidence suggests a link between gas hydrates, gas venting, and slumps and slides on the continental slope. However, which is cause and which is effect is currently unknown.
- Current evidence suggests that gas hydrate decomposition, gas venting, and changes in global climate have occurred at roughly the same time in the past (Kennett, 2003; Dickens et al., 1997). However, again, the issue of cause and effect remains unresolved.

Considering the presentations and discussions, the following statement attempts to summarize the meeting’s purpose and vision for the future of methane hydrate and climate research, and may serve as draft input to ocean methane and hydrate related research plans and legislation:

“Ocean floor sediments host enormous quantities of methane as dissolved gas, gas hydrate, and free gas bubbles. This global reservoir leaks into the sea through a variety of poorly described and understood mechanisms and pathways, ranging from rapid emissions from volcano-like vents to slow seepages over wide-area deep ocean bottom seeps.

Current ocean carbon models assume that most methane escaping from the seafloor does not reach the atmosphere, because of intense biological oxidation in the water column and

sediments. However, methane does reach the atmosphere in localized zones of intense seafloor seepage where methane is rapidly ejected as bubble streams, mud volcanoes, or gas hydrate pieces—forms that may reach the atmosphere before biodegradation depletes methane. These localized areas of "focused methane flow" are continuing to be discovered in the ocean floor, particularly along continental shelves and margins. There is evidence that occasionally in earth's history, massive releases of methane from hydrates may overwhelm the biological methane oxidation process, thus introducing vast amounts of methane over short period of geologic time—enough to significantly increase methane in the atmosphere and change global climate

We must improve understanding: 1) of types, fluxes, and fates of methane emissions from the seafloor, 2) of the role of methane in global and localized oceanic carbon cycles, and 3) of the geologic record of past methane release associated with abrupt climate changes and the potential role that seafloor methane may have played.

Major destructive events, such as the recent tsunami generated by a major sub-sea earthquake in the Indian Ocean, highlight the grave need for better monitoring and understanding of seafloor stability and related forcing factors. Gas hydrates have been implicated in past similar events.

The new Department of Energy strategic plan for methane hydrate studies over the next ten years (2005-2010) includes climate-related research as a funding priority. These efforts should be included in the upcoming re-authorization of the Methane Hydrate Research Act, and NOAA and DoE together should partner to develop the research plan and appropriate funding for these studies, beginning immediately.”

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MacDonald	Ian	Texas A&M- Corpus Christi	Texas A&M Univ-Corpus Christi, 6300 Ocean Dr, ST320, Corpus Christi, TX 78412 imacdonald@falcon.tamucc.edu	(361) 825-2234	Cold Seeps and Fluxes

HYDRATE CONSORTIUM MEETING REPORT: ROLE OF OCEAN CH₄ AND HYDRATES IN GLOBAL CLIMATE CHANGE
A3 **CMDL, Boulder, CO, May 2004**

Last name	First	Affiliation	Email	Phone	Specialty
Matthews	Elaine	NASA	NASA, GISS, 2880 Broadway, NY NY 10025 ematthews@giss.nasa.gov	(212) 678-5628	CH ₄ Budget
McGee	Tom	Univ. Of Mississippi, NURC-NIUST	Univ. of Mississippi, MMRI/CMRET, 220 Old Chemistry Bldg, University, MS 38677 tmm@olemiss.edu	(662) 915-7320	Hydrate, Geophysics
Moore	Barbara	NOAA /NURP	NOAA, NURP, 1315 East West Highway, SSMC3, Rm. 10342, Silver Spring, MD 20910 barbara.moore@noaa.gov	(301) 713-2427 x127	Undersea Technology
Peltzer	Ed	MBARI	Monterey Bay Aquarium Research Institute, 7700 Sandholdt Rd Moss Landing, CA 95039-9644 Etp3@mbari.org	(831) 775-1851	Ocean Chemistry of Greenhouse Gases
Reeburgh	Bill	Univ. of California- Irvine	Univ of CA Irvine, 3323 Croul Hall, Irvine, CA 92697-3100 reeburgh@uci.edu	(949) 824-2986	Measurements of Methane Oxidation Rates and Global Methane Budget
Roberts	Harry	LSU	LSU, Coastal Studies, 304 Howe- Russell, Baton Rouge, LA 70803 hrober3@lsu.edu	(225) 578-2964	Cold Seeps Geology and Geochemistry, Hydrate Flux
Rona	Peter	Rutgers Univ.	Rutgers Univ, 71 Dudley Rd, New Brunswick, NJ 08901-8521 rona@imcs.rutgers.edu	(732) 932-6555 x241	Geology, Geophysics, Slope Stability
Shedd	William	MMS= New Orleans	MMS – New Orleans, 1201 Elmwood Park Blvd., New Orleans, Louisiana 70123, William.Shedd@mms.gov fax 504-736-2905	(504) 736- 2497	Geophysists
Shepard	Andrew	NURC-SEGM	NURC, Univ, of NC at Wilmington, 5600 Marvin Moss Lane, Wilmington, NC 28409 sheparda@uncw.edu	(910) 962-2446	Seafloor Technology
Sloan	Dendy	CO School of Mines	Colorado School of Mines, Center for Hydrate Research, Golden, Colorado 80401 esloan@mines.edu	(303) 273-3723	Hydrates
Tans	Pieter	CMDL	NOAA/CMDL, Mailcode R/CMDL1, 325 Broadway, Boulder, CO 80305 Pieter.Tans@noaa.gov	(303) 497-6678	Atmospheric Measurements of Greenhouse Gases
Taylor	Charles	DOE/NETL	US DOE/NETL PO Box 10940 Pittsburgh, PA 15236-0940 ctaylor@netl.doe.gov	(412) 386-6058	Methane Hydrates
Tedesco	Kathy	NOAA Global Carbon Cycle Program	NOAA/OGP, 1100 Wayne Ave, Suite 1210, Silver Spring, MD 20910 Kathy.tedesco@noaa.gov	(301) 427-2089 x119	Carbon/Climate

HYDRATE CONSORTIUM MEETING REPORT: ROLE OF OCEAN CH₄ AND HYDRATES IN GLOBAL CLIMATE CHANGE
A4 **CMDL, Boulder, CO, May 2004**

Last name	First	Affiliation	Email	Phone	Specialty
Tomer	Brad	DOE/NETL	3610 Collins Ferry Rd, PO Box 880, Morgantown, WV 26507 brad.tomer@netl.doe.gov	(304) 285-4692	Hydrates
Valentine	David	UCSB	University of CA, Dept of Geological Sciences, Santa Barbara, CA 93106 valentine@geol.ucsb.edu	(805) 893-2973	Microbial Geochemistry
Wheat	Geoff	NURC/WCPR	NURC, West Coast and Polar Regions, PO Box 475, Moss Landing, CA 95039-7033 wheat@mbari.org	(831) 633-7033	Geophysics
Whelan	Jean	WHOI	Dept. of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, MS#4, Woods Hole, MA 02543 jwhelan@whoi.edu	(508) 289 2819	Hydrates, Seafloor Geochemistry
White	James	Univ. of Colorado, INSTAAR	Campus Box 450, INSTAAR, Univ. of Colorado, Boulder, CO 80309 james.white@colorado.edu	(303) 492-5494/8437	Stable Isotope Geochemistry, Paleoclimate, Biogeochemical Cycles
Whiticar	Michael	Univ. of Victoria	Univ. of Victoria, Earth & Ocean Sciences, E Building, Rm. 118, PO Box 3050, Victoria BC V8W 2Y2, Canada whiticar@uvic.ca	(250) 721-6514	Hydrates, Seafloor Sampling, Carbon Flux
Wood	Warren T.	Stennis Space Center	NRL Code 7432, Stennis Space Center, MS 39529 Warren.wood@nrlssc.navy.mil	(228) 688-5311	Gas Hydrates
Woolsey	Robert	NURP/NIUST	Univ. of Mississippi, 220 Old Chemistry Building, University, Mississippi 38655 inst@olemiss.edu	(662) 915-7320	Hydrates

APPENDIX B: WORKSHOP AGENDA

Thursday 5/13/04:

Plenary Presentations:

08:00-- Dave Hofmann, NOAA/CMDL Welcome

08:10-- Barbara Moore-- NOAA/NURP, *Why we are here?*

08:20-- Brad Tomer, NETL: *DOE Research into Naturally-Occurring Methane Hydrates*

(Expert talks: 15 min, 5 min questions)

08:30-- Dendy Sloan, Colorado School of Mines: *Hydrates: What and Where are They and How do They Behave in the Ocean?*

08:50-- James Kennett, UC- Santa Barbara: *Methane Hydrates in Late Quaternary Climate Change: Compelling Evidence and Debate for an Outrageous Geological Hypothesis*

09:10-- Gerald Dickens, Rice University: *Why the Global Carbon Cycle Needs Seafloor Methane*

09:30-- Ian MacDonald, Texas A&M: *Transfer of Hydrate Methane to Ocean and Atmosphere: Three Stability Models from Gulf of Mexico*

09:50-- Edward Peltzer, MBARI: *Recent Advances in ROV In situ Observations of Gas Vents and Methane Clathrate Hydrates*

10:10-- BREAK and posters

10:30-- Dick Feely, PMEL: *Gas Hydrates, Carbon Cycle, and Climate: Workshop to Identify Research Issues and Needs—Ocean Carbon Cycle*

10:50-- Elaine Matthews, NASA: *Using Time Series of Methane Emission to Constrain the Global Methane Budget*

11:10-- Lori Bruhwiler, CMDL: *Potential Influence of Hydrates on the Budget of Atmospheric CH₄: Modeling Perspectives*

11:30-- Alan Judd, Univ. of Newcastle: *Current Hydrate Research in Europe*

11:50-- Lunch and poster session

Break-out Sessions:

13: 15-- Jean Whelan, WHOI, Overview of Workshop Goals and Working Group Process

13: 30-- Breakout groups

17:00-- adjourn

1900-- Reception and Dinner (local restaurant)

Friday, 5/14:

Break-out Groups and posters (cont.):

08:30-- Begin in Plenary; Jean Whelan: Review progress and reconvene working groups

10:30-- Break and posters

11:45-- Final Plenary: Breakout groups report out; where do we go from here?

13:00-- Adjourn.

APPENDIX C1: GROUP 1 BREAKOUT NOTES AND WORKSHEETS

FACILITATOR: Dr Jean Whelan
RECORDER: Ann Thorne

Participants:

Geoff Wheat- University of Alaska/NURP, fluid flow from bottom sediments to the ocean, hydrothermal systems
Jim Cimato, Minerals Management Service, Chemical synthesis of hydrates, safety issues
Ed. Brook, Washington State University, paleo-climate on ice core trace gas, atmospheric methane
Bill Shedd, Minerals Management Service, water bottom mapping project
Harry Roberts, Louisiana State University, high resolution geology of continental slope and outer shelf; modern geology; geology of gas hydrates and their associated gases
Art Johnson, exploration geologist, Hydrate Energy International, petroleum systems, source rocks, migration through the system
Dan Belknap, University of Maine, high resolution geophysics in shelf and coastal systems, pockmarks and natural gases
Alan Judd, University of Newcastle, seabed fluid flow including gas hydrates
John Dunne, NOAA/GFDL, earth system modeling of carbon cycling, decadal to centennial
Ian MacDonald, Texas A&M; biology, geology, and oceanography of gas hydrates and their associated gases
Earl Doyle, SHELL (ret.) deep water and geohazards
David Valentine, UC-SB, chemistry and biology interests; microbiology of anaerobic consortia in ocean waters and sediments

SESSION 1, DAY 1—PRIORITY RESEARCH QUESTIONS:

A set of questions was developed by many participants before the meeting and presented by the major themes to the breakout groups. Session 1 was dedicated to reviewing and refining these questions, and adding new ones if desired. Following are suggested priority questions from group 1:

Theme 1—Seafloor Processes:

- 1) What is the true global distribution and abundance of methane and in what form does it occur? Phases: bubbles, hydrates, dissolved, and liquid. Sources: thermogenic, biogenic, and abiogenic.
- 2) What are the controlling processes and rates of formation and degradation of methane in the marine environment? (includes: biological processes, the sediment, and the water column). Shallow, mid, and deep water.
- 3) How have 1 and 2 changed over geologic time?
- 4) Are intermediate waters, which reside at the depth of the methane hydrate reservoir, unstable enough over broad areas to influence the methane hydrate reservoir?
- 5) What factors affect hydrate placements, vulnerability and sensitivity to change?
 - Regional tectonics
 - Geologic setting
 - Depth (e.g. Gulf of Mexico close to the deep ocean floor versus sea-level)
 - Plumbing
 - Latitudinal position
 - Human activities in some settings.

Theme 2—Extreme Events:

- 1) What is necessary to get a significant quantity of methane into the atmosphere?
 - Atmospheric – significant influence of temperature to destabilize hydrates
 - Ocean – How much methane is too much to be processed "normally" by aerobic and anaerobic biodegradation in water and sediments?
- 2) What is the potential role of major slumps on the continental margin on releasing massive methane?

- Slumps, slides, extreme events have the potential to release large amounts of methane all at once. How would such an event be triggered?
- Could you find out by artificially decomposing a hydrate in a confined area of the seafloor and obtaining a methane and carbon budget?
- What are the potential roles of slumps on the continental margin?
- What are the influences of stratigraphy?

Theme 3—Ocean/atmosphere processes:

- 1) What proportion of seabed methane flux is transmitted to the atmosphere from all sources including gas hydrates? What proportion is from hydrates or other microbial and thermogenic methane sources?
- 2) How much methane release is needed to affect the atmospheric inventory?
- 3) What is the fate, storage (seabed) and transport mechanisms of methane within the water column of methane derived from oceanic sources? How much escapes oxidation within ocean waters and sediments?
- 4) What is the evidence of major emissions of methane through the water column to the ocean surface? Are major emissions of methane to the ocean surface being recorded in some way?

SESSION II, DAY 2—APPROACHES AND PARTNERSHIPS:

Group 1 – Theme 1 (Seafloor Processes): At the end of session 1, day 1, the workshop organizing committee and breakout session leaders met to boil down (e.g., avoid redundancy, clarify, simplify) the priority questions in each theme. Four questions were developed related to theme 1 (seafloor processes). The group’s task was to determine possible approaches and potential partners for these questions:

- Q1) What is the true global distribution and abundance of methane and in what form does it occur? Phases: bubbles, hydrates, dissolved, and liquid. Sources: Thermogenic, biogenic, and abiogenic forms.
- Q2) What are the controlling processes and rates of formation and degradation of methane in the marine environment? (includes: biological processes, the sediment, and the water column). Shallow, mid, and deep water.
- Q3) How have 1 and 2 changed over geologic time?
- Q4) What factors affect methane and hydrate placements, vulnerability and sensitivity to change?
 - Regional tectonics
 - Geologic setting
 - Depth (e.g. Gulf of Mexico close to the deep ocean floor versus sea-level)
 - Plumbing
 - Latitudinal position
 - Human activities in some settings.

Table D1-1. Approaches and partners that address seafloor process questions.

Priority Question	Approach	Partners/Piggy-Back
Q1 Q4	<u>Map gas deposits in and under seafloor worldwide</u> . Initially, focus on specific areas; Eventually total coverage should be global. Map: seeps, mud volcanoes, hydrates.	USGS Oil Companies MMS
Q3	Divide each area into: shallow water (gas only), intermediate (gas and gas hydrates) and deep water (gas and gas hydrate) areas. Maps of carbonates (record of present and past gas venting)	International data bases (e.g. IUPAC, see comments in App. E by D. Sloan; D. Hutchinson) ODP DOE NASA
Q1	Satellite data	
Q1	Homogenize world-wide data bases for intercomparison (an immediate critical need for climate community)	USGS MMS

	<p>Integrate whole world data sets via GIS for seeps, carbonates, hydrates as is now being done in UK & by Crimea Group for Black Sea and for hydrates for the whole world except Africa (CODATA HQ in Paris).</p> <p>Critical need: work with CODATA HQ in Paris, which currently has no funding, to finish mapping world's hydrates</p> <p>Apply a statistical approach as currently done in climate community to methane and hydrate deposits, as well as oil and gas. Start with existing patchwork resource assessments for oil and gas and combine with mathematical models to identify geologic environments at a statistical level, assign uncertainties to these, move on, revise, etc. A statistic approach has great initial uncertainty but is refined over years.</p>	<p>NCAR NASA Now being done by UK (ref: Alan Judd)</p> <p>USGS, CMDL, climate community</p>
Q1 to Q4	<p><u>Determine how much gas and gas hydrate exists and how fast it moves between sediment-water-air boxes</u></p> <p>-Prepare series "stereotypical" areas to extrapolate to rest of world (e.g. GC184 in Gulf of Mexico, active thermogenic gas area, and Cascadia in NE Pacific, active biogenic gas area where active means fairly rapid gas movement between boxes) and try to relate to other similar areas worldwide.</p> <p>-Install and monitor methane sensors and profiles in locations now having <i>in situ</i> CO₂ monitors; start at the beach and move out into deeper water. Look at the whole dynamic range of environment which will be different from one place to the next.</p> <p>-Air/sea flux – couple satellite maps with <i>in situ</i> water column measurements. Equip some of the oceanic <i>in situ</i> long term CO₂ equipment with other sensors - e.g. methane.</p>	<p>ORION NEPTUNE VENUS At air/sea interface, Navy OOI</p>
Q2 Q3	<p><u>Determine stability of gas hydrates on short-term and long term time scales</u></p> <p>Need long term temperature measurements in critical areas - bottom waters & in sediment; ocean margins crucial; Polar areas where recent rapid melting of glaciers observed should have first priority</p> <p>Carry out longer time series on annual, decadal time Scales</p> <p>Classify different hydrate types (that is, massive versus dispersed) and determine "typical" stabilities of each</p> <p>We need in-situ work deeper in sediments. Develop science and sampling plan with IODP; as initial step, obtain and analyze samples from IODP.</p>	<p>ORION ODP NSF Polar Programs Coastal Observatories which are well developed Neptune ALPs Big Ocean integrated array and sensor programs</p> <p>IODP</p>
Q3	<p>Millennial time series measurements are needed. Parameters:</p> <p>-temperature and geochemical proxies in high resolution surface sediment cores and ice cores.</p> <p>-Much more high resolution core work on continental margins</p> <p>-Step Back 100K years (Stage 1a-1b transition) - use to gain insight into how climate might be changing now</p>	<p>NSF ODP USGS International partners New "ODP"</p>
Q2, Q4	<p><u>Determine flux of gas from seafloor; how much survives to be vented to atmosphere?</u></p> <p>Focus particularly on: On-going measurements of methane, carbon, CO₂, temperature, and salinity during:</p> <p>-storm events</p> <p>-events which can down-well carbon</p> <p>Place <i>in situ</i> sensors in sediments and in water column to see how hydrates respond.</p>	<p>ORION & Oceanic long term monitoring programs; Coastal Observatories NOAA, NASA Satellite Neptune</p>
	<p><u>Carry out careful budgets of carbon, methane, temperature in important specific seep areas.</u></p>	<p>NSF NOAA</p>

	3) development down hole tool for <i>in situ</i> methane/hydrate monitoring 4) Shallow geophysical monitoring of hydrates 5) 4D seismic data on gas hydrates	Industrial data (for deep hydrates only)
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GROUP 1 DISCUSSION NOTES:

A list of proposed questions was distributed. On day 1, the group was tasked with generating the three most important questions either by using the list or creating new ones. On day 2, they generated proposed approaches and partnerships for the theme 1 questions.

Question 1a – 1a and 1k could be combined. Both distribution and phases need to be discussed.

What techniques should be used to identify hydrates properly? Accurate resource assessments, which are not currently available, require correct identification of hydrate type (type I or II, massive or dispersed, and amount) along with *in situ* pressure, temperature, salinity, and sediment type. Current global estimates are probably off by large amount.

How accessible to the water column is the atmosphere? Some columns and deeper intervals may never see the atmosphere. How available is oceanic methane for interaction with the other cycles? What are these cycles? Where are they located and what are the implications for where venting of oceanic methane might be important? (Note: Approximately the upper 100 m, or the mixed layer of the ocean above the thermocline, generally mixes enough to reach gaseous equilibrium with the atmosphere in approximately 1 year although the exact time and depth vary with latitude, Boecker and Peng, 1982).

What is the real flux of methane making it out of the ocean and where is it oxidized?

Hydrate is a reservoir rather than a source, so we need to understand the processes forming and destroying the reservoir and rates at which these processes act.

There are two separate questions:

1. Where are methane and hydrate located?
2. What are the budgets of methane and hydrate within the carbon budget and what processes control these?

1h, 1i, 1j can be connected.

Can a realistic box model showing amounts, fluxes, and processes be constructed for methane?

There is some evidence that hydrates, in some locations, come and go rapidly and other places where they seem to persist over long time.

One view is a snapshot –

1. Where is the methane?
2. What are processes controlling inputs and outputs in the methane system? We have glimpses of pieces but no clear understanding.

A north-south transect in the northern Gulf of Mexico-- from South Marsh Island 9 just off shore in the north through Eugene Island and to Green Canyon 184 to the south along the upper continental rise-- shows the complexity of gas movement feeding the petroleum system and the gas hydrates in the northern Gulf of Mexico. An enormous amount of gas has flowed through reservoirs to the north, decreasing to the south. At GC184 to the south, gas flow seems to have just begun, yet is sufficient to maintain substantial gas hydrate deposits on the seafloor. A large amount of gas movement is involved over geologic time, so there appears to be plenty of gas to form and replenish the gas hydrates, even if they are disappearing in the presence of Gulf of Mexico warm water loop currents (Whelan et al, in press).

Top issues:

1. how much, where
2. processes, consumption, box model

1g: how can we distinguish hydrate from diagenetic methane versus that formed from gas flow from deeper reservoirs? Is this an important distinction to make? Yes-- much more methane is potentially available to form hydrates if the latter process is important. (Note: A simple modeling approach to the problem describing which parameters and known and which are unconstrained is given in Dickens, 2003).

Are rates of thermogenic and biological production the same? The biological production is a very difficult thing to determine. You can determine the amount of methane, but the rates of production are poorly known. Both sources are feeding the reservoir and the hydrate, so rates of both are important. What are the rates of methane migration? Do we know or are we just guessing? What is happening to hydrates and gases biologically within the sediment?

Thermal portion of gas is produced in deep sediments and collects in a reservoir where the biogenic and thermal methane become intermixed.

Third question focus: proportion of thermogenic methane in hydrates and residence time-- Is there a lot of thermogenic hydrate or not?

1a and 1k – are we talking about the whole world? The meeting focus is climate-- should we talk about the whole world, or parts of it first? Are there major constraints that would make one place more interesting than another?

Study areas are needed that represent good examples of both thermogenic and biogenic sources/sinks, because new seafloor gas seep/hydrate areas are continuing to be discovered in all oceans and seas, particularly in continental margin areas. The Gulf of Mexico is not unique. There is a lot of data from the Gulf of Mexico. However, studies should also be conducted in other parts of the world, which have different settings and processes. We need to get an idea of the range of methane and methane hydrate content in various kinds of systems so we can estimate the range of methane and hydrate values in different settings. Using this approach, the key is to identify and characterize several different prototype areas and then to categorize the rest of the world into these prototypes.

We need to determine which hydrate areas are self-sealing and which continue to leak hydrocarbons.

Gases also need to be measured on the shallow shelf where hydrates can't form. Large amounts of gas are released from shallow shelf environments (Judd, this volume and in press). How much gas is released in these environments as opposed to forming hydrates and how much methane actually gets out to be vented to the atmosphere in both coastal and deeper water areas? Are there other types of oceanic methane releases, in addition to hydrates, that are being vented directly to the atmosphere? What is the importance of mud volcanoes? Methane venting from oceanic sediments to the atmosphere isn't just a deep water phenomenon. Shallow waters and storm events could be more important than continental slope hydrates.

Potential problem using Gulf of Mexico as study site: is it unique or is it similar to some other areas world-wide? We shouldn't box ourselves into a specific study area, but should take advantage of data we have. We know a lot about the Gulf of Mexico and about where hydrate and gas production occur. However, processes of hydrate formation and destruction are not well understood. Bridging may be important. Some of the processes of hydrate formation and destruction may be more similar than we suspect. Spectrum of different types of basins and petroleum systems are involved. We need to understand the continuum.

Beyond this, we've studied various gas vents, but still do not understand the processes of gas and gas hydrate formation and destruction in the top 1000 ft. of the sediment column. Most new wells are studied for 6 meters at the top and then from where logging starts at 200 ft. sub-bottom. We can probably rule out places that there is not much going on, i.e., the North Pacific abyssal plain and places that are not tectonically active.

Did we decide about 1b, the importance of intermediate waters to hydrate stability? This is a fairly central question. 1b seems like a group 2 or 3 question. However, group 2 is talking about extreme release. Our group is looking at the natural processes related to more subtle methane hydrate reservoir instability in the absence of extreme events. There are many possible mechanisms operating on many different time scales. We need a good timescale of the late Cenozoic through the late Holocene to aid our understanding of these mechanisms.

Putting the questions together:

1a, 1i, and 1k – how much, where, physical changes – water, depth, location, sediment
1h 1i and 1j – rates and processes

11 and 1c – Rates and depths of formation of both thermogenic and biogenic methane are needed.

From a climate standpoint, if methane is the issue, then what matters is where the methane is located, its form, and how it changes over time. If hydrate is released from sediment, then a lot more methane trapped below or within the hydrate can also be released. How fast is this release in each case?

There was a group consensus to rewrite the questions.

In terms of processes, a cross-sectional drawing was presented. Different pathways and mechanisms need to be considered from different parts of the cross section: 1) from shallow sediments having primarily biogenic gas, 2) intermediate depths having both thermogenic and biogenic gas, and 3) deep ocean. In the intermediate zone, we're concerned primarily with changes on a geologic time scale.

River systems, deltas, are consistently charged with biogenic methane. If you look at the sediment surfaces, they are populated with mud volcanoes. Recent work appears to show that gas seepage occurs over most major river deltas. When you lower sea level and sediment goes into motion, there can be a very rapid release of methane. River deltas are places where lots of organic matter is deposited, which serves as the precursor to both biogenic and thermogenic methane.

It is observed that when sea levels are low, the methane in atmosphere is low. The world gets colder when the sea level is low. Some suggest rising sea levels might increase methane emissions by warming up permafrost.

The methane in the atmosphere doesn't know if it is coming from a hydrate or not. In terms of climate change, both gases and hydrates need to be considered together.

In intermediate waters, the gas evolution is slowed down a bit by low temp and high pressure.

Projects proposed here may be able to plug into large new initiatives now just starting to install infrastructure to carry out long term monitoring over the whole ocean (e.g. ORION, ALPS, NEPTUNE, etc).

The atmosphere is a global integrator of methane. We don't know how it is influenced by the intertwined methanotrophic and methanogenesis processes occurring in the ocean. C14 methane measurements can help because they tell you how long methane has been out of contact with cosmic rays and the biological carbon sources coming from the surface ocean.

END GROUP 1 NOTES.

APPENDIX C2: GROUP 2 BREAKOUT NOTES AND WORKSHEETS

FACILITATOR: Dr. Tom McGee
RECORDER: Dr. Robin Buchannon

Participants:

Debbie Hutchinson, Dendy Sloan, Ed Peltzer, Edie Allison, Bob Woolsey, Emanuel Gloor, John Miller, Jim White, Dave Butterfield, Peter Rona, Jim Gardner, Gerry Dickens, Lori Bruhwiler

SESSION 1, DAY 1—PRIORITY RESEARCH QUESTIONS:

A set of questions was developed by many participants before the meeting and presented by the major themes to the breakout groups. Session 1 was dedicated to reviewing and refining these questions, and adding new ones if desired. Following are suggested priority questions from group 2:

Seafloor Processes:

1. What is the true global distribution and abundance of methane and in what form does it occur? Phases: bubbles, hydrates, dissolved, and liquid. Thermogenic, biogenic, and abiogenic forms.
2. What are the controlling processes and rates of formation and degradation of methane in the marine environment? (includes: biological processes, the sediment, and the water column). Shallow, mid, and deep water.
3. How have 1 and 2 changed over geologic time?
4. Are intermediate waters, which reside at the depth of the methane hydrate reservoir, unstable enough over broad areas to influence the methane hydrate reservoir?
5. What factors affect hydrate placements, vulnerability and sensitivity to change?
 - a. Regional tectonics/geologic setting
 - b. Depth (e.g. Gulf of Mexico close to the ocean floor, sea-level)
 - c. Plumbing
 - d. Latitudinal position
 - e. Human activities in some settings.

Extreme Events:

1. Does methane change cause climate change or does climate change cause methane change?
2. What are the mechanisms and magnitude of extreme gas release events that can impact climate?
3. How does the proposed relation between stability of hydrate-bearing sedimentary strata beneath continental margins and the release of methane into the ocean and atmosphere actually work?
4. Were methane hydrates an important contributor to atmospheric methane concentrations in the geologic record?

Ocean/Atmosphere Processes:

1. What proportion of the seabed methane flux is transmitted to the atmosphere from all sources including gas hydrates? What proportion is from hydrates versus other reservoirs?
2. How much methane release is needed to affect the atmospheric inventory?
3. What is the evidence of major emissions of methane through the water column to the ocean surface? Are we recording major emissions to the ocean surface?
4. What is the fate, storage (seabed) and transport mechanisms of methane within the water column of methane derived from oceanic sources?

SESSION II, DAY 2—APPROACHES AND PARTNERSHIPS:

Group 2 – Theme 2 (Extreme events): At the end of session 1, day 1, the workshop organizing committee and breakout session leaders met to boil down (e.g., avoid redundancy, clarify, simplify) the priority questions in each theme. Four main questions were developed related to theme 2 (extreme events). The group's task was to determine possible approaches and potential partners for these questions:

Q1) Does methane change cause climate change or does climate change cause methane change?

Q2) What are the mechanisms and magnitude of extreme gas release events that can impact climate?

Q3) How does the proposed relation between stability of hydrate-bearing sedimentary strata beneath continental margins and the release of methane into the ocean and atmosphere actually work?

Q4) Were methane hydrates an important contributor to atmospheric methane concentrations in the geologic record?

Table D2-1. Approaches and partners that address extreme events questions.

Priority Question	Approach	Partners/Piggy-Back
Q1 to Q4 -General approaches	Approach: Constrain gas sources with complete characterization of the C & H isotopes of all methane gas sources.	NSF NOAA IODP Industry
	Approach: - Develop a model for how methane gas is transferred into the atmosphere, and how this can happen over broad (regional) areas. - Determine how much methane is needed to produce climate change on a broad scale. - How good current models are: e.g. how much faith do we put in the current models? - Do we agree that wetlands are the prominent contributor of methane to the environment? - Have the modelers considered both fresh water and marine wetlands?	NSF NOAA IODP NASA USGS
	Approach: Define the quantitative importance of microbes in methane production and destruction.	NSF IODP NOAA DOE (deep biosphere; microbiological mechanisms) NASA (anaerobic organisms in unusual environments)
Q 1 Q2	Study relationship of methane and climate change in the modern ocean and in the geologic record.	
	<i>Approach I:</i> a) Ice core studies Determine temperature changes through time by looking at the isotope compositions and changes (in both marine and ice cores) Attribute a mechanism to these temperature changes; and decide on a cause & effect relationship Determine the age of the methane gas in the cores vs. the age of the ice (or sediments) (14C isotopes) b) Sediment cores studies - inventory cores in hand (both types); where are there gaps in coverage? (Note: In sediment cores, methane is lost during core recovery, so new cores would have to be gathered at interesting sites specifically for <i>in situ</i> methane analyses - how to do this? a) pressure coring or b) possibly via freeze coring. Priority item: Determine if freeze cores are valid for determination of <i>in situ</i> surface sediment CH ₄ amounts and isotope values; if so, develop IODP down hole freeze corer for deeper intervals)	NSF's Office of Polar Program (comprehensive ice core program on-going for next 10 yrs) IODP NSF NOAA NSF IODP
	<i>Approach II:</i> Examine changes in the intermediate water column over time as reflected in continuous cores recovered from intermediate waters along continental rise. Parameters: -Oxygen isotopes in foraminifera from cores	NSF NOAA USGS Existing cores, ODP IODP

	Physical oceanographic modeling; how do circulation patterns change over time? Analyze how intermediate waters responded to temperature changes over broad areas using suitable proxies such as stable isotopes, trace metals (MG/Ca) of foraminifera and/or intermediate depth corals	Academic institution core collections (Lamont, WHOI, Scripps, etc)
Q3 & Q4	Approaches: how do gas hydrates and associated free gas contribute to the presence of methane gas in the atmosphere?	
	<p><i>Approach I:</i> Determine relationship of hydrates to free gas and atmospheric methane via:</p> <ul style="list-style-type: none"> -13C & D isotopes and ratios - Budgets - C, methane, and possibly suitable biomarkers - how much methane escapes the hydrate system? Role of thermal versus methanogenic versus methanotrophic methane and biomarkers and carbon - C and methane budgets through surface sediment, hydrate, water column, and into atmosphere: <ul style="list-style-type: none"> -Specific seep/hydrate locations: Determine rate of methane release from hydrate and determine what fraction is escaping biodegradation and is injected into the surface mixed layer above the thermocline (roughly the top 100m). <i>Potential study locations:</i> GOM GC184 (thermogenic gas); Cascadian Margin (biogenic gas) -Where does this gas come from and what is the effect of hydrate dissociation? -How do the values C & H isotopes of methane change with respect to dissociation of hydrate? (Generally assumed not much, but do we know from measurements?) -Measure <i>in situ</i> P/T regime of water or sediments adjacent to hydrates. -Determine gas chemical and isotopic compositions - relation to P & T regime for specific hydrate types (Type II hydrates stable in lower P and higher T regime than Type I) -Long term temperature monitoring of hydrate with respect to gas evolution and hydrate stability <p><i>Approach II: Test hypothesis: Warming at depth in upper intermediate waters occurs prior to warming in surface waters</i></p> <ul style="list-style-type: none"> -Studies of continuous marine cores looking at temp indicators that suggest methane release: <ul style="list-style-type: none"> - use proxies for water temperatures at depth and at the surface (i.e. stable isotopes and trace metals in foraminifera and/or corals) -Develop new indicators for low temperature sediment history. In same sections of core, compare core temperatures with indicators of water column temperature (U237; foram O18) <p><i>Approach III</i> Carbon and methane budgets at specific seep/hydrate locations to better understand processes affecting seeps & hydrates</p>	<p>IODP - obtain many more pressure cores from hydrate area.</p> <p>NSF IODP</p> <p>NSF NOAA IODP DOE</p> <p>NSF IODP NOAA DOE</p>
	<ul style="list-style-type: none"> -Technology development needed for all of the above: -Improve the procedures for sample recovery to bring the sample back whole for good isotopic analysis -Develop new methods for analysis at <i>in situ</i> P & T at the seafloor - Routine pressure coring device to recover sediments plus hydrates plus free methane. 	NSF IODP ODP samples
Q3	<p><i>Approach I:</i> Define the hypothetical styles of bottom failure (landslides, mud volcanoes, etc.) in relation to proposed gas release <u>methods</u></p>	NSF, DOE, NOAA, USGS, perhaps

Q4	Look at stratigraphic record of these events and correlate them with climate change as reflected in cores <i>Approach II:</i> Model what happens when you have a catastrophic (episodic) event; e.g. what happens to the sediments and gases? <i>methods</i> Produce climate models: do these events release hydrates or vice versa? Can such events influence or trigger measurable atmospheric change?	GHASTLI lab at Woods Hole MMS for resource assessment, hazard studies, etc.
Q3	Map the continental slopes and continental rise (on a global scale) with enough resolution to be able to see landslides, mud volcanoes, pock marks, etc.	
Q3	Design and conduct experiments to determine the temp at which instability occurs	

GROUP 2 DISCUSSION NOTES:

Overview Comments:

After much discussion, it was decided that approaches we defined applied to most of the research questions in some way. Therefore, we began to lump our approaches into broader topics. Overarching needs (or broad approaches) prevailed throughout discussions-- questions/issues/needs that had to be addressed on a more or less generic scale before other things could be addressed:

1. Completely characterize the C & H isotopes of all methane gas sources.
2. Define a mechanism for how methane gas could cause climate change, and conversely, a mechanism for how climate change can cause changes in methane gas concentration.
3. Develop a model for how methane gas is transferred into the atmosphere, and how this can happen over broad (regional) areas.
4. Determine how much methane is needed to produce climate change on a broad scale. Are current models correct; e.g., how much faith do we put in the current models? Do we agree that wetlands are the prominent contributor of methane to the environment? Have the modelers considered both fresh water and marine wetlands (constrained models with marine wetland data)? Some thought that most current wetland methane data might include only fresh water systems. If this is true, there is a problem because wetlands are currently such a large term in the overall carbon budget.
5. Do we know why the methane seems to vary only within very narrow bands?
6. Specifically define the role of microbes in rates and amounts of methane production and destruction.

We then discussed **approaches** for specifically addressing the research questions. Two approaches prevailed: one related to studying methane and climate change in general; the other specifically related to the study of how gas hydrates and associated free gas contribute to the presence of methane gas in the atmosphere.

Approach 1-- Study of ice cores and marine cores:

- We don't necessarily need new cores; there are a lot of cores available, both ice and marine, that if studied thoroughly could provide more answers; we might undertake an extensive inventory of what we have and where gaps in data are, and concentrate any new collection efforts on where these gaps.
- What to do with the cores?
 - Determine temperature changes through time by looking at the isotope compositions and changes, using both marine and ice cores;
 - Again, attribute a mechanism to these temperature changes; and perhaps decide on a cause & effect relationship;
 - Determine the age of the methane gas in the cores vs. the age of the ice or sediments;
 - Regarding the study of Ice Cores: two members of the group stated that the Ice Core Community already has a comprehensive plan of study in place for the next 10 years led by NSF's Office of Polar Programs. This community should review, but does not need to re-invent this scientific plan.
 - Changes in intermediate water column or sediments along the continental slope between the shallow and deep waters-- study these changes through:
 - Oxygen isotopes in foraminifera

- Physical oceanographic modeling; how circulation patterns change: What drives the changes?
- How do intermediate waters respond to changes over broad areas?
- Temp change indicators - proxies
- **Partners/Funding Agencies:** NSF, NOAA, USGS

Approach 2-- Study methane hydrates and their associated free gas and how they contribute to methane in the atmosphere:

- What are the isotopes of C & H that can be attributed to the hydrates (perhaps some specific isotopes or ratios)?
- What is the relationship between the hydrates and the free gas? How to determine this?
- Can the methane get out of the hydrate system? Possibly look at biomarkers; compare to marine isotopic indicators.
- Is the methane that's being released getting to the ocean surface? If it's not getting to the surface, then we suspect hydrate system is not contributing to the atmosphere. Design experiments toward this end.
- Where does gas come from and what is the effect of hydrate dissociation?
 - How do the values of methane change with respect to dissociation?
 - Are some hydrates more vulnerable to dissociation than others?
 - Need **continued studies of marine cores** looking at temp indicators at depth and at surface and indicators that suggest methane release
 - Prior warming at depth (upper intermediate waters) before atmosphere shows increases
 - Need to understand processes operating in this system
- Improve the procedures for sample recovery (technology development)
 - Especially methods for analysis at the seafloor; but also for bringing samples to the surface; must bring samples back whole for good isotopic analysis, and in some way preserve the methane at *in situ* P & T until it can be extracted from the cores (ODP has done that in the past; but improved techniques might be good)
- Define types/modes of bottom failure (landslides, mud volcanoes, etc.) in relation to gas release
 - Define whether or not such events can actually influence the atmosphere
 - Model what happens when you have a catastrophic (episodic) event; e.g. what happens to the sediments and gases?
 - Produce climate models: do these events release hydrates or vice versa?
 - Look at stratigraphic record of these events and correlate them with climate change
- Map continental slopes and continental rise (on a global scale) with enough resolution to be able to see landslides, mud volcanoes, pock marks, etc.
- Design and conduct experiments to determine temperature at which hydrate and sediment instability occurs
- **Partners** should include: NSF, DOE, NOAA, USGS, perhaps GHASTLI lab at Woods Hole (USGS), not MMS (according to the MMS rep here – but yes as far as resource assessment, hazard studies, etc.)

Day 1 (Research Questions) Notes:

2a: critical idea; rephrase to “What are the circumstances in which methane released from hydrates easily gets to the atmosphere vs. doesn't get there?” Define the conditions under which extreme events can release methane to the atmosphere, e.g., temperature and circulatory conditions in the ocean that influence what volume makes it to the surface waters

2a: does this even happen? Is there compelling evidence that extreme events release appreciable methane to the water and atmosphere? There is an indication from ice cores that there has been a doubling of methane through geologic time.

2b: Was free methane an important contributor to atmospheric methane concentrations in the Late Quaternary?

2c: same thing

In general: gas bubbles dissolve within several hundred meters of the bottom; solid hydrate will often get to the sea surface.

Some of the larger episodes of gas venting are not necessarily from hydrates; Russian scientists recorded a lot of gas venting along fault zone off Sakhalin Island; some barges sank; Russians use the venting of methane as precursors to earthquakes.

Even in classic hydrates system (containing massive rather than dispersed hydrate) must look at free gas (e.g., Blake Ridge). We know the systems are dynamic; but must think beyond the hydrate itself.

Critical point: need to include both hydrate and its associated free gas in discussing gas hydrate systems.

What other processes could release a lot of methane, e.g., earthquakes?

If you change temp and pressure, you change the system. Sea Level rise/fall – methane on the shelf and on upper continental rise can be released when sea level falls. However, methane in ice cores is lower in glacial periods.

Propose that methane on shelf is predominantly biogenic rather than thermogenic. Rarely see presence of gas on shelf; but invariably see it on the slope.

One of the key questions: how big are gas and hydrate venting episodes? You must have a certain size event to affect climate. What are the deposits, how large are they, etc.?

From the ice core records, we know how much methane had to be contributed to the atmosphere at various geologic times, but don't know sources.

What are the mechanisms and magnitude of extreme gas release events that can impact climate?

Is a single pulse event enough to drive climate change? We generally think in terms of global events. But pulses can cause other changes that could turn global.

There may be a tight coupling between extreme events gas release to atmosphere. With slow events, the amount of methane that gets oxidized and is not released is greater

What are the masses? What are the fluxes?

Sources of methane to the water column (biogenic, thermogenic, and magmatic) are not well understood.

Can we identify reservoirs that are large enough by themselves to account for extreme changes in methane in the geologic record?

Are there changes in some part of the earth system that could release methane from an ensemble of locations all at the same time?

Can large methane increases in a non-glacial world trigger abrupt climate change?

Does sea level change climate? Or does climate change sea level?

Hydrates and Slumping:

Slumping decreases the normal component of effective stress by effectively lowering the pressure from the overburden, which could destabilize underlying methane hydrate zone.

Sea level fall is invoked as the trigger; which would change the stability field and cause dissociation.

Temperature has a huge effect on stability at all water depths, whereas pressure has a significant effect only at shallow depths.

Changes in temperature and circulation patterns are more likely to release methane than cause slumping. For example, Loop currents in the GOM typically raise the bottom temp 4-7 degrees for several months; but heat doesn't propagate into the sediment very far.

Are there any mechanisms that can destabilize a large enough piece of hydrates to cause a major change in climate?

Can warming of intermediate waters destabilize hydrates on margins, which would cause pressure changes which induce slumping, and release more gas and hydrate? This scenario is consistent with ice core data: more methane in atmosphere during interglacials, or warming.

The modern methane hydrate system is dynamic. Age of methane is older than the surrounding sediments. Age of hydrate is younger than surrounding sediments. **So, can we change flux in and out of the system?** Sea level is a large scale trigger for methane release on a regional scale, as is intermediate water warming; slumping, which is stronger during glacial periods and lower sea level, isn't likely trigger.

What happens in the fossil fuel system? Can methane release turn on and off? Many geologic events through time and space affect release.

If you can change the outputs from these systems, how does the gas then actually get out to the atmosphere?

ACCEPT and combine 2e and 2g: what is the mechanism for getting methane out of the hydrates reservoir and into the atmosphere rapidly?

Does methane change cause climate change or vice versa? Is there a coupling of extreme events and the ability of methane to be released to the atmosphere? Is there a cause and effect relationship here?

What is the role of extensional fracture porosity? Phenomenon by which very fine-grained sediments that are deposited as gels enter into state of tension which produces swarms of small extensional faults, which can act as conduits for circulating fluids. If the fluids include methane and water, large quantities of hydrate could accumulate, or be destroyed by changes in temperature that would not rely on diffusion. Such systems have been called "polygonal fault systems" and are prolific oil and gas reservoirs in places such as offshore Norway. Comments that conventional ideas on oil and gas production do not apply to hydrate accumulations probably are not valid in the context of polygonal systems. Roger Sassen contends strongly that all the hydrates he has seen in the Gulf of Mexico have been in fine grained sediments.

END GROUP 2 NOTES.

APPENDIX C3: GROUP 3 BREAKOUT NOTES AND WORKSHEETS

FACILITATOR: Andrew Shepard
RECORDER: Dr. Carolyn Koh

PARTICIPANTS:

Keith Kvenvolden, John Rona, Elaine Matthews, Charles Taylor, Lori Bruhwiler, Pieter Tans, Bill Reeburg, Ed Dlugokencky, Alan Judd, Ross Chapman

SESSION 1, DAY 1—PRIORITY RESEARCH QUESTIONS:

A set of questions was developed by many participants before the meeting and presented by the major themes to the breakout groups. Session 1 was dedicated to reviewing and refining these questions, and adding new ones if desired. Following are suggested priority questions from group 3:

Seafloor processes:

- 1) What factors affect hydrate placements, vulnerability, and sensitivity to change?
 - Regional Tectonics
 - geological setting
 - Depth (e.g. Gulf of Mexico close to the ocean floor, sea-level)
 - plumbing
 - latitudinal position
 - human activities in some settings.

- 1b) Are intermediate waters, which reside at the depth of the methane hydrate reservoir, unstable enough over broad areas to influence the methane hydrate reservoir?

- 1k) What proportion of methane in marine sediments exist as hydrate, dissolved gas, and free gas? What processes affect mixing and the proportions of these?

- 1h) How rapidly is methane released from hydrate related sources oxidized?

Extreme Events:

- 2a) What role do episodic events play in transmitting methane from the sea bed to the atmosphere? Episodic event defined as detectable change in methane that overwhelms biological oxidation.
 - 2a1) Do ice cores capture episodic events? – Are they hydrate related?
 - 2a2) What are the processes/mechanisms, e.g. gas bubble plume, earthquakes, that cause episodic events.
 - 2a3) What is the role in slumps/wasting?

- 2b) Were methane hydrates an important contributor to atmospheric methane concentrations in the geological records?

Ocean/Atmosphere Processes:

3a) What proportion of the seabed methane flux (including source, flux, fate, consequences, implications to past climate) is transmitted to the atmosphere from all sources including gas hydrates. What proportion is from hydrates (microbial and thermogenic methane sources) versus other sources?

Emissions are usually episodic and vessels may not be around when these occur. Therefore, we want monitoring to be able to detect these. – e.g. Neptune – place sensors in hydrate regions to measure plumes and bubbles.

3a) What is the evidence of major emissions of methane through the water column to the ocean surface? Some experiments have been performed, but these are very limited and there is controversy on how to interpret the results. Are we observing and recording major emissions to the ocean surface?

How much methane release is needed to affect the atmospheric inventory?

3b) What is the fate, storage (seabed) and transport mechanisms of methane within the water column of methane derived from oceanic sources?

- role of the feedback to the oxygen minimum zone?
- partitioning of methane between atmospheric release versus biological oxidation?
- role of dirty (with oil) versus clean methane bubbles?
- hydrate-armored versus gas only?

SESSION II, DAY 2—APPROACHES AND PARTNERSHIPS:

Group 3 – Theme 3 (Ocean/atmosphere processes): At the end of session 1, day 1, the workshop organizing committee and breakout session leaders met to boil down (e.g., avoid redundancy, clarify, simplify) the priority questions in each theme. Three main questions were developed related to theme 3 (ocean/atmosphere processes). The group’s task was to determine possible approaches and potential partners for these questions:

Q1) What are the water column processes, pathways, and interactions that affect methane during its transit from the sea floor to the atmosphere? e.g.,

- Bubble types (dirty/oily, clathrate–armored)
- dissolution
- oxidation rate measurements

Q2) How large a methane release from the seafloor is needed to transit the ‘oxidizing gauntlet’ and to measurably affect the global atmospheric budget?

Q3) What is the evidence for major sea floor releases of methane to the ocean surface?

Q4) Are intermediate waters, which reside at the depth of the methane hydrate reservoir, unstable enough over broad areas to influence the methane hydrate reservoir?

Table D3-1. Approaches and partners that address ocean/atmosphere process questions.

Priority Question	Approach	Partners/Piggy-Back
Q1 Q2 Q3	OBSERVING SYSTEM to support synoptic studies of flux from the seafloor to the sea surface:	Neptune NSF ORION, new ocean observing initiatives
	<u>Sea Floor Component:</u> -observatories at hydrate beds, target ‘flux’ indicators,” e.g. mud volcanoes, and background sites -array for continuous monitoring, including seismic, visual, acoustic, chemistry -side scan sonar data calibrated with geochemistry to determine how much methane gets into water column - Characterization of mud volcanoes which could be big contributor to atmospheric methane - start with seafloor geophysical data -Spare radiotelescopes to survey for mud volcanoes observed in seismic data	JIP, hydrate consortium NSF EU, side scan sonar data USGS Petroleum industry EU and international survey efforts Navy NASA
	<u>H₂O column component:</u> array for continuous monitoring, including seismic, visual, acoustic, chemistry throughout water column -Survey cruises to measure methane and its rate of oxidation Integrate methane sensors into existing observing stations and various transits by NOAA and other vessels,	NOAA vessels NSF, long-term ocean observing network Neptune Venus (Canadian) International long term observing programs
	<u>Surface Component:</u> -physical gas sampling devices	TAU BUOYS, ARGO floats

	<p>-new satellite sensors that can see CH₄???</p> <p><u>At air-sea interface</u></p> <p>- flux sensing devices sensitive to all gases present</p> <p>-develop rapid response in-situ sensors to measure rapid changes in individual gas fluxes at air-sea interface</p>	<p>NASA</p> <p>NSF</p> <p>Navy</p>
<p>Q1</p> <p>Q2</p> <p>Q3</p>	<p>Observation program strategy should:</p> <p>-target extreme events</p> <p>-cover representative environments</p> <p>-regional network including background stations</p> <p>-build on existing programs</p> <p>-Consider important processes (e.g. oxidation max., O₂ minimum layer)</p> <p>-Program to be based on accurate maps</p> <p>Sentinel stations:</p> <p>-long-term, real-time, common parameters, networked-</p> <p>-customized for geological/environmental settings</p> <p>-to measure dissolved methane, bubbles of methane; gas seep, gas vents, hydrates, etc.</p> <p><u>Parameters (examples):</u></p> <p>-CO₂</p> <p>-temperature (water and air)</p> <p>-salinity</p> <p>-particulates</p> <p>-met. Data (T, humidity, wind)</p> <p>-waves (shallow seas)</p> <p>-biology (microbes, fluorescence) for methane oxidation rate</p> <p>Devise way to move out from sentinel station as needed (via AUV?)</p>	<p>NSF</p> <p>Long term ocean observatory programs, national (ORION, Neptune, etc)</p> <p>International long-term observatory programs</p> <p>NIUST/NOAA program, IOOS</p> <p>NSF, NIUST</p>
<p>Q1</p>	<p>Tracer studies: -look for those specifically concentrated or depleted by hydrates</p> <p>-ratio of methane to inert tracers (e.g. Xenon, SF₆) emitted from seeps by collecting samples using a submersible vehicle.</p> <p>-mobile platforms</p> <p>-known seep or perturbation sites</p> <p>-follow the water mass for greater than 24 hour experiments</p> <p>- AUV development</p>	<p>NSF</p>
<p>Q1</p> <p>Q2</p> <p>Q3</p>	<p>Modeling:</p> <p>-we need 'appropriate models' (ranging from simple box models to ocean GCM models) to integrate and estimate the methane flux from the sea floor to the atmosphere, and measure methane concentrations throughout the ocean and incorporate ocean geochemistry</p> <p>-Start with D. Feely's model (which is for CO₂) and incorporate methane into this model?</p>	<p>NSF</p>

GROUP 2 DISCUSSION NOTES:

Need synoptic studies to assess flux from the sea floor to the sea surface, (cf. experiments by MacDonald). In MacDonald's case, he had oil present so methane could be followed to surface; this is only applicable in petroleum areas. Need an array of *in situ* measurements continuously through the water column.

Sea surface measurements are dependent on winds; only way to monitor/measure this right at air/sea surface boundary layer is using sonars (CODARS).

NOAA is measuring atmospheric methane all the time, but question is where does this methane come from?

Need to integrate methane sensors into existing observing stations and various surface ship transits by NOAA and other vessels, i.e. do not re-invent wheels.

Need to measure methane from all seafloor sources, not just methane hydrates. Methane hydrate may be a source and is a good flux indicator; manifestation of seep/leaky environment.

Use **OCS oil/gas platforms** (over 4000 in Gulf of Mexico EEZ) as sensor platforms and offshore research bases/labs.

Once the gas reaches the surface, is there a model to say what happens to the gas? Yes, there are plenty of dispersion models for this. **Need flux sensing devices at sea surface to collect all gases present in large volumes.**

Capturing bubbles at seafloor is done, but need to expand, e.g., use many 5 m² tubes to collect gas over 10 km² area. Ian MacDonald knows where to deploy capture devices and sensors, using seeped oil as a tracer. We know where the mud layers/volcanoes are (can see in seismic records); these should be priority sample sites.

Time constant for methane oxidation depends on the concentration in the water column. Water column sampling cruises (cf. Dick Feely) to measure methane and the rate of oxidation should be continued and expanded.

In EU, there are a lot of side scan sonar surveys to determine how much methane gets into the water column. Need to set up a **Sentinel station** to see if methane is increasing or decreasing in the water column; this could be done in the Gulf of Mexico. The sentinel buoy would be applicable to any case, i.e. gas seep, gas vents, hydrates, etc. Develop prototype station that meets requirements in Table D3-1 listed above and test in a location where we know there are seeps of methane. Could move a sentinel station, but would not want to do this often. **Need to be able to move out from sentinel stations, using mobile sampling platforms, e.g., AUVs.**

Use **tracers** to assess flux, e.g. ³He which is stable, quantify the ratio of this isotope and see how fast gets destroyed. Hydrates preferentially incorporate large noble gases such as Xe and Ne (tried to look at Xe, Ne, methane ratios).

Modeling is needed, but not just box models; other models (e.g. ocean dynamic models) exist that could be used. It would be good to know about the ocean surface system as well as we know about the atmosphere. Ocean GCM models already exist and have biological systems coupled/integrated into them. It makes sense to start with existing models and modify these to incorporate methane.

END GROUP 3 NOTES.

APPENDIX D: POSITION PAPERS

Following the meeting, participants were invited to submit "position papers" or additional comments they wished to see included in the report:

Sloan, D.	2
Roberts, H.	3
Rona, P.	4
Judd, A.	5
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Summary Thoughts on Climate Change After the NOAA Hydrates and Climate Change Conference May 13-14, 2004,

by Dendy Sloan, Center for Hydrate Research Colorado School of Mine, May 15, 2004

A few central points arise after the NOAA Conference on Climate Change:

1. While hydrates may provide an entrée into the area of climate change, in fact the consensus of the community is that hydrates are presently a minor . Two senior members of the methane budget community estimated the hydrate contribution at 5Tg y⁻¹ (Bill Reeburgh) and 10 Tg y⁻¹ (Keith Kvenvolden) out of a total of about 600 Tg y⁻¹.
2. Thus the topic of our study should be much broader than just hydrates, and the associated research should be renamed, “Methane Gas Contributions to Climate Change.”
3. Climate change did not play a significant role in the Methane Hydrate Act of 2000, and it probably will not play a significant role in any subsequent act, such as the proposed follow-on Methane Hydrate Act of 2005.
4. However, because the methane in hydrates is twice the equivalent of all other fossil fuels combined, it is important, both for current, historical, and future purposes, to keep track of the hydrate and their potential to contribute to climate. Particularly, it is important to study hydrates at locations where they are under the most jeopardy for dissociation in today’s geosphere. These places include the Arctic margins and the pockmark evolutions.
5. Such an effort requires international cooperation. One major source of such cooperation is CODATA (<http://www.codata.org>), a 50 year old international organization headquartered in Paris, whose purpose is to gather and share databases on scientific subjects. Over the last three years the CODATA Hydrate Task Force has held regional meetings on five major continents (China, Europe, India, Japan, North America, Russia) to alert the international community of this need. During the next three years (2005-2008), a comprehensive hydrate database will be generated, to include hydrate geoscience and mapping, physical-chemistry, and engineering applications. It is vital for major research organizations (e.g. NOAA, CGS, USGS, GFZ, IODP, USDOE, etc.) to participate in the generation and maintenance of this database. The 2004 International CODATA meeting, held in Berlin, November 8-10, 2004 (<http://www.CODATA.org/04conf>), will have a special session to discuss this database.

Summary thoughts of Harry Roberts, University of Louisiana, after conference (May 27, 2004):

I think the take home message for me is that we need to have a better understanding of the global methane budget in order to have faith in our climate models. Because we are at a high sea level stand, I suspect that gas hydrates play a minimal role as compared to times when our continental margins are under less hydrostatic pressure and bathed in warmer water. I think the fact that many of the world's complex continental shelves and margins, like the Gulf of Mexico example, are presently and constantly leaking hydrocarbon gases into the water column and atmosphere is an important process that needs quantification. At the moment we don't even have order of magnitude estimates of this methane source. With the national and international push for the standardization and deployment of ocean observing systems (both coastal and deep ocean), the global climate change community needs to push for development of reliable methane and carbon dioxide sensors that can be deployed as parts of these systems. Measurements should be made both in the water and atmosphere. These near real-time sources of methane and carbon dioxide data from the marine realm would be extremely valuable for calibrating existing and future climate models.

I also think the workshop pointed out the need to understand climate changes in the past (particularly in the Pleistocene) with regard to the current global warming trend. The clathrate gun theory is just that, but I didn't hear much at the workshop that made me doubt that hydrates could be major players in the global climate change arena. In my estimation we have a long way to go to understand the role of hydrates in climate change and slope failure. Timing is a key issue when talking about hydrate decomposition and these two possible responses. We really don't have very good time constraints on either slope failure and or methane spikes in the atmosphere vs. climate change. Solving these problems should keep us all in business for a long time!

Summary thoughts by Peter Rona, Rutgers University, May 14, 2004 at end of conference:

Has sea-floor failure ever had an effect on global warming?

Determine the style, extent, and timing of sea-floor failure features that release gas into the ocean (methane, carbon dioxide) and the relation of the gas release to climate change. These features include pockmarks, collapse structures, rotational slumping, gravitational gliding, and mud volcanoes. The approach is to map and determine relations between sea-floor failures and gas flux in selected areas of gas hydrates representative of major tectonic settings (active and passive continental margins such as Hydrate Ridge on the Oregon margin, and the Hudson Canyon region on the Atlantic margin, respectively; a sediment drift like the Blake Ridge; and a salt basin like the Gulf of Mexico).

Are the oceans an insignificant source of methane?

Alan Judd

School of Marine Science and Technology

University of Newcastle upon Tyne

U.K.

The current paradigm, reflected in atmospheric methane budgets accepted by IPCC (the Intergovernmental Panel for Climate Change) and other international authorities, is that the oceans are an insignificant methane source, providing approximately 2% of the global source (Houghton *et al.*, 1996). However, this estimate is based on a very small and poorly constrained database (Lambert and Schmidt, 1993). It is also widely believed that gas hydrates are the only seabed sources of methane, yet methane is widespread in marine sediments from inter-tidal zones to the deep ocean trenches.

Although microbial methanogenesis is widespread in marine sediments, microbial utilization removes the majority of the methane produced, inhibiting escape through the seabed. This is true of all locations, except where there are unusually high rates of methanogenesis and where seabed fluid flow is focused geologically. Such focusing also enables methane derived by geological (thermogenic and abiogenic) processes deeper within the Earth's crust to migrate towards the seabed. Focusing is associated with migration pathways such as faults, gas chimneys, and mud volcanoes. Migrating methane may be sequestered by gas hydrates, but only where pressure (water depth) and temperature are suitable.

At any location, including those with gas hydrates, if the methane flux exceeds the rate of microbial utilization, seepage occurs and methane-rich water or gas bubbles escape into and rise through the water column. Concentration gradients cause methane to pass from bubbles into the water. Depending on water depth, temperature and salinity, and the initial bubble size, bubbles may completely dissolve, or escape to the atmosphere. Bubble life is extended within the gas hydrate stability zone where a skin of hydrate inhibits loss to the water. This enables seabed methane bubbles to rise to within 300 to 400 m of the sea surface before the solution process begins. Where thermogenic methane is associated with oil, a film of oil coats bubble surfaces, restricting methane solution, and enabling transport to the sea surface regardless of water depth. Although these situations increase the proportion of seabed methane reaching the surface, generally the greater the water depth the smaller the proportion of methane that reaches the sea surface. So, seeps in the relatively shallow waters of the continental shelves and coastal zones are more likely to escape to the atmosphere. However, even in deep waters a proportion of methane reaching the top 200 m or so will reach the atmosphere as a result of sea surface mixing processes.

Mud volcanoes deserve special mention as sources of atmospheric methane (or, in some cases, CO₂). These features occur both on land and offshore in zones of tectonic compression (e.g. accretionary prisms) and rapid sedimentation (e.g. deep sea fans). There is a spectrum of activity styles. Some mud volcanoes de-gas continuously but with relatively modest flux rates, some exhibit periodic vigorous activity, and some erupt catastrophically producing enormous volumes of gas over periods of a few hours or days (some of which ignites to produce flames hundreds of meters tall). Methane from such eruptions, and vigorous escapes from other reservoirs released, for example, during earthquake events, is likely to escape directly to the atmosphere.

Estimating the flux and utilization rates at every stage from seabed to atmosphere (methane generation, seabed utilization, seabed flux, seawater solution and utilization, and sea surface flux - see Fig. 1) is essential if the contribution to the atmosphere is to be quantified. Each of these estimates presents challenges. However, there is little point in attempting these estimates if geologically-focused seabed fluid flow is a rare phenomenon.

A GIS database compilation of English language publications about seabed fluid flow and its indicators (seeps, mud volcanoes, pockmarks, cold seep biological communities, methane-derived authigenic carbonates, etc.- see Fig. 2) clearly demonstrates that this is not the case (Judd, 2002a). In fact seabed fluid flow is distributed throughout the world's seas and oceans in a wide variety of geological and oceanographic contexts: on active and passive continental margins, at plate boundaries and intra-plate sites - at water depths ranging from inter-tidal to >7,500 m in ocean trenches (Judd, 2003a). Bearing in mind the limitations of the geographical coverage and public availability of suitable data, it is clear that seabed fluid flow is of more than academic interest.

Judd, 2003b estimated that 3.6 Tg methane y^{-1} escapes through the sea surface flux from marine mud volcanoes, and Kvenvolden *et al.* (2001) suggested a total sea surface flux of 10 to 30 Tg methane y^{-1} (best estimate 20 Tg) from all seabed sources. It is emphasized that gas hydrates provide only a small proportion of these present-day fluxes; the majority is derived from coastal and continental shelf sources. Furthermore, these estimates are additional to water column methane sources of methane. Conventional oceanographic surveys which estimate methane concentrations in the water and sea surface methane fluxes are unlikely to recognize localized fluxes such as those described above. Consequently available estimates of the ocean methane flux may considerably underestimate the true flux.

The above discussion focuses on the present day methane budget, but considerable variations may be expected during periods of transition in glacial / inter-glacial cycles. Because sub-seabed methanogenesis processes are unaffected by surface conditions, the migration of methane to the seabed is likely to remain constant over periods of geological time. At these times the relative significance of gas hydrates is likely to change. The strength of the other sources will vary according to:

- i) variations in sea level: during glacial periods the lowering of sea level reduces the proportion of the seabed methane flux lost to the water column;
- ii) the extent of seabed ice and permafrost and sea-surface ice: during glacial periods the increased extent of ice and permafrost restricts the fluxes from the seabed and the sea surface. High latitude seabed permafrost and gas hydrates are known to trap gas (Bondarev *et al.*, 2002), and sea surface ice inhibits sea/air gas exchange (Lammers *et al.*, 1995). Consequently the reservoirs of methane trapped in sub-seabed reservoirs and held in solution in sub-sea surface water respectively will progressively increase over time, reducing the flux to the atmosphere. Conversely, during warming these reservoirs will be progressively released as the warming front migrates towards the poles. Evidence of catastrophic gas releases associated with warming at the end the last glacial have been reported from the North and Barents Seas (Judd *et al.*, 1994 and Long *et al.*, 1998 respectively - Fig. 3)).
- iii) The locations of major centers of deposition: During interglacial periods organic-rich sediments accumulate in coastal sites (estuaries, deltas etc.), providing prolific sources of shallow water microbial methane. In contrast the lowered sea levels of glacial periods cause terrestrial sediments to be swept across the continental shelves to be deposited in the deep sea fans of the continental rise. Here, microbial methane production will be sequestered by gas

hydrates (particularly once sea level rises again), to be released when hydrostatic pressure drops during the next glacial advance.

Judd *et al.* (2002b) argued that the above processes result in variations in methane fluxes from different parts of the globe as glacial / interglacial cycles progress. Both positive and negative feedback are provided to both global warming and global cooling. Although further work is required to quantify the relative strengths and influences of these processes, it seems that the net effect may be that they act as a 'geological thermostat', limiting extremes of climate.

In order to quantify the processes discussed above, two approaches are required. Firstly, individual generation, sequestration and flux processes require quantification. Secondly, it is necessary to ascertain the global distribution of locations of active seabed fluid flow. The second approach, in particular, necessitates an international effort, but considerable progress could be made with the aid of existing data sets (including those of the offshore petroleum industry).

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Figures follow:

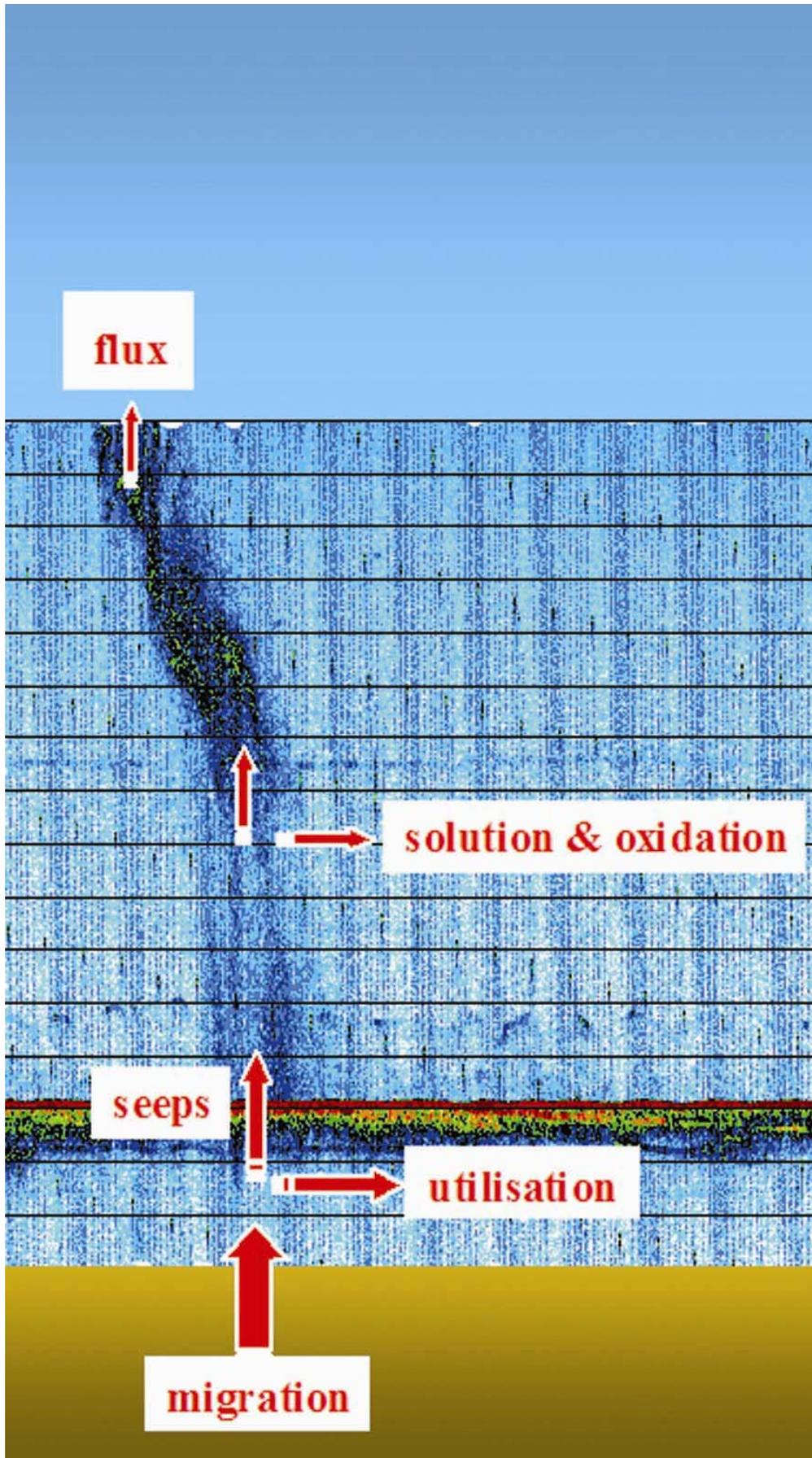


Figure 1. Fluxes and utilization of methane from geologically focused seabed fluid flow. The background shows a methane-rich seep plume from the Norwegian North Sea (water depth 74 m) recorded by parametric acoustic profiler.

Image courtesy of Prof. Dr. Gert Wendt, Rostock University, Germany.

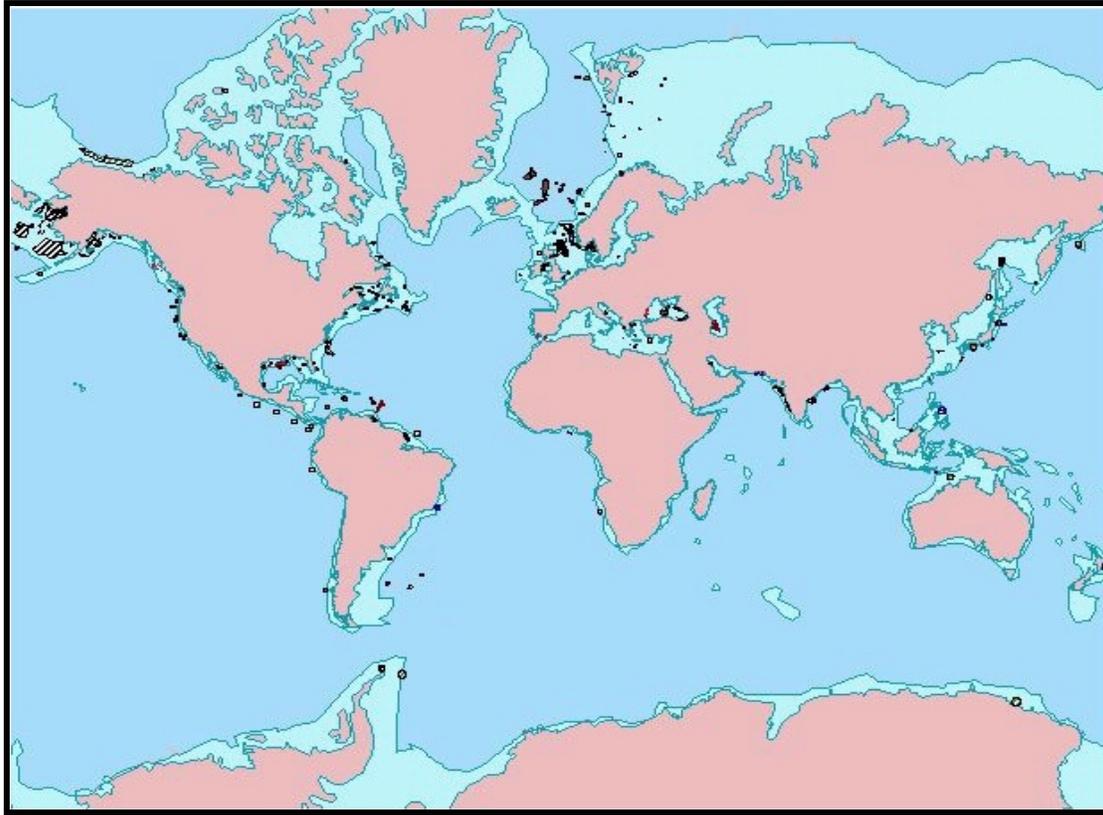


Figure 2: Distribution of gas seeps and indicators of gas seeps (pockmarks, mud volcanoes, gas hydrates, chemosynthetic benthic biological communities, methane-derived authigenic carbonate etc.). From the MAGIC GIS database (described by Judd *et al.*, 2002a).

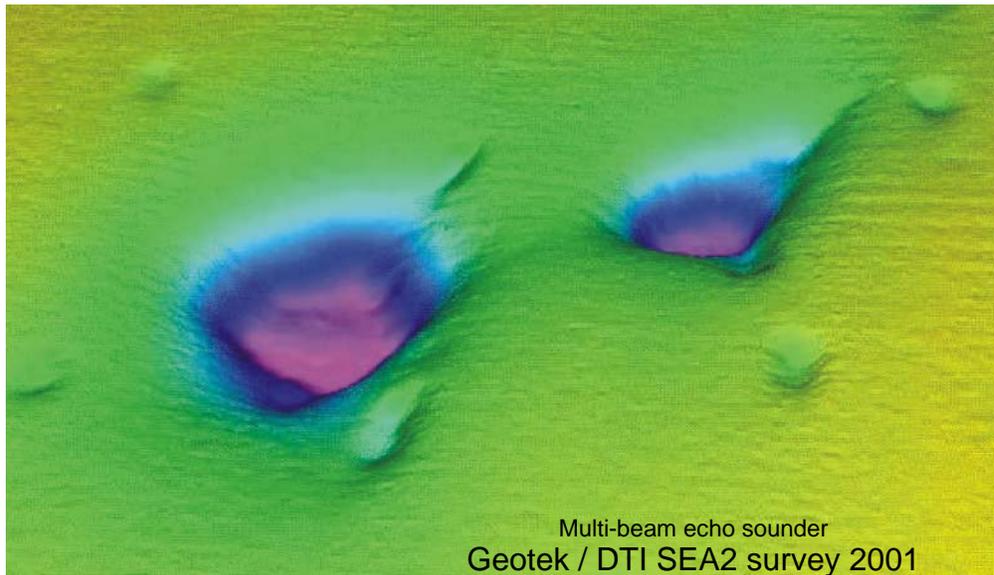
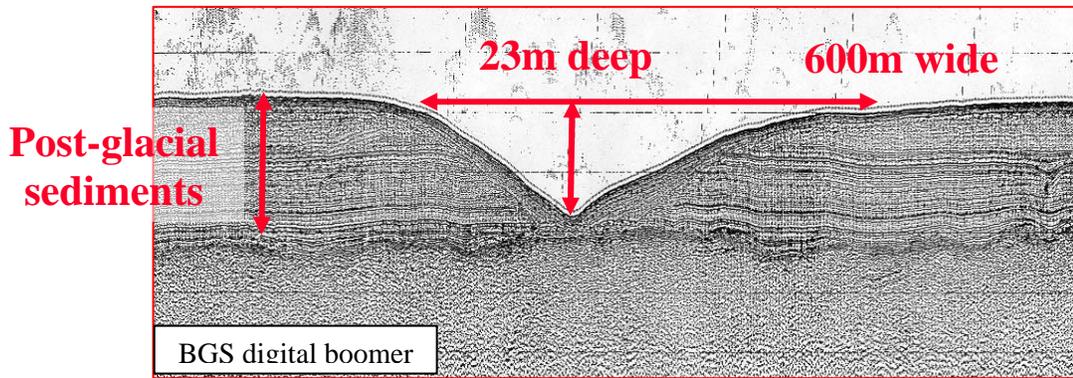


Figure 3: Giant pockmarks in the U.K. sector of the North Sea. These pockmarks were formed when gas trapped beneath seabed permafrost was released as the permafrost melted about 13,000 year ago (see Judd *et al.*, 1994, 2002b).

Top: Seismic profile of the pockmark shown on the left of the lower figure. Note the sediment that partially infills the feature. This has been dated by micropaleontology (Judd *et al.*, 1994).

Bottom: Seabed image showing two giant pockmarks and several much smaller 'normal' pockmarks.

Image acquired as part of the UK government's Strategic Environmental Assessment of part of the North Sea (SEA2) and reproduced by kind permission of Geotek Ltd.

A Role for Industry in Understanding Seafloor Methane Venting and the Global Carbon Cycle

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The discussion at the end of the May workshop mentioned some potential involvement with industry on the issue of natural methane release from the seafloor. I would like to add a few thoughts to this topic.

Understanding hydrocarbon migration is a critical factor in oil and gas exploration, and is an area of focus at most oil companies. This is especially true in deepwater areas where the cost of drilling a single exploratory well is often more than \$30 million. The daily rate for the latest generation of drill ships is typically over \$200,000. While much is made of using seismic indicators to select exploration targets, the costs are such that understanding the entire petroleum system at a proposed location is advantageous.

The proposed program we discussed in Boulder will primarily focus on the shallow subsurface (upper km), an interval of generally less interest to the industry. And yet, when we take a “petroleum systems” view, the entire interval from deep source rocks to the sea floor is very much linked. Thus, from a purely geological standpoint, there is great overlap between the goals of our project and the goals of industry.

Industry has a number of resources that would be of use to a climate change project if they could be made available. First is data. This includes very high quality seismic data, often with special processing of the shallow subsurface section for geohazards work. Second is the technical staff with experience at interpreting seismic data with an eye for timing and migration of hydrocarbons. Third is well and borehole data. This includes both conventional well data (although often quite sparse and of low quality in the shallow subsurface) and geotechnical data taken from shallow boreholes prior to setting platforms. Last are the platforms. These could serve as a base from which seafloor data could be gathered and transmitted back to shore.

Most companies have been reluctant to participate in this type of project in the past. Most likely, they have not seen any particular benefit for them and the potential for some adverse results. To overcome this resistance, it will be necessary to show strong benefits and low cost or risk. The first benefit is the improved understanding of hydrocarbon migration through the shallow subsurface as noted above. The second benefit is more strategic and addresses a different concern of the industry: global climate change. In the popular press and in much of the public mind, the oil industry is the ultimate “bad guy” on the climate issue. While the industry is often quite defensive on this issue, it has also taken a number of steps to cut greenhouse gas emissions. These include significant reductions in venting and flaring. The industry might well embrace a project that sought to quantify natural methane venting.

The difficulty is in developing contacts within the industry. Twenty years ago, each company had a position of “Chief Geologist”, a scientist with a long-term outlook and good contacts with industry and academia. As companies have reorganized into profit centers and business units, the position of Chief Geologist has been eliminated or significantly altered at most companies. Finding the right individuals at various companies will be difficult, but may add an important dimension to understanding the role of seafloor methane venting in the global carbon cycle.

Can marine methane hydrates drive abrupt climate change? Rough estimates and proposed modeling framework

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Abstract:

We present a rough estimate of the sensitivity of climate to methane hydrate destabilization after the “Methane Hydrate Gun” hypothesis of Kennett et al. (2000). We then lay out a modeling framework for refining the estimate on potential climate implications and list the currently missing ingredients needed for such an attempt. A simple “back of the envelope” calculation based on Dickens (2003) for the magnitude of effect and sign of the feedback for the observed climate warming of the last century as a potential trigger for the “methane hydrate gun” indicates the following: If the timescale of release is set by thermal molecular diffusion of heat through the sediments, then the release of methane hydrates is too low to lead to a positive feedback. If, in contrast, there is a mechanism for releasing all hydrates within the zone destabilized by observed warming over the timescale of a century, then a positive warming feedback which would sustain additional, continuing release most of marine hydrates would occur. While observations of methane cycling over the last century do not support such catastrophic releases as having yet occurred, little is known to constrain the potential for such releases in the future. The central missing ingredients are the global 3D distribution, amount and form of CH₄ hydrates, an understanding of the process of heat transfer within the sediment and within CH₄ hydrates and the fraction of hydrate CH₄ that reaches the atmosphere once released from the ocean floor.

Case study of current climate change: Can greenhouse warming be amplified through methane hydrate disassociation?

First we assess the degree of warming that has occurred over the last century. The globally averaged warming at the earth surface in the last century caused by the 2 W m⁻² anthropogenic climate forcing has been estimated as 0.6 °C (IPCC 2001 report). In the Levitus et al (2000) study, this corresponds to a 0-300 m ocean warming of 0.31 C and to a 0-3000 m warming of 0.06 °C over 40 years, or 0.08 °C/century below 300 m. Arbic and Owens (2001) suggest that the warming in the 1000-2000 m range was much larger in the Atlantic – 0.5 °C/century. As an upper limit, let’s assume that roughly a 1 °C surface change can effect a global 0.5 °C deep ocean change over 100 years.

Given this warming, we next estimate how much methane could be released. At 1000 m, a 0.5 °C change is equivalent to lowering the methane (CH₄) stability depth by 200 m given the average thermal structure of the ocean. If there are 10000 Pg C in hydrates (Dickens 2003), and they are evenly spread over a depth range of 1000-3000 m, then 1000 Pg C would be in the ocean volume affected by the warming and could potentially be destabilized over the 100 years. However the subsurface sediments are buffered to temperature changes through the diffusion boundary. Given a seawater thermal molecular diffusion coefficient of $1 \times 10^{-7} \text{ m}^2 \text{ sec}^{-1}$, and a sediment porosity of 0.3, this gives a depth of penetration of 7 m over the 100 years, assuming a linear perturbation. Assuming these deposits are dispersed within the upper 100 m gives only a net loss of 70 Pg C of CH₄.

We can then determine the response of atmospheric methane. Assuming all of this CH₄ is released to the atmosphere directly, and further assuming an 8 year atmospheric lifetime for this CH₄ with respect to reaction with hydroxyl radical, gives an average increase of 6 Pg CH₄ over this period, or more than a doubling of atmospheric CH₄ (current inventory 4.8 Pg C). This would also add 35 Pg C to atmospheric CO₂ (current inventory 700 Pg C) assuming a CO₂ atmospheric lifetime of 50 years with respect to ocean uptake.

This subsequently provides a quantifiable greenhouse response. Given the IPCC 2001 estimates of CH₄ radiative forcing, doubling the CH₄ concentration adds about 0.6 W m⁻², or 30% of the current forcing. The related CO₂ forcing is 0.15 W m⁻². This would serve to warm the deep ocean by, at most, another 0.19 °C after the initial 0.5 °C trigger. Thus, the stimulus-response factor is much less than one, and the system is stable on the 100 year timescale. That is to say that the feedback is damped relative to the initial perturbation and thus does not lead to a catastrophic release of all the ocean hydrates. Still, the response has a quite large impact on the CH₄ cycle, and a fairly strong impact on the CO₂ and heat budgets.

Problems with this “back of the envelope” calculation:

- 1) Atmospheric CH₄ oxidation timescale is nonlinear due to hydroxyl radical consumption, so a doubling of CH₄ could increase the lifetime of CH₄; answering this correctly requires an atmospheric chemistry model.
- 2) Looking at shorter timescales would add seasonal and inter-annual variability and potentially increase the amount of hydrate exposed; this would require a climate model and perhaps a sediment model.
- 3) Looking at longer timescales would require a more detailed description of sediment-water interactions, also requiring a sediment model.
- 4) This model assumes all CH₄ is reaching the atmosphere directly. If this is not true – particularly in the case of slow disassociation – an explicit treatment of the ocean biogeochemistry of CH₄ is required. This would severely reduce the amount of CH₄ released to the atmosphere, but could have large effects on ocean chemistry.
- 5) This model ignores catastrophic disassociation events such as slumping; how much positive feedback is there in the alteration of the sediments during disassociation? For example, if all 30 m of CH₄ were lost in the 200 m zone – 1000 Pg C – this would provide a linearized atmospheric warming of 25 °C!!! Certainly, we know that this has not happened over the last 100 years so it is only an upper limit, but it does beg the question of how quickly CH₄ hydrates can be eroded under temperature change – we really have no idea.
- 6) This model assumes an extremely simple distribution of CH₄ hydrates (a flat, thin, 100 m layer of hydrates evenly distributed over the 1000 m to 3000 m depth range with a global inventory of 10000 Pg C). Knowledge of the real distribution, particularly with respect to regional variations in ocean temperature and its variability, would improve the simulation, and require both a better map and a climate model.
- 7) This model assumes a static CH₄ hydrate reservoir - are its dynamics important?
- 8) This model only describes deep hydrates. What about the shallow ones?

Current informational impediments to more detailed modeling:

- 1) Distribution – latitude, longitude and depth distribution in sediments as well as chemical phase.
- 2) Mechanism of heat transfer in sediments and hydrate-sediment mixtures – is it just molecular diffusion through the porous medium or does the mechanical alteration of the medium through disassociation of hydrates increase the diffusivity?
- 3) How much of the methane is released to the atmosphere directly by bubbles? What controls this – interaction of five processes: size distribution of initial bubbles which determines vertical velocity, increase in bubble size with decreasing pressure determined by initial depth, dissolution of methane, N₂, O₂, and CO₂ gas exchange with bubble, impediment to gas transfer by oil films and, finally, impediment to gas transfer by hydrate film formation.
- 4) If most of the CH₄ is dissolved into seawater, what is its fate with respect to biological oxidation?
- 5) How certain is the phase diagram for hydrates?
- 6) Are there globally significant catastrophic processes (such as a meteorite, global earthquakes, slumping or tsunamis) that may also serve as a trigger?
- 7) Optional: knowledge of the isotopic signature of the hydrate reservoir for application to ¹³CO₂.

How would such modeling proceed?

- 1) Sediment and sediment pore water model including the thermodynamics (and mechanics?) of hydrates based on distribution of hydrates. The sediment model would need to be developed.
- 2) Physical climate model of ocean and atmosphere – e.g. the GFDL climate model.
- 3) Ocean biogeochemical model (for at least CO₂ and CH₄ cycling) - e.g. adding CH₄ to the GFDL model of Dunne.
- 4) Mechanics of ocean-atmosphere bubble transfer – would need to be developed based on observations.
- 5) Atmospheric chemistry, e.g. Mozart model being used at GFDL.
- 6) Optional: Modeling of the ocean, land and atmospheric ¹³CO₂ cycle.

What would be the value of such a more detailed simulation?

- Quantify direct effects of methane release
- Assess role of seasonal-interannual variability
- Quantify strength of climate feedbacks
- Specify regional sensitivities (particularly the arctic)
- Suggest observational strategies in the ocean and atmosphere that confirm or disprove model results.

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A few informal ideas for research into methane and global change

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Assessment of global geological release of methane from the lithosphere (i.e., from rocks).

A challenge in modeling methane and global climate change is to develop reliable quantitative estimates of global geological release of methane from the lithosphere and, of greater importance to the climate change modeling community, the amount that successfully reaches the atmosphere. As a geologist, I am best suited to estimate the former, i.e., the release from the lithosphere, here assumed to be from subsurface sedimentary or other rock sources, e.g., mud volcanoes, gas seepage from leaky petroleum systems, dissociation of gas hydrates etc. Some of this geological component is biogenic (i.e., from methanogenic bacteria), but it is essentially methane released from deeper sources. (The biological component I consider to be the release from surface sources, such as cows, termites, productivity from salt marshes, and other non-geological sources, which is not what I am considering here).

Two possible strategies for developing this global estimate are (a) to map and measure the features where methane is being released. A. Judd has a pretty good sense of the types of features to map and where they might be. This approach has the disadvantage of being very time consuming (for field work) and expensive (for field and interpretive work), not to mention probably unrealistic for yielding a reliable number within the next decade or several decades. (b) to use the methodology developed by the community that does energy assessments. This community uses statistical methods to combine geological models with mathematical uncertainties (and other economic and technological information) to estimate in-place resources, recoverable resources, and economically developable resources. The advantage of this approach is that it gives numerical estimates of uncertainties with ranges of possible values (which are of course dependent on the geological and mathematical models); it also is a technique that can produce a number within a few years (as opposed to many years with the mapping effort). Assessments undergo revisions as new information is learned, i.e., the methodology is well suited to periodic revision as more knowledge is gained. *My recommendation is that this "assessment" approach should be used for doing a methane inventory.*

Current researchers with this kind of expertise reside in academia (especially the mathematical modelers) and in the federal agencies that conduct these kinds of assessments, USGS (for terrestrial national and global assessments of energy resources) and MMS (for offshore national energy and mineral assessments). MMS has a new project for undertaking an offshore methane hydrate assessment, focused initially on the Gulf of Mexico (see Bill Shedd's contribution for more information on this). Using an energy assessment approach has great opportunities for integrating diverse disciplines and expertise.

- (1) Experiment to monitor intermediate water temperature changes and effects on the subbottom environment.

The “clathrate gun” hypothesis lists the warming of intermediate bottom waters at the onset of deglaciation as a possible mechanism for warming sediments, which in turn leads to dissociation of methane hydrate and massive release of methane to the atmosphere, which is a positive feedback for climate warming. This is a potentially testable hypothesis through conducting an experiment to monitor the history of intermediate bottom water temperatures (and potential effects on subsurface sedimentary temperatures). By designing an experiment in a region where hydrates are known to occur, the experiment might yield insights into whether hydrate dissociation actually occurs. An obvious place to locate such an experiment is where intermediate bottom waters undergo temperature changes for multi-year periods (e.g., during an El Niño event) and where hydrates also occur (e.g., off Peru). Measurements of bottom water temperatures and subsurface temperatures are necessary, so it may involve drilling, “corking,” and instrumenting a well-hole. The broader research community should be engaged in making the final decision about the most suitable location. Note that long-term temperature measurements of bottom water have been recorded off Norway, and there is a proposal to drill and instrument a nearby well to extend the record and also obtain subsurface temperatures. It is unclear to me whether this hole satisfies the conditions of measuring intermediate water and having hydrate proximal hydrate deposits.

Comments from Ross Chapman, University of Victoria, May 13-14, 2004

1. Workshop summary

The workshop was organized to bring hydrate scientists and together with climate scientists to determine the major issues related to the role of gas hydrates in global climate change. There is a fundamental knowledge gap in the transfer processes that link hydrates in the sediment and methane in the atmosphere. The transfer involves a system that includes the ocean sediments, the water column and the atmosphere. We have to look at issues such as the quantities in the storage component of the system (the sediments); the transfer mechanism and the transfer rate of methane from the storage reservoir to the water; the evolution of the methane in the water; the vertical and horizontal distribution of methane in the water; and finally the transfer of methane from the water to the air at the sea surface.

It's difficult to know where to start in suggesting experiments, because one of the most fundamental problems is the detection of seep sites. That is, where do we do the experiments to monitor the flow of gas? There are some obvious sites, but it's also true that there may be many more that we don't know about. The experimenters will have to choose specific sites and determine the flow conditions at those sites. Some obvious examples are the Gulf of Mexico (Green Canyon; Keithley Canyon; Bush Hill), Hydrate ridge, and Barkley Canyon. I think the basic requirement however is to choose sites where there is hydrate on the sea floor, so that you have a system that is easily observed. There is also a need to know as much as possible about the plumbing system that brings the methane to the sea floor, so this means having a good amount of multichannel seismic data for the sites. Related to the plumbing question, is the type of methane. Is the hydrate bacterial or thermogenic? The flow rate in the sediment may depend on what type of methane comprises the hydrates, since thermogenic hydrates are often associated with very strong hydrocarbon seeps.

The critical points in the system are at the interfaces. My experience is with the sediment/water interface, so I would advocate experiments that measure the quantity of methane in the pore water, and in the ocean water at the sea floor. These measurements have to ensure that the samples are recovered and the gases are analyzed at *in situ* pressure (and temperature if possible). We have been doing this at the Barkley Canyon site already, and are going to continue the measurements in June of this year. Measurements like we have done provide some basic information about the carbon flow. There is also a quantity of carbon that is taken up by biological systems in the sediments, and the measurements that we have made do not address this question. How much methane in the sediment is consumed by microbial activity? There is also a question of the hydrate distribution around the seep site. How much hydrate is beneath the sea floor? We can see outcrops in a few specific places, but is this the whole story?

We also need to measure factors that may affect the flow of methane and the dissociation of hydrates, such as temperature and salinity (in the water, in the sediment and in the hydrate itself) over a long period of time, and the biological activity over time.

The next problem is to make measurements of the vertical distribution of the quantity of methane. We have done this using the submersible, taking water samples immediately above the sites where we sampled the pore water. Measurements like this are very useful, and require very specific navigation. You can't simply drop niskin bottles from a ship over the general area.

The most recent release of a large quantity of methane was at the Barkley Canyon site, where a commercial fishing boat accidentally snagged about a half ton of hydrate and brought it to the surface. (I think we have seen the site where the hydrate used to be, i.e. a big hole in the hydrate patch) It would have been interesting to monitor the quantities of gas in a 'controlled' release such as happened to the fishing boat.

2. Partnership with the NEPTUNE project.

NEPTUNE is an international (US and Canada) project to instrument the sea floor off the west coast of British Columbia, Washington and Oregon with fiber optic and power cable. The infrastructure provides a new capability to make long term measurements of ocean and sea floor processes over a regional spatial scale.

The Neptune project is the perfect infrastructure for making the measurements that are required to answer the questions about the transfer of methane from marine gas hydrates to the ocean and to the atmosphere. The sea floor cables provide the means to instrument a hydrate site with physical (seismic), chemical and biological sensing systems that can monitor the state of the hydrate system below the sea floor, on the sea floor and in the water, over a long period of time. Furthermore, there is also the option of linking the sea floor measurements with measurements in boreholes that exist from previous Ocean Drilling Program legs in the region (e.g., Legs 146 (1992) and 204 (2002)).

The Canadian portion of the infrastructure has been funded, and is now in the process of determining the initial experimental program of the infrastructure. There are four research themes in the Canadian program, one of them being Hydrates and Fluid flow. A first workshop was held in Victoria on 3-5 May, 2004, and a second workshop is planned for 27-29 September. The goal of the workshops is to develop initial proposals for installing experimental systems for community experiments at the node sites of the Canadian network. As a result of the first workshop, the trunk cable layout will be designed to connect with one or more of the sea floor hydrate sites that are known on the northern Cascadia Margin.

There is a clear benefit in partnering with existing research programs to realize the objectives in acquiring new experimental data on methane gas transfer from hydrates. The NEPTUNE project provides an opportunity that is consistent with the time frame for the experimental program that was discussed at the NOAA workshop. Further interaction and collaborative work can be explored at the forthcoming NEPTUNE workshop in September.

Proposal for a Study to Estimate Methane Flux Rates into the Atmosphere from Natural Gas and Oil Seeps from the Gulf of Mexico, Bill Shedd, MMS

The sources and flux rates of methane reaching the atmosphere are of great concern to atmospheric scientists because of methane's effectiveness as a greenhouse gas. Many of the human activities that introduce methane to the atmosphere have been modeled and their relative contributions estimated; however, the contribution from natural seepage of methane from the oceans worldwide is poorly understood and needs to be studied to better estimate the total impact of methane on the atmosphere. The Gulf of Mexico provides an excellent location to conduct such a study because of its many known seeps and the wealth of data available to the U. S. Government and academia.

The Minerals Management Service (MMS) has used its extensive proprietary database of seismic data to map bathymetric and amplitude anomalies in the northern Gulf of Mexico. Through submersible dives to the seafloor with Dr. Harry Roberts of Louisiana State University, correlation with data collected by Dr. Ian MacDonald of Texas A&M from his dives to study chemosynthetic communities, and correlation with piston core data collected by GERG of Texas A&M and others, investigators conclude that most of these anomalies are created by oil and gas seeps. Through mapping efforts, 145,000 square miles of the deepwater Gulf of Mexico have been evaluated to determine the distribution of the seeps.

What remains to be estimated are the methane flux rates from the specific sites. Many of the sites studied exhibited a slow, dispersed flux rate where it would be a challenge to measure the actual flux rate. While many of the other sites in the Gulf, though, exhibit moderate to rapid flux rates that are easily visible by direct observation from the submersible, as plumes on high resolution fathometer plots, and as persistent oil slicks on the ocean surface observed on satellite data. These sites exhibit a unique geophysical acoustic signature: where most of the seismic amplitude anomalies are strong positive reflections due to the presence of authigenic carbonates, gas hydrates and chemosynthetic communities, rapid flux pluming sites are often strong negative reflections due to the high gas saturation in the sediments. The seafloor is acoustically slower than seawater and much slower than the surrounding strong high positive amplitude anomalies.

The MMS proposes to collaborate with NOAA to estimate methane flux rates in a part of the Gulf of Mexico. Local flux rates can then be extrapolated to the rest of the Gulf using a combination of: 1) the MMS's database and maps, 2) satellite imagery to identify active, persistent oil slicks on the sea surface sourced from the seafloor, 3) other remote geophysical methods (fathometer surveys or other ship borne technology from which amplitude can be extracted and related to measured flux rate), and 4) *in situ* flux rate measurement using technology similar to Dr. Harry Robert's "bubble-ometer" (a cone with a hole at the top, where a small, hinged cone resides that fills with gas, swings up to release the gas; being connected to a counter and timer, and knowing the volume in the small cone, the local flux rate can be measured).

The MMS is partially funding Dr. Robert Woolsey of the University of Mississippi in the design and construction of a vertical seismic array that will monitor natural gas hydrate flux and stability at one of the core holes that the DOE funded hydrate JIP is scheduled to drill in the fall of 2004. This ongoing data collection, along with the proposed study, will be invaluable to our knowledge of methane flux and the role that hydrates play as a source/sink for methane in the ocean and atmosphere.

Geologic Methane Emissions and the Global Atmospheric Methane Budget (Received July 5, 2004)

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The current global atmospheric methane budget (IPCC, 2001) does not take into account naturally occurring, geologically-sourced, fossil methane emissions. This omission of natural methane emissions from this budget needs to be rectified in order to better understand the global methane cycle. The purpose here is to (1) identify the geological sources of methane to the atmosphere, (2) estimate their source strengths (annual rates of methane release, and (3) adjust the global atmospheric methane budget to reflect the contribution of geologically-sourced, fossil methane.

The total amount of methane entering the atmosphere each year is about 598 (rounded to 600) Tg (Tg = teragrams = 10^{12} g), of which about 576 Tg is destroyed, mainly by oxidation. The corresponding current total atmospheric burden of methane is about 4850 Tg, giving rise to an average atmospheric surface abundance of about 1745 ppm (IPCC, 2001). The presently recognized sources of atmospheric methane can be organized under two main categories, natural and anthropogenic. Natural sources include wetlands, termites, oceans, fresh water, wild ruminants, natural forest fires, and gas hydrates. Anthropogenic sources include fossil fuel (petroleum and coal) energy use, landfill and waste treatment, domesticated ruminants, rice agriculture, and biomass burning.

Most of the sources in both categories emit methane generated by active biological (microbial) processes. Two exceptions are biomass burning and natural forest fires in which methane results from incomplete combustion of vegetation. Another important exception is the source identified as 'fossil fuel energy use' where petroleum (oil and natural gas) and coal are exploited, and the released methane is non-biological (non-microbial), i.e., geological in origin. This methane has been generated in the geological past by thermal processes acting on ancient (fossil) biological materials.

According to IPCC (2001), 82% of the methane in the atmosphere results from present or past microbial (methanogenic) activity, and 18% is "old" or "fossil," i.e., geological. Such a percentage distribution balances the global atmospheric methane budget from the perspective of both the ¹³C and ¹⁴C isotopic abundances of methane and accounts for the mean stable carbon isotopic composition (-47.3‰) of the surface atmosphere. Thus, of the 600 Tg y⁻¹ of methane entering the atmosphere, about 110 Tg y⁻¹ is fossil or geological and the remainder is microbial. Even in the gas hydrate source, the methane is mainly microbial in origin (Kvenvolden, 1995).

Any newly identified source of methane emission to the atmosphere must be constrained by the results of IPCC (2001) which represents the current consensus. If the total amount of methane entering the atmosphere is about 600 Tg y⁻¹, then the postulated methane emission from natural geological sources cannot be added to this total, but must be accommodated within the total. In order to maintain the isotopic (¹³C and ¹⁴C) balances, the postulate methane emissions from natural geologic sources must be accommodated within the 110 Tg y⁻¹ of fossil or geological methane now attributed only to anthropogenic exploitation of fossil fuels, mainly natural gas and coal.

Natural methane emissions from geological sources are all natural gas seeps, and they include macro-seeps, which have visible manifestations, such as bubbles, when the seeps are underwater, and micro-seeps, which are invisible and usually are detected by chemical measurements. Mud volcanoes are special macro-seeps; the exits of these natural seeps are volcano-like in appearance. Gas hydrate, a solid form of methane and water, is often associated with macro-seeps, including mud volcanoes, under special conditions of pressure and temperature; however, most methane in gas hydrate is microbial in origin, and not the result of thermal processes. Minor methane emissions result from

magmatic volcanism, geothermal processes, and from tectonism at mid-ocean ridges. Kvenvolden and Rogers (in press) summarizes the estimates of fossil methane emissions to the atmosphere from geological sources as shown in the Table below:

<u>Geological Source</u>	<u>Methane Flux (Tg y⁻¹)</u>
Natural Macro-seeps	25
Micro-seeps	7
Mud Volcanoes	5
Magmatic Volcanoes	4
Geothermal Areas	3
Gas Hydrate	1
Mid-ocean Ridges	0
TOTAL	45

This estimate of 45 Tg y⁻¹ of geological methane reaching the atmosphere is conservative but agrees remarkably well with a 50 Tg y⁻¹ methane flux estimate by Etiope (2004). Because this methane is isotopically heavy in terms of ¹³C and devoid of ¹⁴C, it can only be accommodated in the global atmospheric methane budget within the 110 Tg y⁻¹ currently assigned by IPCC (2001) to fossil fuel usage. Therefore, the amount of methane emission attributed to fossil fuel usage should be reduced by 45 Tg y⁻¹, leaving only 65 Tg y⁻¹ to be attributed to the anthropogenic exploitation of fossil fuels and partitioned between coal mining and petroleum (natural gas) production.

The affect of geologically-sourced methane on current global climate change is considered to be minimal because it is part of the background emission of methane that has been going on throughout much of geologic time. Massive releases of gas-hydrate methane, however, could impact significantly the atmospheric methane budget by adding large amounts of mainly microbially sourced (¹³C depleted) methane to the ocean/atmosphere system. Such massive injections of methane from gas hydrate may have affected global climates in the past and could influence climates in the future. The extent of this influence, however, cannot yet be predicted, given current understanding.

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Comments by Jean Whelan, July 21, 2004

a) Potential for Interfacing some aspects of the future oceanic hydrate monitoring program to the developing Ocean Observatories Initiative (OOI)

A substantial weakness of the current DoE hydrate research programs is the almost total absence a coherent plan to make the quantitative *in situ* observational measurements on seafloor hydrates which are badly needed to underpin the rest of this part of the DoE hydrate initiative. This workshop report could help by recommending that consideration be given to interfacing hydrate research on the seafloor, wherever possible, with the Ocean Observatories Initiative (OOI) and ORION (Ocean Research Interactive Observatory Networks) programs currently in the planning stages from NSF (<http://www.coreocean.org/orion/>; also see Dietrich et al. 2003). OOI is a new initiative in which NSF would fund installation of a worldwide infrastructure of continuous seafloor observatories throughout the world's oceans. This program has a very high priority for some funding in the next fiscal year in the NSF budget as well as continuing funding over the next several years. The current plan is for the initiative to be fully funded within the next 6 years. Some of the Canadian parts of the program, Neptune and Venus, have already been funded.

The OOI program interfaces with other international hydrate programs and ocean monitoring efforts, such as those underway in a number of EU nations and in Japan. My impression is that the Europeans and Japanese are generally ahead of the US with respect to seafloor observations of hydrates and their associated cold seeps. The OOI will make possible long time series *in situ* measurements on many types of ocean floor hydrates. The program will also provide more power than has previously been available to specific locations of the ocean floor which will increase the possibilities for *in situ* experiments on sea bottom methane hydrates, even in deep parts of the ocean.

The advantage of hooking the newly developing OOI and future hydrate monitoring programs together would be the ability to apply new tools being developed by the OOI for hydrothermal research to seafloor gas hydrates and cold seeps. For example, real time streaming video from the seafloor will allow real time response to an event (Dietrich et al. 2003), such as a volcanic eruption or a gas eruption of a hydrate associated mud volcano.

At the present time, no OOI sites are proposed in the Gulf of Mexico, although the program covers other areas of known seafloor hydrates and gas seeps worldwide (e.g., the Neptune and Venus sites in the NE Pacific which cover the Cascadian Margin and many sites over most of the world's continental margins where more and more hydrates are continuing to be found). The OOI will provide the infrastructure to carry out *in situ* seafloor observations on hydrates over fairly large areas and over varying periods of time.

Combining seafloor long-term monitoring with new IODP drill holes would offer new opportunities for long term monitoring of the basic *in situ* properties of different types of seafloor hydrate deposits, including both the massive and diffuse types, data which we currently lack. For example, one possible experiment (proposed by C.Paull of MBARI) in the ORION report would involve deliberate destruction of sub seafloor hydrates of various types within a drill hole and then continuously monitoring of *in situ* changes in a variety of geochemical and geophysical properties within the hydrate, the surrounding sediments, as well as within the overlying water column and atmosphere. The OOI makes available at the seafloor the large amounts of heat (power) to decompose the borehole hydrate.

b) Unsolved "Basic Science" issues on seafloor gas hydrates - the missing link between their potential role as a future resource, in bottom sediment instability, and as a trigger for global climate change

A weakness with the past seafloor hydrate programs with respect to resource potential has been the implicit assumption that seafloor hydrates will behave like conventional oil and gas reservoir deposits. This assumption has not been demonstrated and is probably wrong - seafloor and sub-seafloor hydrate deposits are comprised primarily of biogenic gases which have generation and migration histories very different from those of normal "petroleum" resources in almost every respect. For example, application of the "Petroleum System" method of evaluating oil and gas prospects which is widely used by industry requires definition of source, migration fairway, and evaluation of timing of oil generation versus timing of reservoir formation and filling history. Viewing seafloor hydrates from this perspective, prospects for producible methane at or below the seafloor look grim for the diffuse type of seafloor hydrate for which the source is too shallow and too dilute to be of much use in filling of a conventional reservoir.

A number of hydrate researchers feel strongly that economic quantities of gas hydrate from the seafloor will come massive deposits that are generally localized, hard to locate and characterize, and result from some mechanism, such as gas migration along fractures and faults, for delivering large amounts of methane to a single location (e.g. Hovland and Judd, 1988; Judd and Hovland, in prep.; Roberts and Carney, 1997; Sassen et al., 2001). A concerted effort is required to develop better methods for detecting and measuring *in situ* properties of these more focused seafloor hydrates and their commonly associated gas flows than is currently available. There is a critical need to be able to better detect and to characterize these more massive seafloor and sub-seafloor hydrate deposits if an accurate estimate is ever to be made of the true size of the oceanic hydrate resource and an estimate made of what part of this might be commercially exploitable.

In summary, basic knowledge required to find and produce large deposits of biogenic gas and associated gas hydrate deposits in and under the seafloor is almost totally lacking. Gaining this fundamental knowledge needed to make this evaluation would also go a long way toward enabling other more neglected parts of the hydrate initiative regarding seafloor stability and global climate change.

c) Investigation of the relationship between seafloor hydrates and gas flow

Seafloor gas hydrates are commonly associated with gas flows. Various theories of the source and importance of this gas is a matter of considerable disagreement within the scientific community at present. Is the gas the result of hydrate dissociation and related only to climatic aspects of hydrates? Or is the gas seepage related to hydrate formation/destruction processes possibly making it relevant to exploring for and assessing the extent and concentration of worldwide hydrate deposits?

Two very different hypotheses currently exist for the origin of the free and seeping gas associated with hydrates: 1) the gas comes from a deeper source, either thermogenic or biogenic, and forms a hydrate deposit whenever high enough pressures and low enough temperatures are present for hydrate formation. In this scenario, the hydrate is viewed as a capacitor in a very dynamic methane flow system (e.g. Dickens, et al, 1997; Zatsepina, et al, 1997); 2) methane to form hydrates is derived from local in-situ sediment sources of biogenic methane produced by anaerobic methanogenic bacteria and archaea so that hydrate amounts and lifetimes of the methane hydrate deposit can be estimated from *in situ* pore water profiles of methane and sulfate (e.g. Xu and Ruppel, 1999, Ruppel, 2000, and Valentine et al., 2001). In scenario 2, the hydrate and associated seeping gas are primarily a function of

the relative rates of hydrate replenishment via upward methane diffusion from the sediments below and hydrate decomposition due to interactions with warmer water column temperatures above.

These two scenarios of methane hydrate formation and maintenance are very different and knowing which is correct significantly impacts the amount and concentration of methane ultimately recoverable from any particular ocean floor hydrate deposit. The very rough topography of many of many seafloor gas hydrate deposits (Roberts and Carney, 1997) is more consistent with a very heterogeneous gas flow associated with hydrates and scenario 1.

The key data needed to distinguish these two hypotheses are methane flux measurements, or the amount of methane per unit time flowing through and equilibrating with a particular gas hydrate deposit: How much, how fast, and where is methane venting from bottom seeps into the water column? How much methane is venting through the water column and in sediment pore waters? How much of this methane is coming from an underlying gas hydrate deposit versus an underlying gas reservoir versus *in situ* sediment (biogenic) sources? How fast is the methane moving and what is its rate of venting? How fast is the methane being biodegraded both in sediments and in the water column? Where is the gas venting occurring and how widespread is it? Is methane venting very localized or pervasive over a wide area? Are chunks of hydrate being carried to the surface waters by bubble streams emanating from hydrate deposits even in deep water? The heterogeneity of these systems makes them very difficult to study.

The developing OOI initiative and new methods of continuous measurement of chemical and biological properties of both the water column and sediments surrounding both kinds of hydrates offer new opportunities to find and characterize both kinds of seafloor hydrates so amounts of gas potentially available can be evaluated using a much better knowledge base than is currently available. The OOI also provides opportunities to monitor the biota surrounding and dependent on the gas hydrate.

In addition, if the hydrate is in equilibrium or in steady state with seeping gas, then methane venting from surface seeps could be used to explore for underlying gas hydrate deposits. This method would constitute the ocean analog of one of the earliest successful land-based oil exploration methods: surface "sniffing" where surface gas and oil "shows" were used to find underlying gas and oil reservoirs. Present day "sniffing" depends on coupling surface geochemical anomalies, such as elevated gas or oil concentrations in surface sediments, with subsurface geophysical data showing the subsurface plumbing connecting the surface seep to underground gas sources and reservoirs. In the case of oceanic gas hydrates, this approach is often made difficult because seep features are covered by water. However, manifestations of this gas venting are often not subtle and may involve mud volcanoes and slope instabilities as well as large gas hydrate deposits (e.g. Roberts and Carney, 1997; Hovland, 2000; Driscoll, 2000). Styles of gas venting often vary both temporally and spatially, within a relatively small area. The OOI and ORION initiatives will offer new opportunities understand and better utilize the relationships between seafloor hydrates and seeping gas in gas resource exploration and production as well as in better understanding the relationships between gas and gas hydrates on slope stability and on global climate change.

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(NOTE Reeburgh also did recent review for new Wiley "Chemical Oceanography" volumes)