Naval Research Laboratory

Washington, DC 20375-5320

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4th International Workshop on Methane Hydrate Research and Development

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14. ABSTRACT

The Fourth Workshop of the International Committee on Gas Hydrates Research and Development was held during 9-11 May 2005 in Victoria, British Columbia, Canada. Invited national agency representatives and international researchers from university, government, and industry convened to assess research priorities and to promote international collaboration on methane hydrate research. The 2.5-day workshop included plenary lectures and panel discussions, conducted as a working event where all participants engaged in open discussions to develop collaborative methane hydrate studies. The workshop was organized by the Centre for Earth and Ocean Research at the University of Victoria, Victoria, British Columbia, Canada; the Marine Biogeochemistry Section at the Naval Research Laboratory, Washington, DC, USA, the Hawaii Natural Energy Institute of the University of Hawaii, Honolulu, Hawaii, USA, and in cooperation with the Institute for Energy Utilization, AIST, Hokkaido, Japan; the Department of Physics and Technology at the University of Bergen, Bergen, Norway; the Office of Naval Research - Global; the Geological Survey of Canada, and the United States Department of Energy. This series of annual international methane hydrate research and development workshops was initiated during March 2001 at the University of Hawaii. Subsequent workshops have been held in Washington, DC, USA, and Vina del Mar, Chile. At the previous three meetings, the focus was on presentation of research results on selected hydrate themes, and description of national hydrate research programs. The workshops have resulted in international field and laboratory collaborations between U.S., Canadian, Japanese, Chilean, and German scientists working on methane hydrate exploration off the coasts of the U.S., Canada, Chile, and Japan.

At the Victoria workshop, the objective was more ambitious. A primary goal was to begin discussions on developing plans for continuing the collaborative scientific work among the nations. It is our conviction as organizers of the workshop that the national research programs could greatly benefit by combining resources to carry out experiments, and sharing the results of the research. The workshop was organized around four themes that included: 1) Methane Hydrate Resource Characterization and Distribution, 2) Methane Hydrates Kinetics, Dissociation and Biogeochemistry, 3) Environmental Concerns: Seabed Stability and Ecosystem Health, 4) Methane Hydrate Future Development.

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Overview

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Acknowledgements

The workshop committee would like to acknowledge sponsorship provided by the Office of Naval Research Global, the Geological Survey of Canada and the Department of Energy, National Energy Technology Laboratory.

4TH INTERNATIONAL WORKSHOP ON METHANE HYDRATE RESEARCH AND DEVELOPMENT

Victoria, BC, Canada, May 9-11, 2005

Scientific Committee:

Dr. Ross Chapman, Center for Earth and Ocean Research (CEOR) at the University of Victoria, Victoria, British Columbia, Canada, chapman@uvic.ca

Dr. Richard Coffin, Marine Biogeochemistry Section, US Naval Research Laboratory, Washington DC, USA, rcoffin@ccs.nrl.navy.mil

Dr. Bjørn Kvamme, Department of Physics, University Of Bergen, Norway, bjorn.kvamme@fi.uib.no

Dr. Stephen Masutani, Hawaii Natural Energy Institute, Univ. of Hawaii, Honolulu Hawaii, USA, stephenm@hawaii.edu

Workshop Organizing Committee:

Ms. Sonia Wolff, ONR Global, Santiago, Chile, Sonia_Wolff@onr.navy.mil

Mr. Nicholas Langhorne, ONR Global, London, England, nlanghorne@onrifo.navy.mil

I. INTRODUCTION:

The 4th **International Workshop on Methane Hydrate Research and Development** was held in Victoria, BC, Canada from May 9-11, 2005. The Workshop organizers were Dr. Ross Chapman, Center for Earth and Ocean Research (CEOR) at the University of Victoria, Victoria, British Columbia, Canada, Dr. Richard Coffin, Marine Biogeochemistry Section, US Naval Research Laboratory, Washington DC and Sonia Wolff, Assistant Director, Office of Naval Research Global LA.

The Workshop was sponsored by the Center for Earth and Ocean Research at the University of Victoria, British Columbia, Canada; the Marine Biogeochemistry Section at the Naval Research Laboratory, Washington, DC, USA; the Hawaii Natural Energy Institute of the University of Hawaii, Honolulu, Hawaii, USA; and in cooperation with the Energy Technology Research Institute, AIST, Japan; the Department of Physics and Technology at the University of Bergen, Bergen, Norway; the Office of Naval Research-Global; the Geological Survey of Canada and the United States Department of Energy. Building on the success of the three previous international workshops on methane hydrates, this workshop was seen as an excellent opportunity to promote open discussion to identify the most important questions in hydrate research that can be addressed by collaborative international experiments.

The workshop included plenary lectures and open discussions in breakout sessions that were conducted as a working event where all participants had the opportunity to contribute. The objectives at this meeting were to promote open discussion to identify knowledge gaps in hydrate research, and set research priorities that could be addressed by collaborative international experiments. It was our conviction as workshop organizers that the national research programs could greatly benefit by combining resources to carry out experiments, and by sharing the results of the research.

The breakout sessions were organized in four theme topics. The discussions in each group were facilitated by a session leader, who was assisted by a rapporteur to record the discussions that took place. The theme topics included:

1. ***Methane Hydrate Resource Characterization and Distribution***: This session focused on current hydrate exploration in marine and arctic environments. In addition to surveys of the hydrate characterization and distribution, session topics included geophysical, geochemical and biological parameters that are relevant to the field survey.

    - Session Chair: Dr. Warren T. Wood, Geophysicist, Marine Geosciences Division, U. S. Naval Research Laboratory

2. ***Methane Hydrates Kinetics, Dissociation and Biogeochemistry***: This session was intended to combine laboratory, field and theoretical investigations of physical, chemical and biological influence on hydrate stability, molecular content and lattice saturation.

    - Session Chair: John Ripmeester, Group Leader, Steacie Institute of Molecular Sciences, National Research Council of Canada

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Manuscript approved August 24, 2006.

3. ***Environmental Concerns: Seabed Stability and Ecosystem Health***: Research topics in this session included the influence of coastal hydrates on industrial platform stability, ocean carbon cycling, global warming and coastal inhabitant safety. Research focus between the nations was be integrated to address this broad range in topics.

    - Session Chair: Frederick Colwell, Microbiologist in the Biotechnology Department at the Idaho National Laboratory, operated by Battelle Energy Alliance

4. ***Methane Hydrate Future Development:*** Discussions during the three previous International Workshop on Methane Hydrate R & D have revealed different national focuses in hydrate research. Efficient integration of research between nations requires incorporation of the national goals within the collaborative research plan. This session combined discussion on the participants' research objectives and the intermediate steps to accomplish the goal.

    - Session Chair: Art Johnson, President, Hydrate Energy International

The discussions in each theme group focused on the priorities of the research that should be done to address knowledge gaps, selection of appropriate sites for field studies, description of technologies and techniques for geophysical, geochemical and biological data acquisition, and identification of collaborative research partners. A central goal across all the groups was to establish connections between experimental work in the field and laboratory research. Although there were no formal sessions for orally contributed papers, participants were given the opportunity to display posters at the workshop, and to present briefings on specialized research that was relevant to the discussions in the breakout groups. Summaries of the discussions are presented below in Section 4. A final plenary session focused on integration of the ideas from the four sessions, and summarized the recommendations.

II. WORKSHOP SCHEDULE:

HYDRATES IV WORKSHOP PROGRAM
LAUREL POINT INN

Sunday, 8 May			
TIME			
4:00PM-8:00PM Marble Lobby	Registration		
7:00PM Salons ABC	Happy Hour		
Monday, 9 May			
TIME	**SESSION**	**SPEAKERS**	
7:00AM-8:00AM Terrace Room	Breakfast		
8:00AM-10:00AM Salons ABCD	**Main Plenary** Session Chair: Ross Chapman University of Victoria	**Charles Paull**: Does Gas Escape from Gas Hydrate Deposits? **Scott Dallimore**: Characterization and distribution of gas hydrates at the Mallik field, Mackenzie Delta, Canada **Stefan Buenz:** Gas hydrates and free gas in submarine slope failures: The Storegga Slide case study **Richard Coffin**: Biogeochemical Evaluation of Hydrate Rich Sediments	
10:00AM-10:30AM Terrace Room	Coffee Break		
10:30AM-12:30AM Salons ABCD	**Main Plenary** Session Chair: Richard Coffin Naval Research Laboratory	**Dendy Sloan**: Hydrate Kinetics **Frederick Colwell:** Rates of Biological Methane Production in Marine Sediments **Kirk Osadetz:** Societal and structural trends affecting has hydrate research in Canada **Art Johnson:** Gas Hydrate: The Paths Forward	
12:30PM-1:30PM Terrace Room	Lunch		
1:30PM-3:30PM Salon A: Theme 1	Methane Hydrate Resource Characterization and Distribution	**Chair: Warren Wood** Marine Geosciences Division, U. S. Naval Research Laboratory	**All sessions**: Open discussion on knowledge gaps and barriers in hydrate research
1:30PM-3:30PM Salon B: Theme 2	Methane Hydrates Kinetics, Dissociation and Biogeochemistry	**Chair: John Ripmeester** Steacie Institute for Molecular Sciences, National Research Council of Canada	
1:30PM-3:30PM Salon C: Theme 3	Environmental Concerns: Seabed Stability and Ecosystem Health	**Chair: Frederick Colwell** Biotechnology Department Idaho National Laboratory, (Battelle Energy Alliance)	
1:30PM-3:30PM Salon D: Theme 4	Methane Hydrate Future Development	**Chair: Art Johnson** Hydrate Energy International	
3:30PM-3:45PM Terrace Room	Coffee Break		

TIME	SESSION	SPEAKERS	
3:45PM-5:45PM Salon A: Theme 1	Methane Hydrate Resource Characterization and Distribution	**Chair: Warren Wood**	**All Sessions**: Priorities for new experimental research
3:45PM-5:45PM Salon B: Theme 2	Methane Hydrates Kinetics, Dissociation and Biogeochemistry	**Chair: John Ripmeester**	
3:45PM-5:45PM Salon C: Theme 3	Environmental Concerns: Seabed Stability and Ecosystem Health	**Chair: Frederick Colwell**	
3:45PM-5:45PM Salon D: Theme 4	Methane Hydrate Future Development	**Chair: Art Johnson**	

Tuesday, 10 May

TIME	SESSION	SESSION CHAIR	SPEAKERS
7:00AM-8:00AM Terrace Room	Breakfast		
8:00AM-10:00AM Salon A: Theme 1	Methane Hydrate Resource Characterization and Distribution	**Chair: Warren Wood**	**All Sessions**: Formulate plans for collaborative experiments. Focus on experimental sites, use of existing infrastructure and programs.
8:00AM-10:00AM Salon B: Theme 2	Methane Hydrates Kinetics, Dissociation and Biogeochemistry	**Chair: John Ripmeester**	
8:00AM-10:00AM Salon C: Theme 3	Environmental Concerns: Seabed Stability and Ecosystem Health	**Chair: Frederick Colwell**	
8:00AM-10:00AM Salon D: Theme 4	Methane Hydrate Future Development	**Chair: Art Johnson**	
10:00AM-10:30AM Terrace Room	Coffee Break		
10:30AM-12:30PM Salon A: Theme 1	Methane Hydrate Resource Characterization and Distribution	**Chair: Warren Wood**	**All Sessions**: Formulate plans for collaborative experiments. Focus on experimental sites, use of existing infrastructure and programs.
10:30AM-12:30PM Salon B: Theme 2	Methane Hydrates Kinetics, Dissociation and Biogeochemistry	**Chair: John Ripmeester**	
10:30AM-12:30PM Salon C: Theme 3	Environmental Concerns: Seabed Stability and Ecosystem Health	**Chair: Frederick Colwell**	
10:30AM-12:30PM Salon D: Theme 4	Methane Hydrate Future Development	**Chair: Art Johnson**	
12:30PM-1:30PM Terrace Room	Lunch		

Tuesday, 10 May			
TIME	**SESSION**	**SESSION CHAIR**	**SPEAKERS**
3:30PM-3:45PM Terrace Room	Coffee Break		
3:45PM-5:45PM Salon AB	Results and Discussions: - Methane Hydrate Resource Characterization and Distribution - Methane Hydrate Future Development	**Chairs:** **Warren Wood** **Art Johnson**	Integration of research across hydrate research themes. Develop links between experimental research in the field and in laboratories
3:45PM-5:45PM Salon CD	Results and Discussions: - Methane Hydrates Kinetics, Dissociation and Biogeochemistry - Environmental Concerns: Seabed Stability and Ecosystem Health	**Chairs:** **John Ripmeester** **Frederick Colwell**	
7:30PM Terrace Room	Dinner		
Wed., 11 May			
TIME	**SESSION**	**SESSION CHAIR**	**SPEAKERS**
8:00AM-9:00AM Terrace Room	Breakfast		
9:00AM-12:00AM Salon ABCD	**Summary and Closing Remarks**		Ross Chapman Richard Coffin

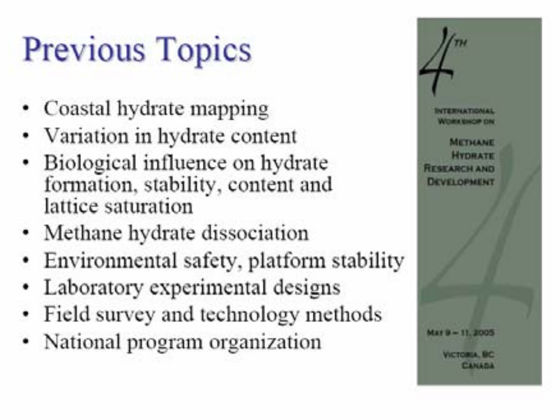
III. WORKSHOP PRESENTATIONS:

A. Opening Remarks:

1. ***Introduction.*** Ross Chapman, CEOR-UV and Richard Coffin, NRL.

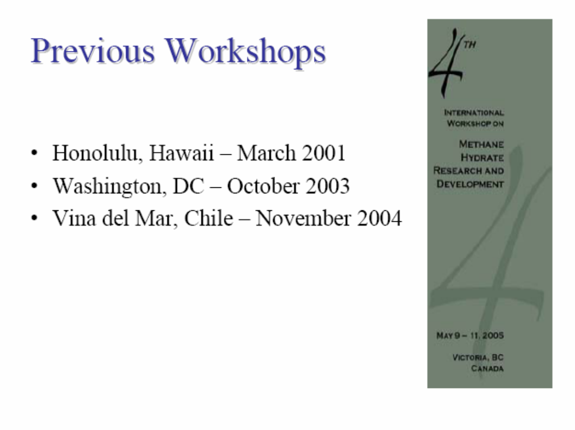
4th International Workshop on Methane Hydrate Research & Development

Chairs:
Ross Chapman, SEOC, University of Victoria, Victoria, BC
Richard Coffin, Marine Biogeochemistry Section, NRL-DC
Stephen Masutani, Hawaii Natural Energy Institute, University of Hawaii, HI
Bjørn Kvamme, Department of Physics, University of Bergen, Norway



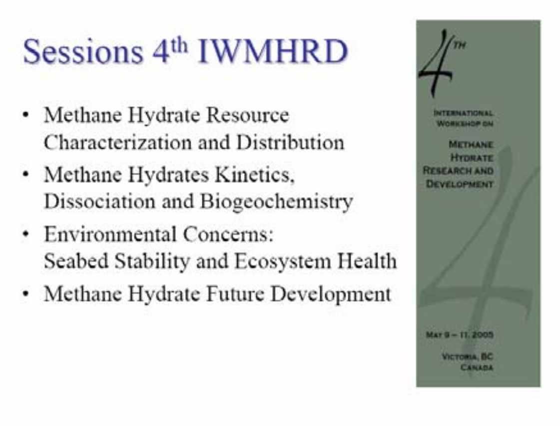
Previous Topics

- Coastal hydrate mapping
- Variation in hydrate content
- Biological influence on hydrate formation, stability, content and lattice saturation
- Methane hydrate dissociation
- Environmental safety, platform stability
- Laboratory experimental designs
- Field survey and technology methods
- National program organization



Previous Workshops

- Honolulu, Hawaii – March 2001
- Washington, DC – October 2003
- Vina del Mar, Chile – November 2004



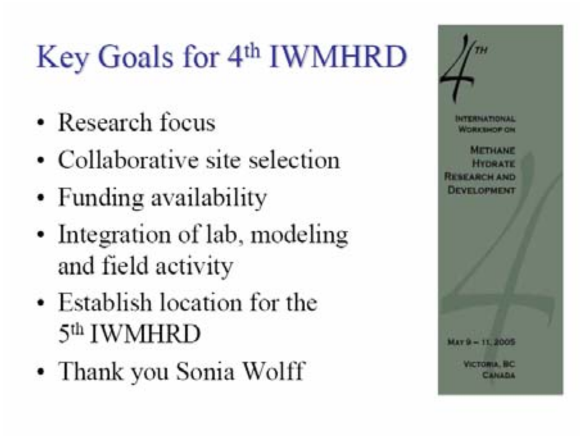
Sessions 4th IWMHRD

- Methane Hydrate Resource Characterization and Distribution
- Methane Hydrates Kinetics, Dissociation and Biogeochemistry
- Environmental Concerns: Seabed Stability and Ecosystem Health
- Methane Hydrate Future Development

International Collaboration

Change in Approach for 4th IMHRD

- Limit presentations to topic overviews
- Share science with poster presentations
- Plan international collaboration
- Integrate advanced technology on research approaches
- Share technology to support a broad basic and applied research goals
- Complete workshop with collaborative project plan(s) and commitment(s)

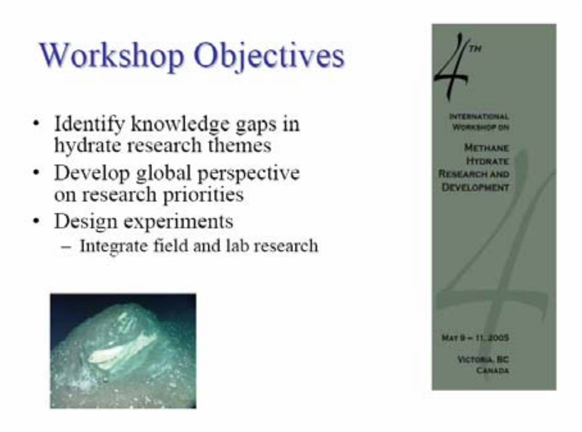


Key Goals for 4th IWMHRD

- Research focus
- Collaborative site selection
- Funding availability
- Integration of lab, modeling and field activity
- Establish location for the 5th IWMHRD
- Thank you Sonia Wolff

Workshop goals

- Plans for effective field and laboratory research
- International participation
  - Sharing technology and infrastructure
  - Exchange of data, knowledge

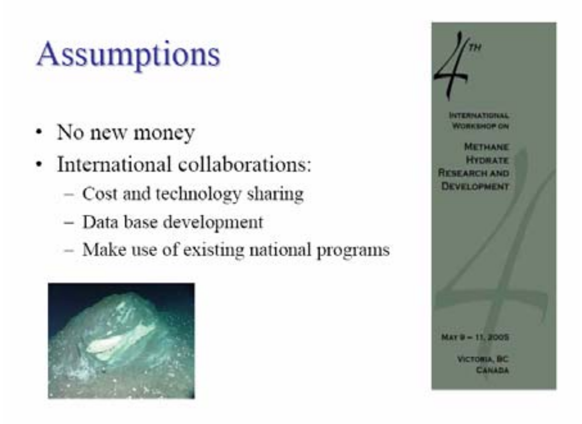


Workshop Objectives

- Identify knowledge gaps in hydrate research themes
- Develop global perspective on research priorities
- Design experiments
  - Integrate field and lab research

Opportunities for effective collaboration

- Data 'mining'
  - Sharing existing data from lab and field
- Create inventories
  - International expertise
  - Methods and technology
  - Data and results
  - Models

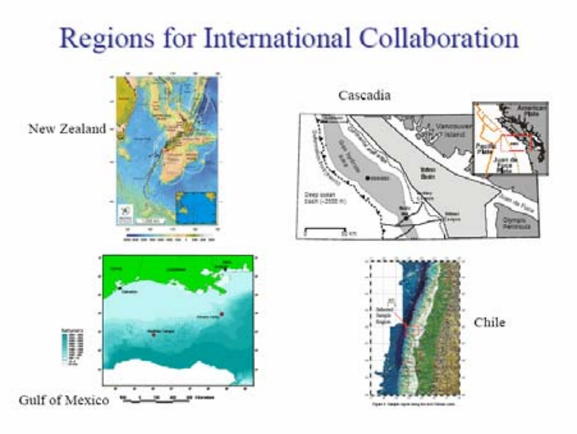


Assumptions

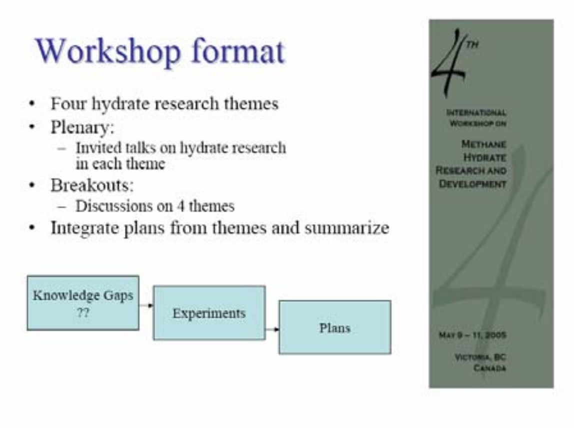
- No new money
- International collaborations:
  - Cost and technology sharing
  - Data base development
  - Make use of existing national programs

New experiments

- 'Remote' participants
  - IODP Cascadia 311: Sept-Oct 2005
    - Michael Riedel: Co-Chief Scientist
  - ROPOS: submersible dives
- International sites
  - New Zealand, Chile, Gulf of Mexico Western Europe



Regions for International Collaboration



Workshop format

- Four hydrate research themes
- Plenary:
  - Invited talks on hydrate research in each theme
- Breakouts:
  - Discussions on 4 themes
- Integrate plans from themes and summarize

Knowledge Gaps ?? → Experiments → Plans

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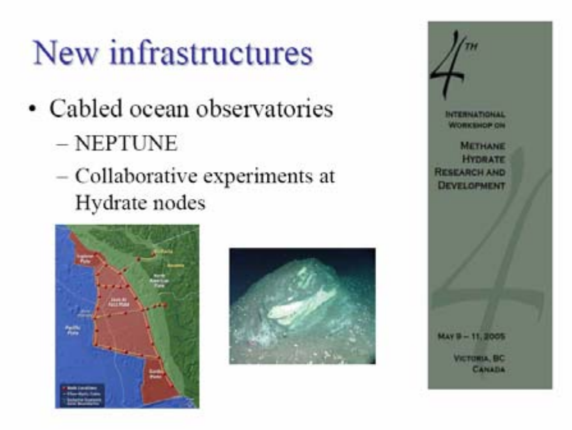
MAY 9 – 11, 2005
VICTORIA, BC CANADA



New infrastructures

- Cabled ocean observatories
  - NEPTUNE
  - Collaborative experiments at Hydrate nodes

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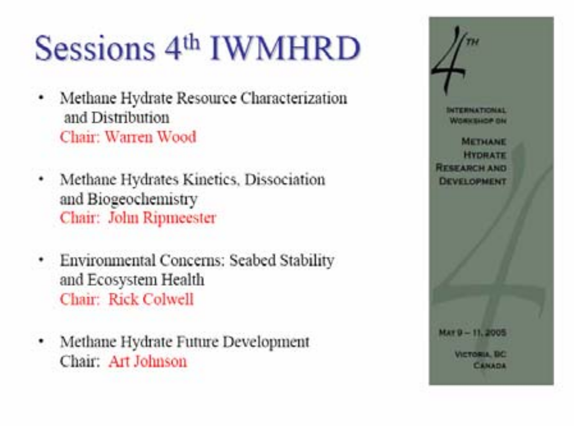

Sessions 4th IWMHRD

- Methane Hydrate Resource Characterization and Distribution
  Chair: Warren Wood
- Methane Hydrates Kinetics, Dissociation and Biogeochemistry
  Chair: John Ripmeester
- Environmental Concerns: Seabed Stability and Ecosystem Health
  Chair: Rick Colwell
- Methane Hydrate Future Development
  Chair: Art Johnson

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B. Invited Presentations:

1. ***Does gas escape from gas hydrate deposits?*** Charles Paull, MBARI.

A copy of the presentation was not available for this report. The following text is a review of the presentation.

The focus of this presentation was gas flux from hydrates and related seafloor slumping and thermal decomposition. Regions for focus in the presentation were Storrega Margin and the Candian Arctic Shelf. This topic was addressed with geochemical data from cores to assess gas leakage due to diffusion. Methane concentrations in core porewater is not a good indicator of the profiles, alternately sulfate gradients can be used as an indirect parameter for the vertical methane profiles. This approach is applied with the assumption that the surface sediment vertical methane profile occurs through anaerobic methane oxidation with sulfate serving as the terminal electron acceptor. The depth of the sulfate and methane gradient is proportional to the vertical methane diffusion.

Interpretation of slumping with analysis of porewater gradients in regions such as the Storegga Slide is observed with non conservative vertical sulfate profiles. Similar shifts in the hydrate stability zone were observed in the analysis of piston core porewater analysis, with non conservative profiles in samples from the Beaufort Sea on the Canadian Arctic Shelf.

These data suggest that there are gas losses, however, fieldwork has not confirmed this estimate that has been interpreted from porewater sulfate profiles. In current studies, gas venting is associated “pingos” that form with ice formation and melting. In marine systems it is expected that these structures form because of fluid pressure from decomposing gas hydrates.

Methods: Cores and seismic profiles, vibracores on PLFs, and some ROV work.

2. ***Characterization and distribution of gas hydrates at the Mallik field, Mackenzie Delta, Canada.*** Scott Dallimore, Canadian Geological Survey.

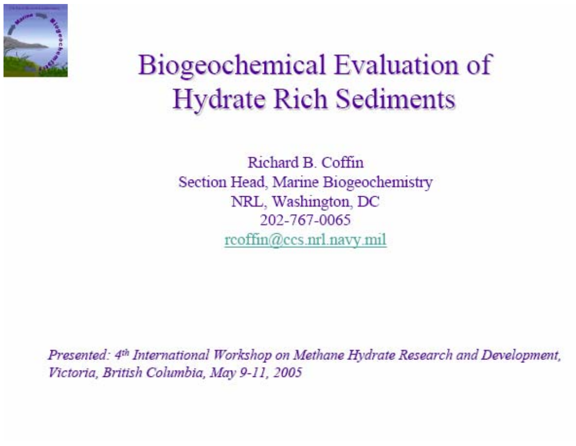
A copy of the presentation was not available for this report. The following text is a review of the presentation.

This presentation provided an overview of methane hydrate exploration on the Mallik Wells, in the Mackenzie Delta, Canada. Information included an overview of lessons learned, discussion on the comparison of terrestrial and marine hydrate bearing regions, and an overview of topics pertaining to hydrate contribution to the natural gas reserve and global warming.

Part of the presentation included the difference in hydrate exploration in coastal waters and Arctic tundra. In the evaluation of hydrates in these diverse environments standard protocol include stability curves, sediment and soil gas compositions to determine if a suitable reservoir exists. In these systems, the hydrate burial depths and gas sources (thermogenic vs. biogenic) are different. The difficulty in survey marine systems results in few quantified estimates of hydrate distribution. On the other hand, Arctic gas hydrates have been found in 50% of the wells that have been drilled.

The major conclusion from this presentation was that experimental exploration of methane hydrate deposits on the Mackenzie Delta was successful. Future studies need to incorporate economic evaluation with an integration of topics such as the methane hydrate quantity, distribution, prospecting strategies, production technology, quantification of environmental, economic and policies issues for determination of the energy resource potential.

3. ***Biogeochemical Evaluation of Hydrate Rich Sediments.*** Richard Coffin, Naval Research Laboratory.



Biogeochemical Evaluation of Hydrate Rich Sediments

Richard B. Coffin
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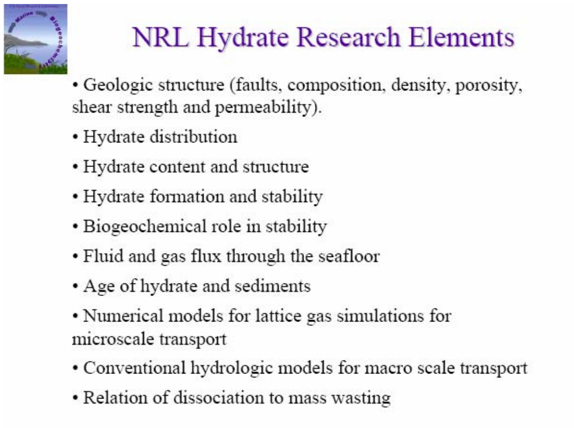
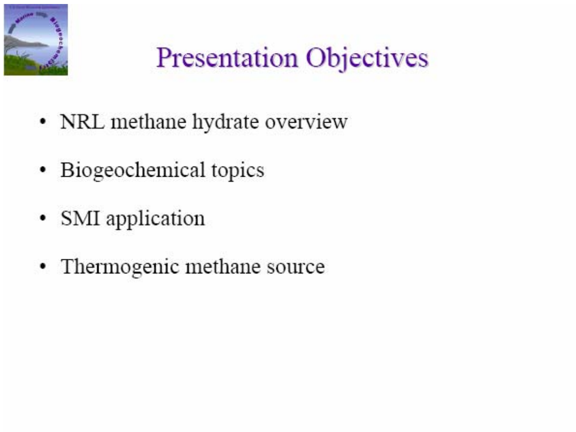
Presented: 4th International Workshop on Methane Hydrate Research and Development, Victoria, British Columbia, May 9-11, 2005



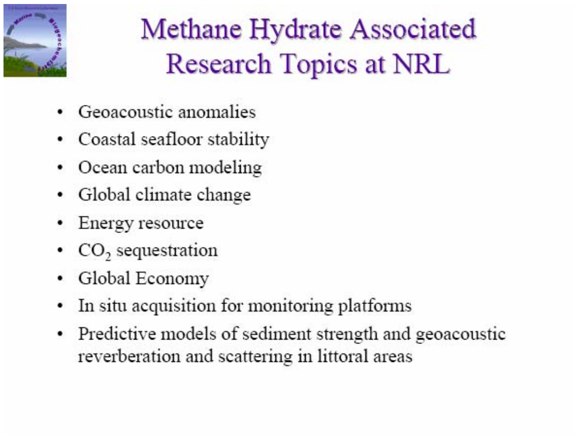
NRL Hydrate Research Elements

- Geologic structure (faults, composition, density, porosity, shear strength and permeability).
- Hydrate distribution
- Hydrate content and structure
- Hydrate formation and stability
- Biogeochemical role in stability
- Fluid and gas flux through the seafloor
- Age of hydrate and sediments
- Numerical models for lattice gas simulations for microscale transport
- Conventional hydrologic models for macro scale transport
- Relation of dissociation to mass wasting



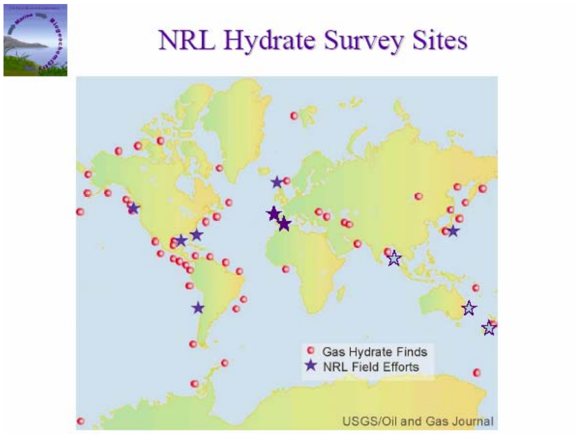
Presentation Objectives

- NRL methane hydrate overview
- Biogeochemical topics
- SMI application
- Thermogenic methane source



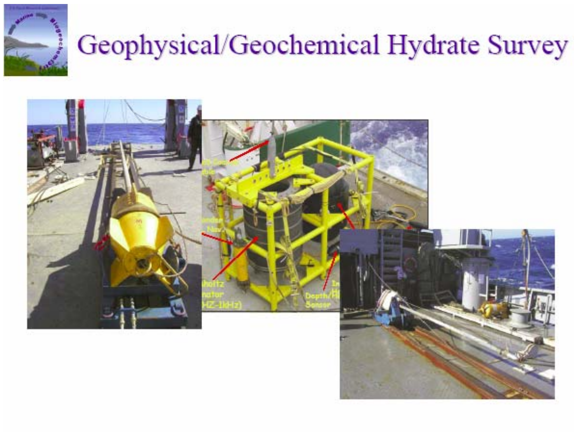
Methane Hydrate Associated Research Topics at NRL

- Geoacoustic anomalies
- Coastal seafloor stability
- Ocean carbon modeling
- Global climate change
- Energy resource
- CO_2 sequestration
- Global Economy
- In situ acquisition for monitoring platforms
- Predictive models of sediment strength and geoacoustic reverberation and scattering in littoral areas



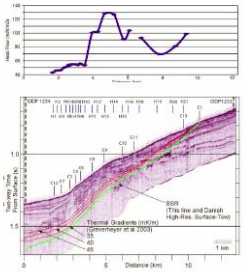
NRL Hydrate Survey Sites

USGS/Oil and Gas Journal



Geophysical/Geochemical Hydrate Survey

Evaluation Mid Chile Coast



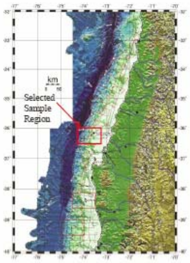
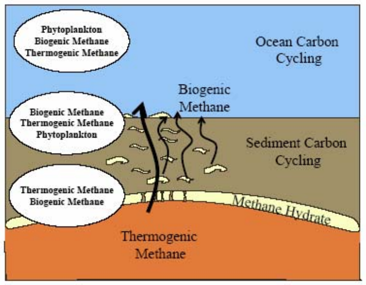


Figure 1: Sample region along the mid Chilean coast.

Source and Fate of Methane



Geochemical Parameters

- Gases (Methane, Ethane, Propane)
- Sulfate
- Chloride
- Hydrogen Sulfide
- DIC concentration
- *Percent Organic Carbon*
- *Stable Carbon Isotope Analysis (CH_4, DIC, POC)*
- *$\Delta^{14}C$ Sediment Organic Carbon*

Carbon Isotope Analysis

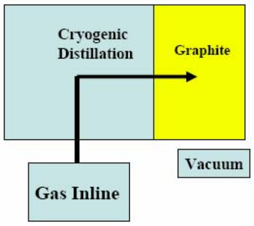
$\delta^{13}C$

$\Delta^{14}C$

$$X^nC = (C_{sample\text{-}h/l}/C_{standard\text{-}h/l}) - 1 \times 1000$$

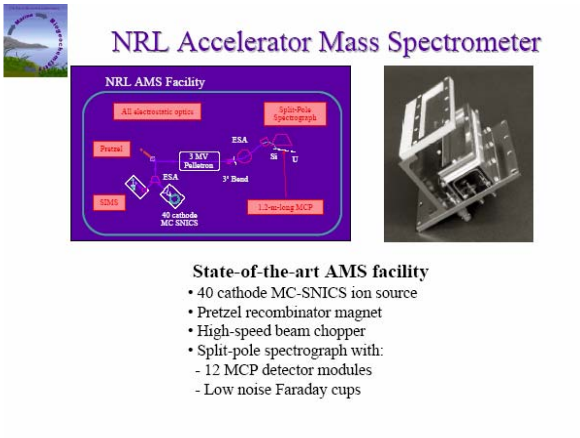
On Board Lab

NRL Graphite Laboratory



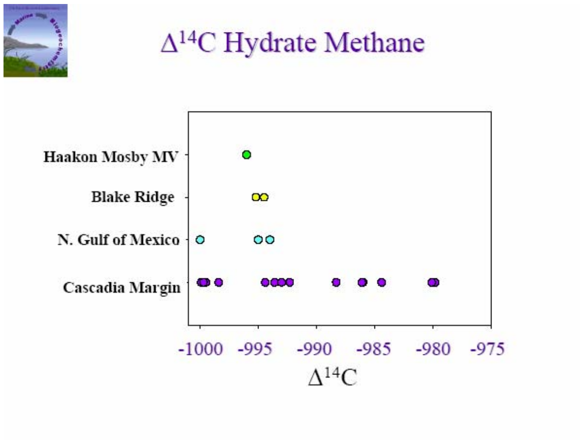
Instrumentation
- GC cryogenic trap
- 10 port graphite line
- 6 port cryogenic distillation line
- methane oxidation system
- UV oxidation system
- solid organic combustion system
- GC/IRMS/ITMS

$\Delta^{14}C$ and $\delta^{13}C$ Parameters
- Dissolved organic and inorganic carbon
- Particulate organic and inorganic carbon
- Biomarkers
- Methane
- Ethane to Hexane

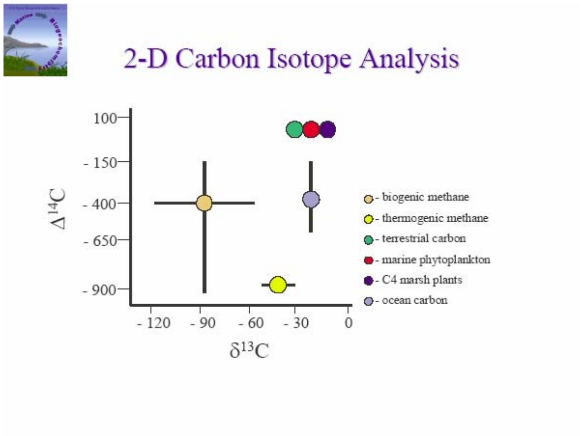


NRL Accelerator Mass Spectrometer

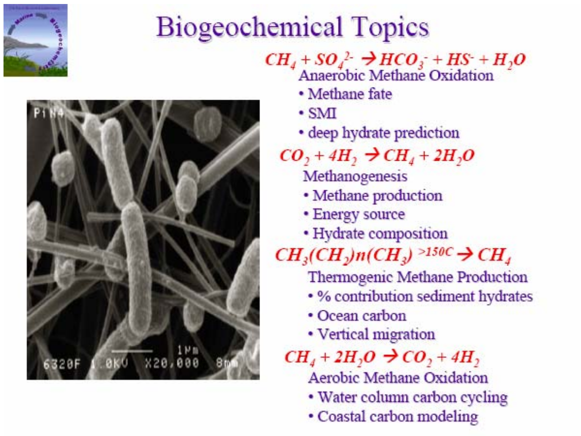
State-of-the-art AMS facility
- 40 cathode MC-SNICS ion source
- Pretzel recombinator magnet
- High-speed beam chopper
- Split-pole spectrograph with:
  - 12 MCP detector modules
  - Low noise Faraday cups



$\Delta^{14}C$ Hydrate Methane



2-D Carbon Isotope Analysis



Biogeochemical Topics

$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$

Anaerobic Methane Oxidation
- Methane fate
- SMI
- deep hydrate prediction

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

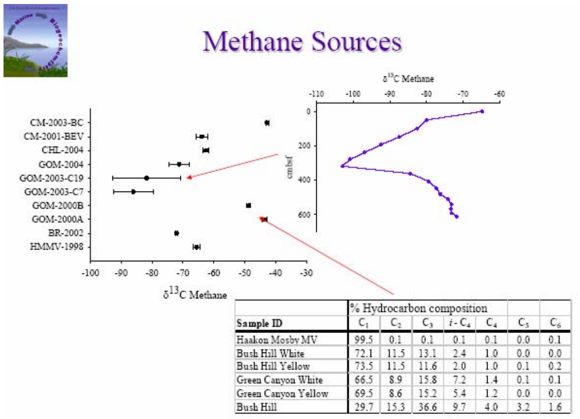
Methanogenesis
- Methane production
- Energy source
- Hydrate composition

$CH_3(CH_2)n(CH_3)^{>150C} \rightarrow CH_4$

Thermogenic Methane Production
- % contribution sediment hydrates
- Ocean carbon
- Vertical migration

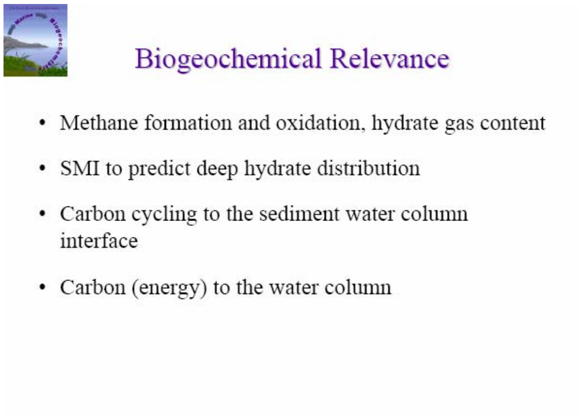
$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

Aerobic Methane Oxidation
- Water column carbon cycling
- Coastal carbon modeling



Methane Sources

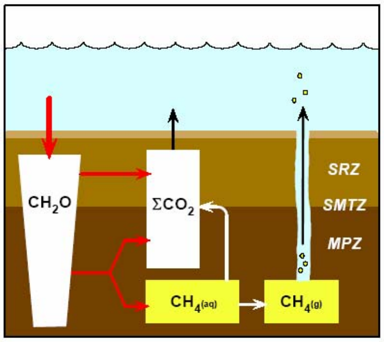
	% Hydrocarbon composition						
Sample ID	C_1	C_2	C_3	$i-C_4$	C_4	C_5	C_6
Haakon Mosby MV	99.5	0.1	0.1	0.1	0.1	0.0	0.1
Bush Hill White	72.1	11.5	13.1	2.4	1.0	0.0	0.0
Bush Hill Yellow	73.5	11.5	11.6	2.0	1.0	0.1	0.2
Green Canyon White	66.5	8.9	15.8	7.2	1.4	0.1	0.1
Green Canyon Yellow	69.5	8.6	15.2	5.4	1.2	0.0	0.0
Bush Hill	29.7	15.3	36.6	9.7	4.0	3.2	1.6



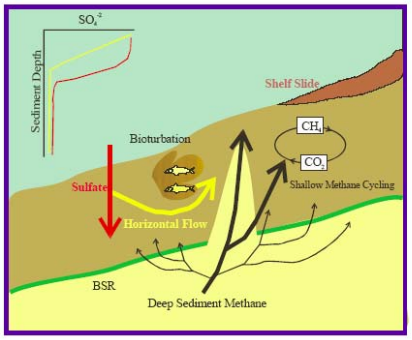
Biogeochemical Relevance

- Methane formation and oxidation, hydrate gas content
- SMI to predict deep hydrate distribution
- Carbon cycling to the sediment water column interface
- Carbon (energy) to the water column

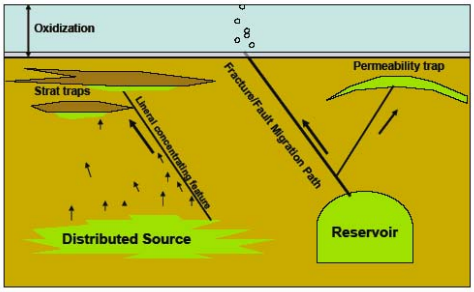
Microbial Methane Cycling



Concave Up Methane Profile

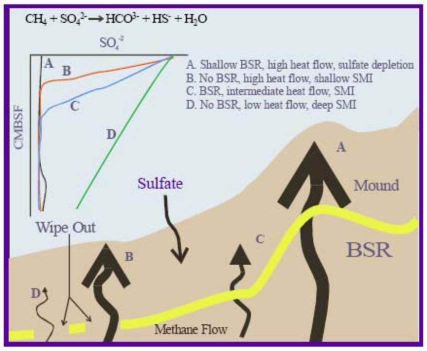


Thermogenic Methane

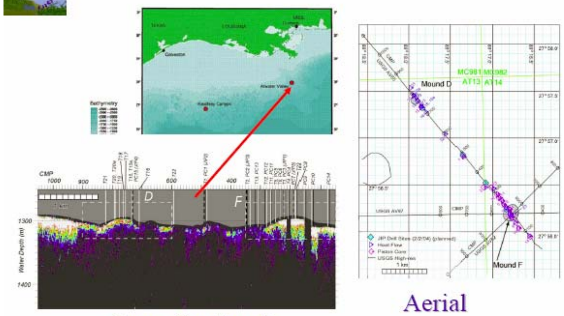


Anaerobic Methane Oxidation

Vertical Methane Flow

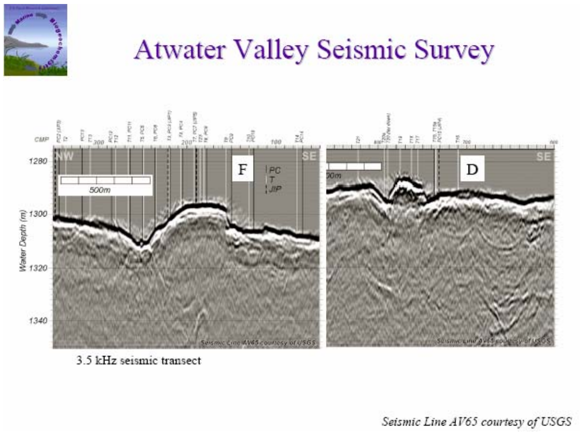


Atwater Valley Sites



Aerial

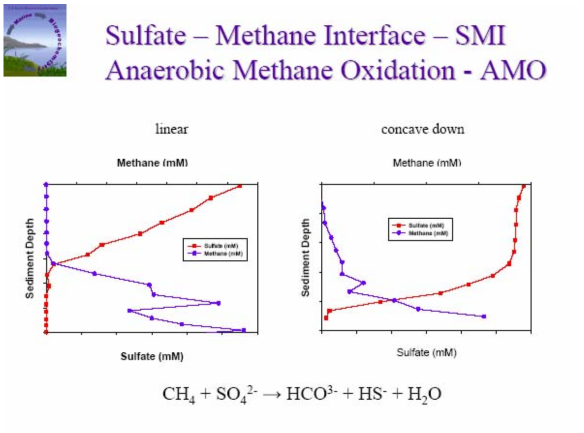
Cross Sectional



Atwater Valley Seismic Survey

3.5 kHz seismic transect

Seismic Line AV65 courtesy of USGS

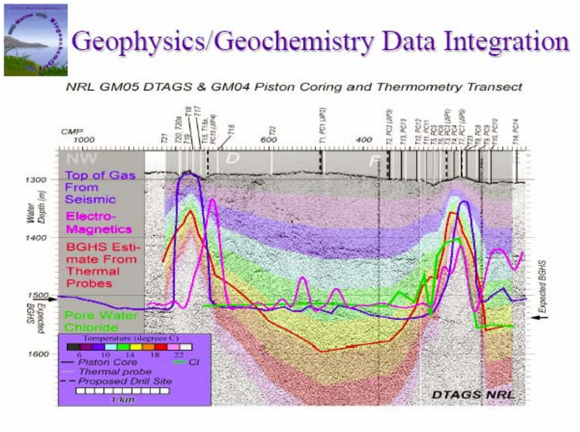


Sulfate – Methane Interface – SMI
Anaerobic Methane Oxidation - AMO

linear

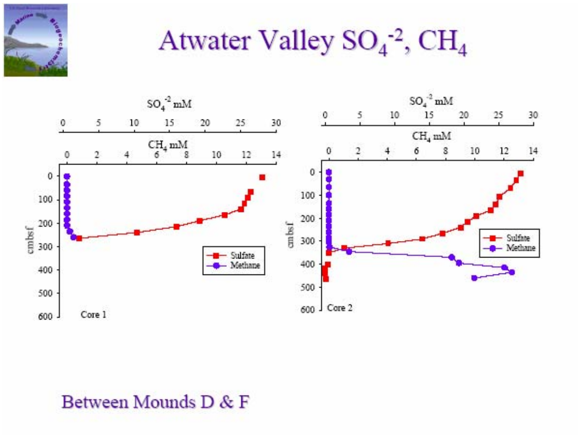
concave down

$CH_4 + SO_4^{2-} \rightarrow HCO^{3-} + HS^- + H_2O$



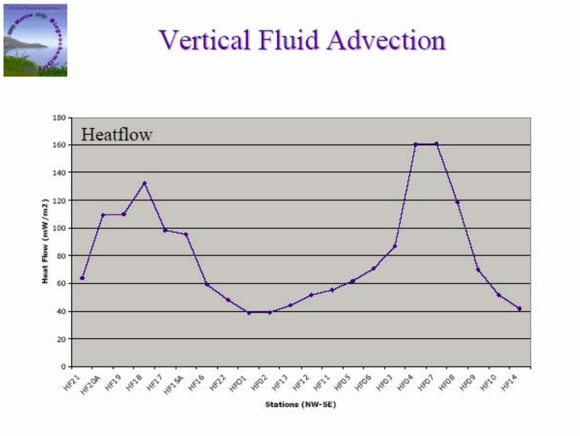
Geophysics/Geochemistry Data Integration

NRL GM05 DTAGS & GM04 Piston Coring and Thermometry Transect

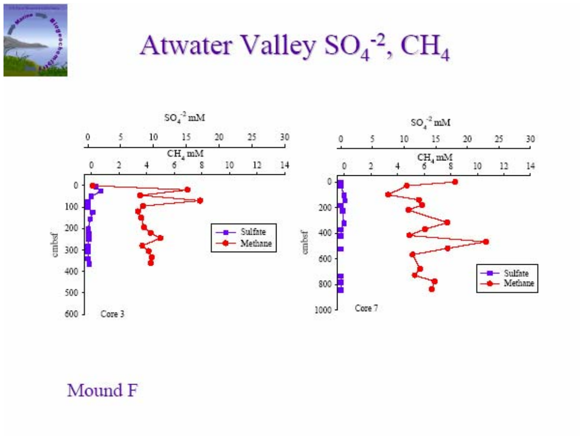


Atwater Valley SO_4^{-2}, CH_4

Between Mounds D & F

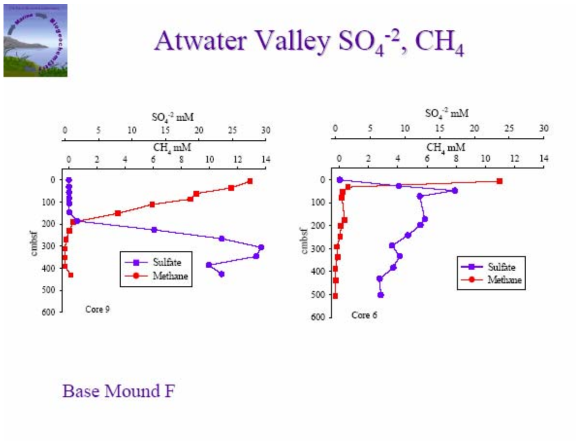


Vertical Fluid Advection



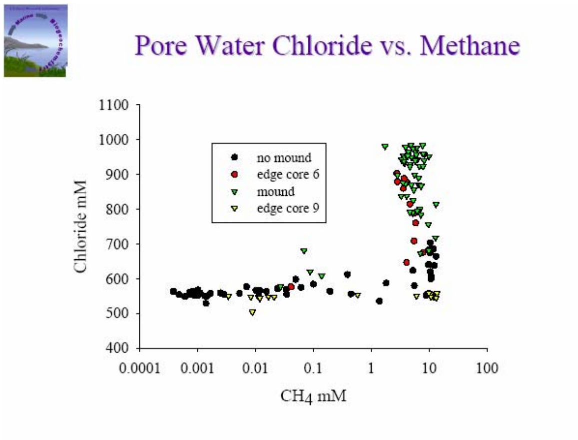
Atwater Valley SO_4^{-2}, CH_4

Mound F

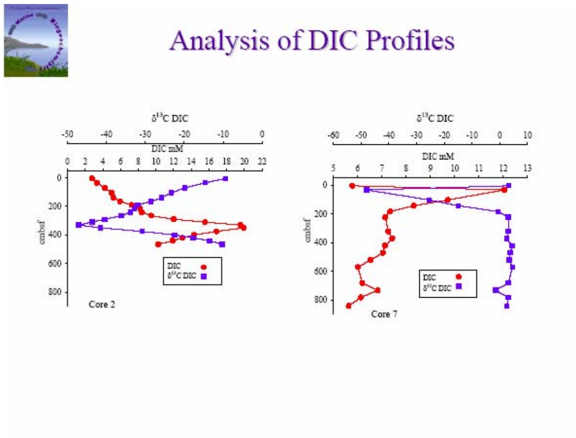


Atwater Valley SO_4^{-2}, CH_4

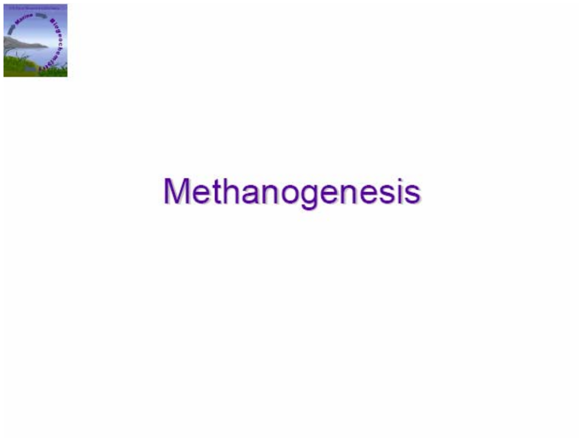
Base Mound F



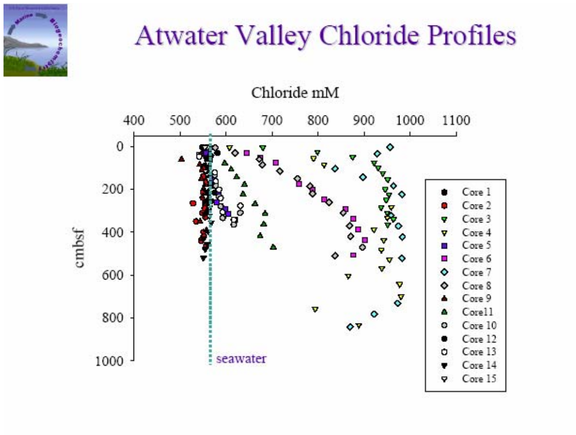
Pore Water Chloride vs. Methane



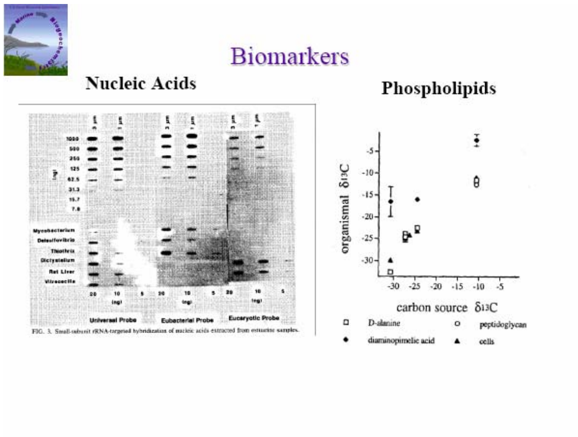
Analysis of DIC Profiles



Methanogenesis



Atwater Valley Chloride Profiles

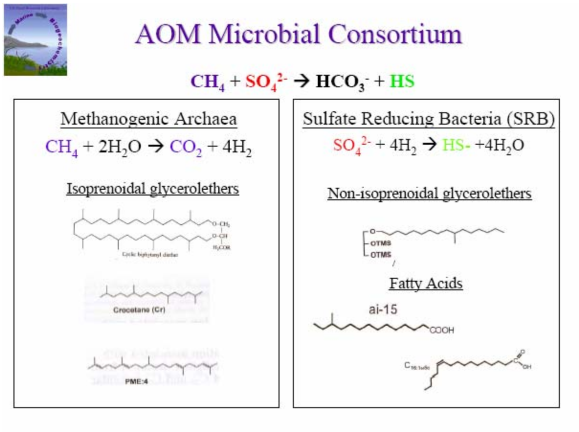


Biomarkers

Nucleic Acids

Phospholipids

FIG. 3. Small-subunit rRNA-targeted hybridization of nucleic acids extracted from estuarine samples.



AOM Microbial Consortium

$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS$

Methanogenic Archaea

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

Isoprenoidal glycerolethers

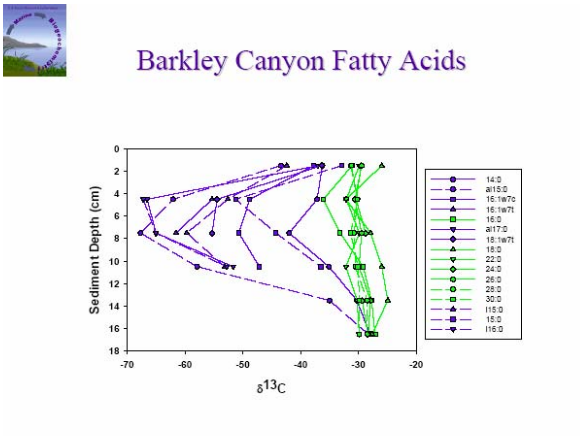
Sulfate Reducing Bacteria (SRB)

$SO_4^{2-} + 4H_2 \rightarrow HS\text{-} + 4H_2O$

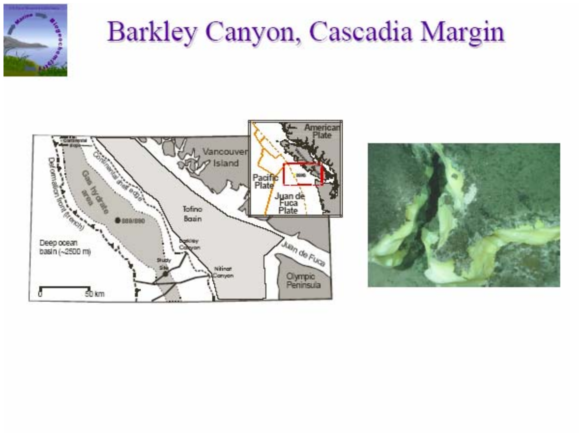
Non-isoprenoidal glycerolethers

Fatty Acids

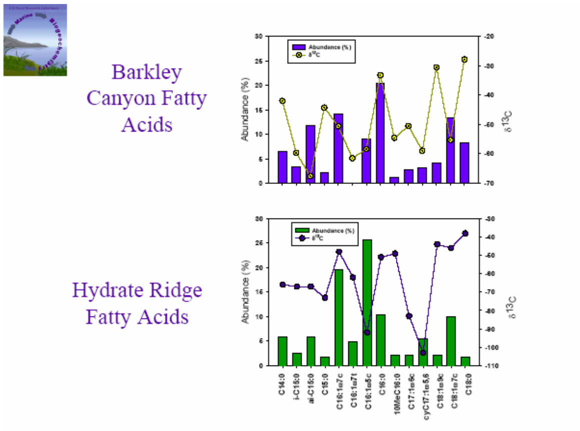
Thermogenic Methane Production



Barkley Canyon Fatty Acids

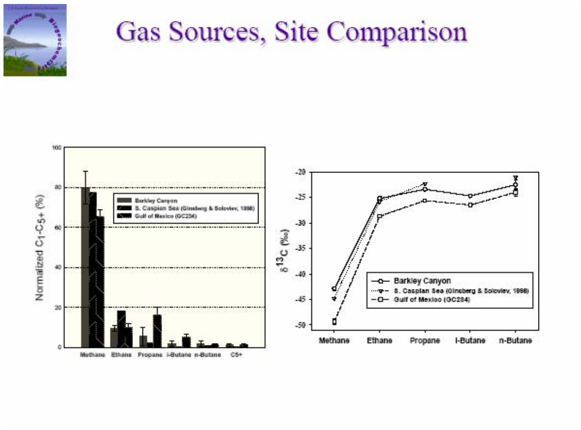


Barkley Canyon, Cascadia Margin



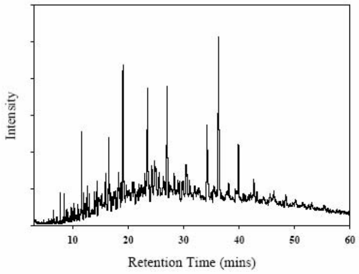
Barkley Canyon Fatty Acids

Hydrate Ridge Fatty Acids



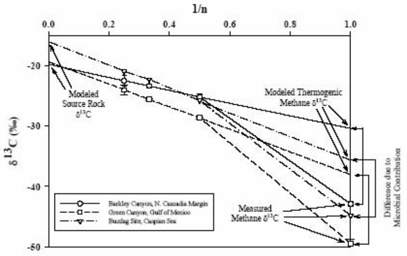
Gas Sources, Site Comparison

Gas Speciation

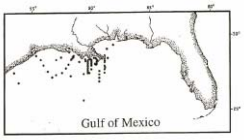


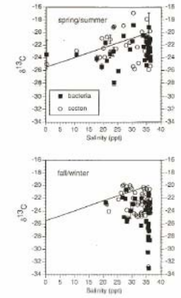
Aerobic Methane Oxidation

Microbial Influence



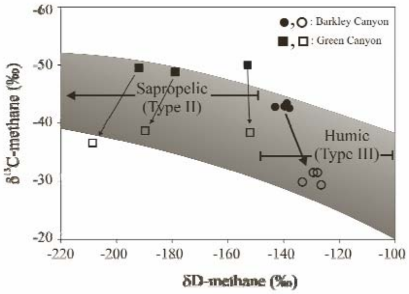
Methane Contribution to Bacterioplankton



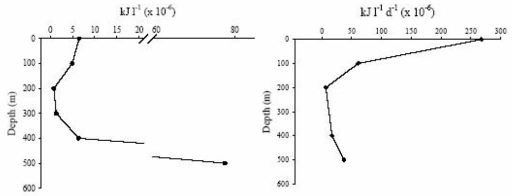


Kelley et al., 1998 Limnol. Oceanogr.

δ13C & δD Methane

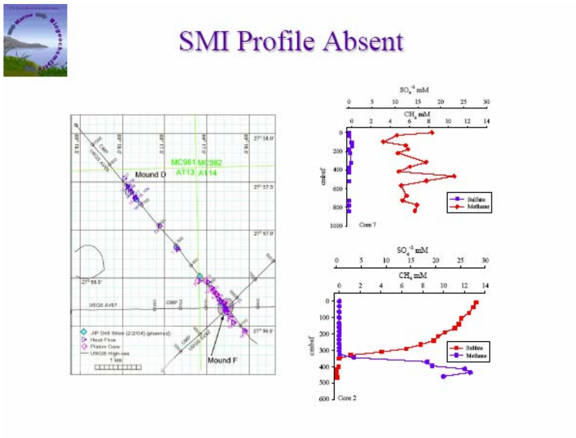


Energy Comparison of Carbon Cycling

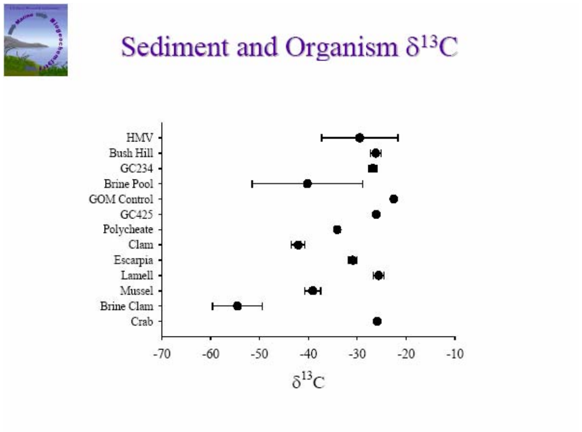


Depth m	CH_4 nM	PE_{CH4} kJ (x 10^{-6})	BPROD nM C d^{-1}	RE kJ (x 10^{-6})	PE/RE
0	128.6	6.5	65.8 (103.3, 28.3)	268	0.024
100	87.6	5.0	15.0 (7.50, 22.5)	61.1	0.082
200	13.9	0.8	1.67 (1.67, 1.67)	6.8	0.074
300	23.1	1.4	n.d.	n.d.	n.d.
400	108.2	6.4	4.17 (5.83, 2.50)	17	0.37
500	1288.7	77.6	9.17 (10.8, 6.17)	37.3	2.08

PE potential energy
RE is required energy



SMI Profile Absent



Sediment and Organism $\delta^{13}C$

4. ***Societal and structural trends affecting gas hydrate research in Canada.*** Kirk Osadetz, Geological Survey of Canada.

Abstract

Canada depends critically on petroleum as its primary energy source, the driving force for investment growth and the source of its record (2004) trade surplus. Switching to natural gas is part of Canada's Kyoto strategy. It has immense gas hydrate resources and it has also provided and hosted leading gas hydrate research and researchers. One might conclude that Canada should remain a research leader, but the future is challenging because of a "market-driven" energy policy and a restructuring of public research funding. Market demand and price drive supply, and corporate demand drives energy research. Restructuring will make the universities and industry the primary science-providers, while transforming government institutions, historical contributors to gas hydrate research, into facilitators. A public interventionist S&T roadmap like that which realized the potential of Canadian bitumen is unlikely. Changes are being made slowly, making for a contemporary "business as usual" environment, but with change appearing inevitable. Industry recognizes the new environment without embracing gas hydrates as an economically competitive potential supply. Lack of transportation, uncertainties in well performance and the minimization of geotechnical risks have pushed gas hydrates deep into the corporate agenda. Long-term success requires that gas hydrate research is championed by industrial demand and that reservations regarding economic competitiveness are successful addressed.

Societal and Structural Trends Affecting Gas Hydrate Research In Canada

Kirk G. Osadetz
Natural Resources Canada
Geological Survey of Canada (Calgary)
kosadetz@nrcan.gc.ca

Pathways

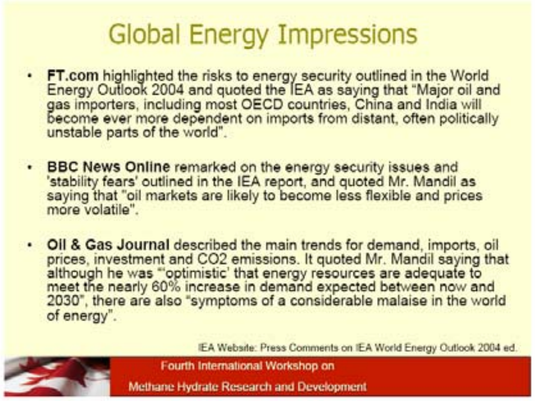
- The **Technology Push Model** or "Innovation Pyramid" (basic science -> design and engineering -> manufacturing -> marketing -> sales).
    - The current general model of Canadian R&D.
    - Climate change GH R&D is the type model.
- The **Market Pull Model** (market need -> development -> manufacturing -> sales).
    - For Commodity Demand, are supplies short or is it access?
    - For Industrial Demand, are there unforeseen events?
    - Flow assurance GH R&D is the type model.
- The **Curiosity Driven Model** (the method of the Dead European Guys).
    - The "Dogbert" model of "Success by Pilfering Office Supplies" .

"The public saw technology and thought it was Science"

Edmund Burke

Acknowledgements

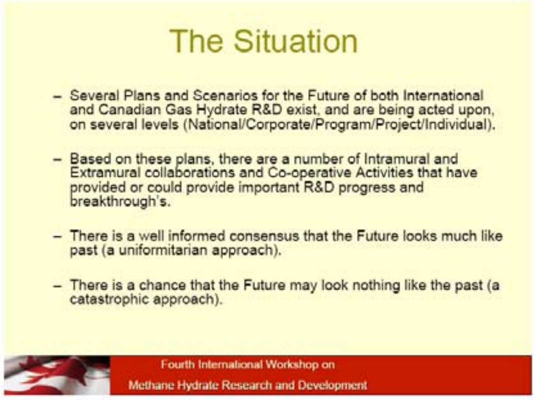
- Jack Smyth, Privy Council Office, The Chief Scientific Advisor's Office.
- Yvan Hardy, Chief Scientist, Natural Resources Canada.
- Don Simpson, The Innovation Expedition.
- George Eynon, Canadian Energy Research Institute.
- Thomas S. Ahlbrandt , United States Geological Survey, Denver, Vice Chairman, Ad Hoc Group of Experts on Supply of Fossil Fuels,United Nations Framework Classification for Energy and Mineral Resources.
- Jillian Nimblett and Clinton Tippett, Shell (Houston and Calgary).
- Ken Potma and Tadahiro Okazawa, Imperial Oil Ltd. (Calgary)
- Scott Dallimore, Fred Wright, David Mosher and Roy Hyndman, Earth Sciences Sector.
- Steve Hancock, APA Petroleum Engineering Ltd. (Calgary)



Global Energy Impressions

- **FT.com** highlighted the risks to energy security outlined in the World Energy Outlook 2004 and quoted the IEA as saying that "Major oil and gas importers, including most OECD countries, China and India will become ever more dependent on imports from distant, often politically unstable parts of the world".
- **BBC News Online** remarked on the energy security issues and 'stability fears' outlined in the IEA report, and quoted Mr. Mandil as saying that "oil markets are likely to become less flexible and prices more volatile".
- **Oil & Gas Journal** described the main trends for demand, imports, oil prices, investment and CO2 emissions. It quoted Mr. Mandil saying that although he was "'optimistic' that energy resources are adequate to meet the nearly 60% increase in demand expected between now and 2030", there are also "symptoms of a considerable malaise in the world of energy".

IEA Website: Press Comments on IEA World Energy Outlook 2004 ed.



The Situation

- Several Plans and Scenarios for the Future of both International and Canadian Gas Hydrate R&D exist, and are being acted upon, on several levels (National/Corporate/Program/Project/Individual).
- Based on these plans, there are a number of Intramural and Extramural collaborations and Co-operative Activities that have provided or could provide important R&D progress and breakthrough's.
- There is a well informed consensus that the Future looks much like past (a uniformitarian approach).
- There is a chance that the Future may look nothing like the past (a catastrophic approach).

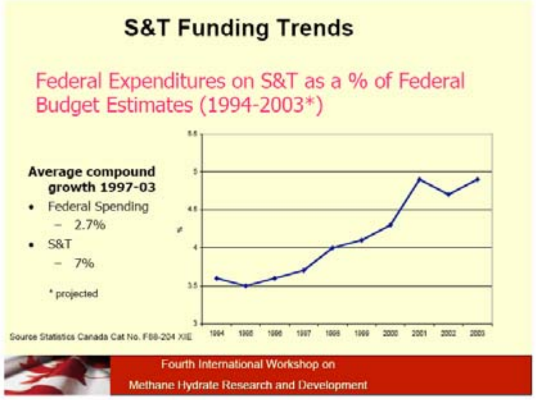
APEC Energy Security Strategy

- APEC Energy Ministers (in Manila) agreed that access to adequate, reliable and affordable energy is fundamental to achieving the region's economic, social and environmental objectives....
- The importance of these efforts is further highlighted by the recent rise in global oil prices and its potential impact on economic growth and sustainable development within the APEC region.
- To meet this challenge:
    - **They support the creation of a competitive and transparent marketplace for gas trade...**
    - **Recognizing that some Member Economies consider nuclear power as an option for their energy mix ...**
    - **They support research on the potential of methane hydrates as a future energy source and direct the EWG to communicate research developments within their economies.**
- Support for Gas Hydrates Fuel Research was explicity endorsed by the APEC Economic leaders 21 November 2004 as part of the Energy Security Initiative – energy security, sustainable development and common prosperity (CAIRNS)
- http://www.apec.org/apec/leaders__declarations/2004.downloadlinks.0007.LinkURL.Download.ver5.1.9

A Recent Canadian Energy Snapshot

- Canada produced 45% more energy than it consumed in 2002.
- Canada has been a net producer for 37 years and it is a significant exporter of energy, primarily to the United States.
- In 2001 alone, Canada exported energy products worth $55.1 billion, which represented 14% of all exports. Exports = two-thirds of Canada's annual oil and over one-half of natural gas production.
- On a per capita basis, each Canadian consumed ~353 gigajoules of energy in 2002, compared with ~222 in 1967. (30-litres of gasoline contain ~gigajoule).
- *Human Activity and the Environment 2004 edition*

Fourth International Workshop on
Methane Hydrate Research and Development



S&T Funding Trends

Federal Expenditures on S&T as a % of Federal Budget Estimates (1994-2003*)

Average compound growth 1997-03
- Federal Spending
  - 2.7%
- S&T
  - 7%

* projected

Source Statistics Canada Cat No. F88-204 XIE

Fourth International Workshop on
Methane Hydrate Research and Development

Uniquely Canadian Considerations

- A Net Energy Exporter.
- A "Free" Integrated North American Energy Market.
- Natural Gas Hydrate Resources are co-located with Stranded Conventional Petroleum Resources.
  - Gas Hydrates Compete in a Resource-rich Environment.
- A Kyoto Signatory.
  - Fuel and Climate R&D are commonly administered separately.
- A Changing Social Structure for Science.
  - The Migration of Science Performance out of Government.

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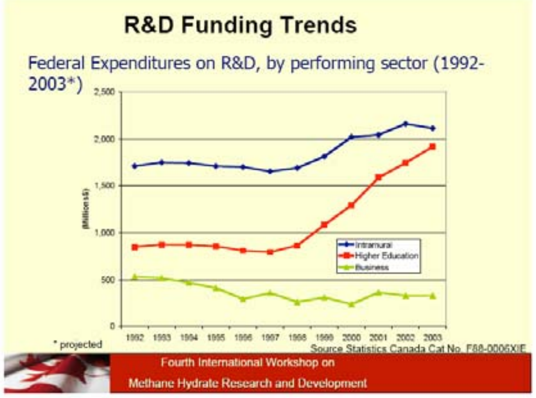

R&D Funding Trends

Federal Expenditures on R&D, by performing sector (1992-2003*)

* projected

Source Statistics Canada Cat No. F88-0006XIE

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Canada's National System of Innovation

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Priorities in Knowledge Performance

- Address key challenges for the university research environment.
  - A Government Focus on Educational Institutions as the providers of basic science.
- Renew S&T capacity to respond to emerging public policy, stewardship and economic challenges and opportunities.
  - Transformation of Government R&D from Science Performance to Science Facilitation in Academia and Industry.
- Encourage innovation and the commercialization of knowledge in the private sector.
  - Reverse the trend of declining Canadian Industrial R&D.

Modified from NRCan Chief Scientist's Presentation

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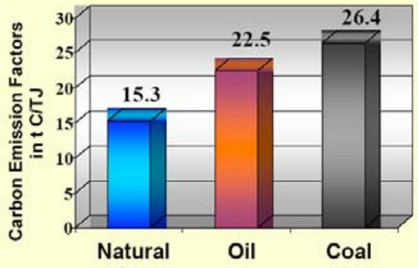
The Implications of Science Models for GH R&D

- The Technology Push Model or "Innovation Pyramid" (basic science -> design and engineering -> manufacturing -> marketing -> sales).
    - Several opportunities are present, in climate foresight; GHG sequestration and energy supply.
- The Market Pull Model (market need -> development -> manufacturing -> sales).
    - Commodities: not expected in a resource "rich" setting.
    - Industrial Demand: opportunities related to both energy extraction (geohazards) and environment (enhanced recovery).
    - There is a relationship between MP and TP, as indicated by Climate change.
- The Curiosity Driven Model .
    - A difficult proposition.

Natural Gas is A "Cleaner" Fossil-Fuel Energy Source



Market Pull – Climate Change

Canada will spend $10 billion over seven years to help Canada cut its average greenhouse gas emissions by 270 megatonnes a year in the five years 2008 to 2012.

It is committing to:

- Draw 20 per cent of its electricity from renewable sources by 2010.
- Replace its vehicles more quickly and with fuel-efficient alternatives including hybrids.
- Create three funds to:
- Buy greenhouse gas emission credits from other countries.
- **Invest in new technologies to help industrial large emitters meet GHG targets.**
- Develop renewable energy ($1.8 in the February 2005 budget).
- Implement conservation and efficiency measures.

74 per cent of the targets will be achieved through the actions of individual Canadians, even though individuals are responsible for only 23 per cent of Canada's emissions.

http://www.climatechange.gc.ca/english/ccplan.asp

Market Pull –Hazards

- As conventional petroleum exploration, particularly for crude oil, moves into more challenging terrestrial (Arctic) and marine (Deep Water) settings the hazards posed by gas hydrates to Exploration and Production increases.
- Potential Hazards Include:
    1. Open-hole instability caused by dissociation and associated free gas.
    2. Well head and casing integrity.
    3. Hydrate formation subsea equipment.
    4. Seafloor Instability.
    5. Flow Assurance.
- Most of 53 GH papers presented at the 2005 OTC addressed GH Hazards.

Market Pull – Climate Change

Market Pull is expected to:

- Increased demand for natural gas.
- Increased opportunities for GHG emission reduction and sequestration, especially from large point source emitters, such as natural gas and tar sands/heavy oil plants.

GH R&D opportunities can be expected with respect to:

- Carbon dioxide separation and sequestration.

Technology Push – Climate Change

- **The entire climate change issue is a technology push/foresight issue.**
    - **The role of gas hydrates in climate change, past, present and future remains an important general topic to address.**
- **There is an interaction between market pull and technology push.**
    - **Motivated by Public Policy and International Treaties several industries will considering GHG segregation and sequestration, possibly in hydrates as an opportunity for both science and technology R&D.**
    - **Activities that produce high purity Carbon Dioxide for enhanced oil recovery or coal bed methane recovery are expected to be economically favourable.**
    - **Long distance transportation of carbon dioxide is feasible (e.g. The Alamo Oregon to West Texas carbon dioxide pipeline).**
    - **Related GH R&D will have to meet economic tests, but these might be "facilitated" by regulation and policy.**

Technology Push - Energy Supply

- Destruction Demand.
  - Industrial demand reduced in response to high current prices (N.W. U.S.A. Aluminum Industry.
- Competition From Other Sources of Supply.
  - GH's compete with both co-located conventional resources and more favorably located non-conventional resources for incremental supply
- Gas Composition Disadvantages.
  - The "drying" effects of hydrate formation and lower reservoir pressures have a cost.
- Cost and Lack of Infrastructure.
  - Most GH's are located in difficult environments where the costs of production and infrastructure are high.
- North American Security of Supply.
  - Many analysts believe that natural gas prices will fall to $4.50/MMBtu, which, like high storage values, makes resource scarcity unlikely.

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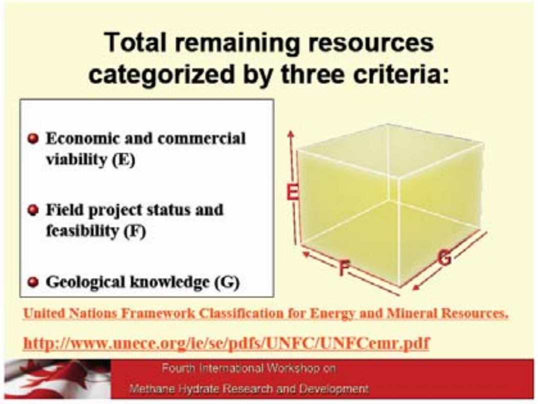

Total remaining resources categorized by three criteria:

- Economic and commercial viability (E)
- Field project status and feasibility (F)
- Geological knowledge (G)

United Nations Framework Classification for Energy and Mineral Resources.

http://www.unece.org/ie/se/pdfs/UNFC/UNFCemr.pdf

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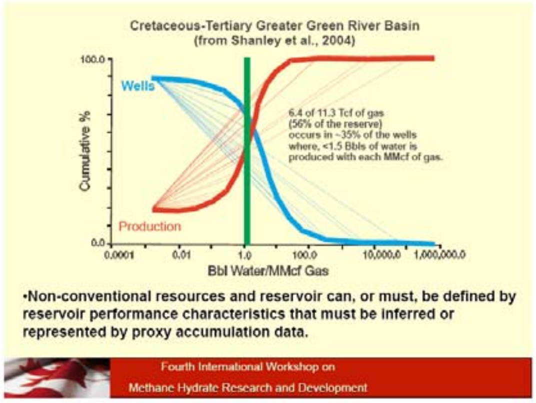

Cretaceous-Tertiary Greater Green River Basin
(from Shanley et al., 2004)

•Non-conventional resources and reservoir can, or must, be defined by reservoir performance characteristics that must be inferred or represented by proxy accumulation data.

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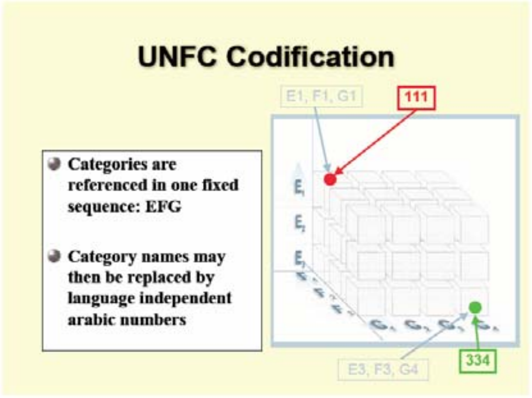
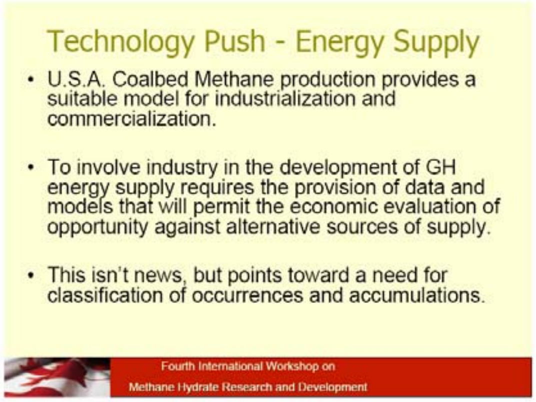


UNFC Codification

- Categories are referenced in one fixed sequence: EFG
- Category names may then be replaced by language independent arabic numbers



Technology Push - Energy Supply

- U.S.A. Coalbed Methane production provides a suitable model for industrialization and commercialization.
- To involve industry in the development of GH energy supply requires the provision of data and models that will permit the economic evaluation of opportunity against alternative sources of supply.
- This isn't news, but points toward a need for classification of occurrences and accumulations.

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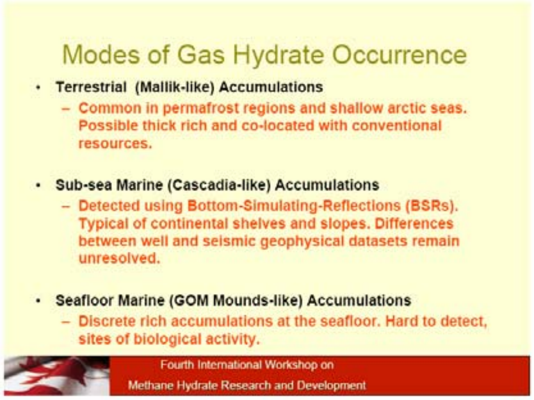

Modes of Gas Hydrate Occurrence

- Terrestrial (Mallik-like) Accumulations
  - Common in permafrost regions and shallow arctic seas. Possible thick rich and co-located with conventional resources.
- Sub-sea Marine (Cascadia-like) Accumulations
  - Detected using Bottom-Simulating-Reflections (BSRs). Typical of continental shelves and slopes. Differences between well and seismic geophysical datasets remain unresolved.
- Seafloor Marine (GOM Mounds-like) Accumulations
  - Discrete rich accumulations at the seafloor. Hard to detect, sites of biological activity.

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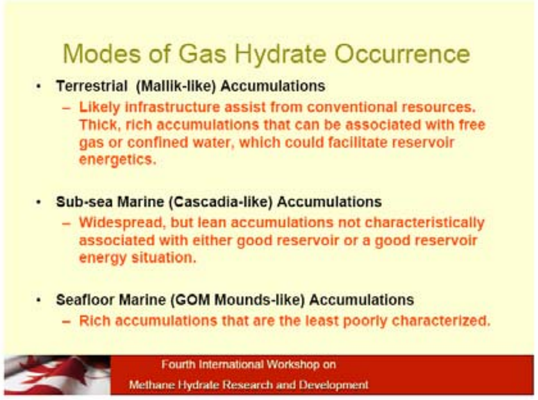

Modes of Gas Hydrate Occurrence

- **Terrestrial (Mallik-like) Accumulations**
  - Likely infrastructure assist from conventional resources. Thick, rich accumulations that can be associated with free gas or confined water, which could facilitate reservoir energetics.
- **Sub-sea Marine (Cascadia-like) Accumulations**
  - Widespread, but lean accumulations not characteristically associated with either good reservoir or a good reservoir energy situation.
- **Seafloor Marine (GOM Mounds-like) Accumulations**
  - Rich accumulations that are the least poorly characterized.

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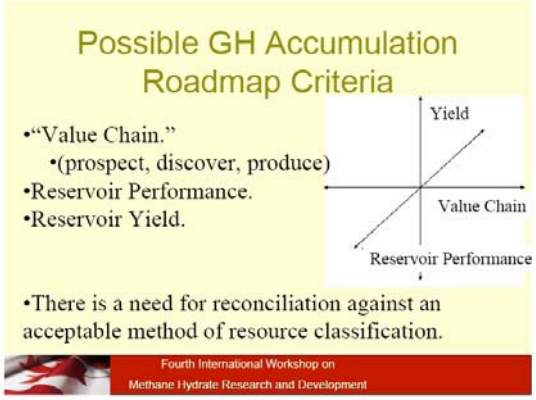

Possible GH Accumulation Roadmap Criteria

•"Value Chain."
  •(prospect, discover, produce)
•Reservoir Performance.
•Reservoir Yield.

•There is a need for reconciliation against an acceptable method of resource classification.

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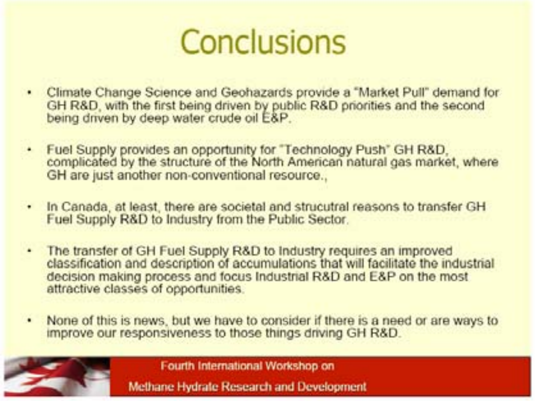

Conclusions

- Climate Change Science and Geohazards provide a "Market Pull" demand for GH R&D, with the first being driven by public R&D priorities and the second being driven by deep water crude oil E&P.
- Fuel Supply provides an opportunity for "Technology Push" GH R&D, complicated by the structure of the North American natural gas market, where GH are just another non-conventional resource.,
- In Canada, at least, there are societal and strucutral reasons to transfer GH Fuel Supply R&D to Industry from the Public Sector.
- The transfer of GH Fuel Supply R&D to Industry requires an improved classification and description of accumulations that will facilitate the industrial decision making process and focus Industrial R&D and E&P on the most attractive classes of opportunities.
- None of this is news, but we have to consider if there is a need or are ways to improve our responsiveness to those things driving GH R&D.

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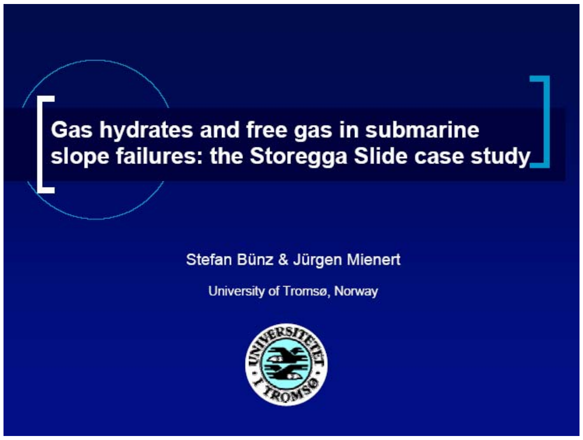
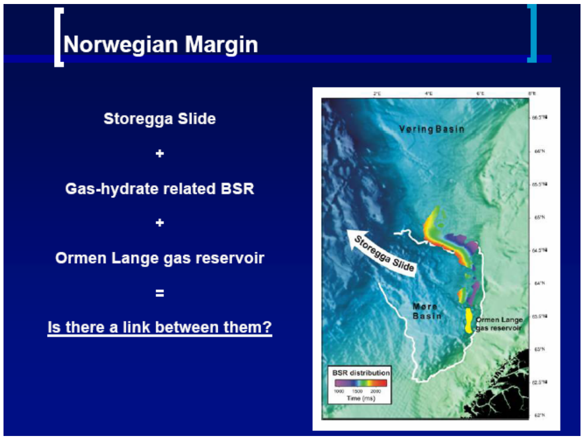
5. ***Gas hydrates and free gas in submarine slope failures: the Storegga Slide case study.*** Stefan Buenz, University of Tromsø***.***



Gas hydrates and free gas in submarine slope failures: the Storegga Slide case study

Stefan Bünz & Jürgen Mienert

University of Tromsø, Norway



Norwegian Margin

Storegga Slide

+

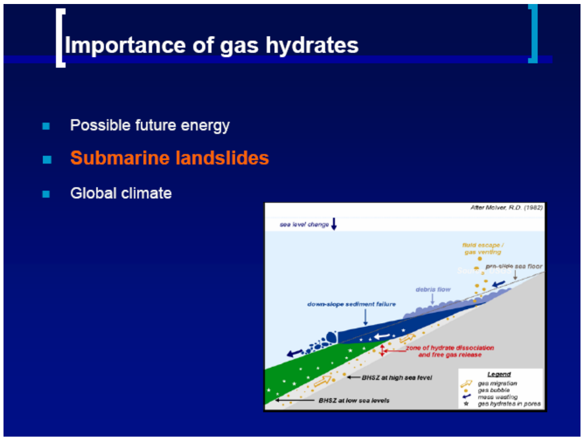
Gas-hydrate related BSR

+

Ormen Lange gas reservoir

=

Is there a link between them?



Importance of gas hydrates

- Possible future energy
- **Submarine landslides**
- Global climate

References

- Marine Geology, COSTA - Continental Slope Stability, Volume 213, Issues 1-4, Pages 1-504
- Marine and Petroleum Geology, Ormen Lange, An integrated study for the safe development of a deep-water gas field within the Storegga Slide Complex, NE Atlantic continental margin, Volume 22, No. 1-2, Feb. 2005

Gas hydrate and free gas as geohazard

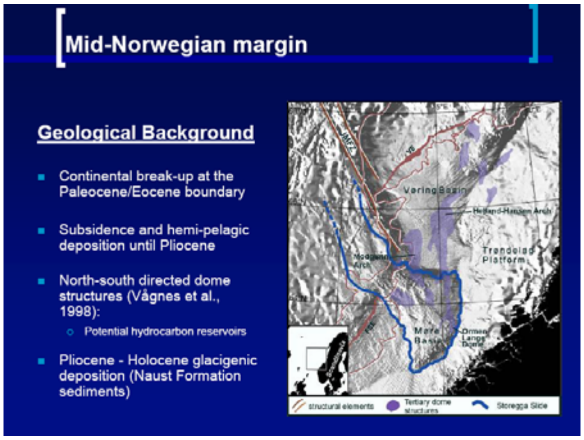
- Seafloor failure
- Drilling (overpressures, gas blow-out)
- Seafloor pipelines

Outline

- Geological background of the mid-Norwegian margin
- The Storegga Slide
- Possible involvement of gas hydrate on the development of the slide
- Impact of gas on slope failure
- Summary

Key to understanding submarine slope failure

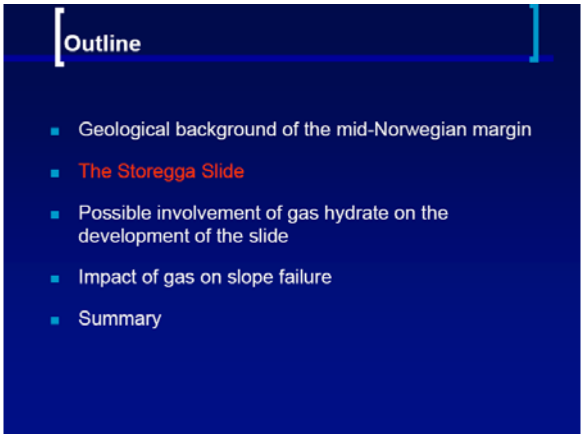
- Increase of pore pressure within sediments decreases effective soil strength.
- Possible processes:
  - high sedimentation rates during peak glaciations
  - gas hydrate dissociation
  - Gas charging of shallow sediments
  - Diapirism
  - Earthquakes



Mid-Norwegian margin

Geological Background

- Continental break-up at the Paleocene/Eocene boundary
- Subsidence and hemi-pelagic deposition until Pliocene
- North-south directed dome structures (Vågnes et al., 1998):
  - Potential hydrocarbon reservoirs
- Pliocene - Holocene glacigenic deposition (Naust Formation sediments)



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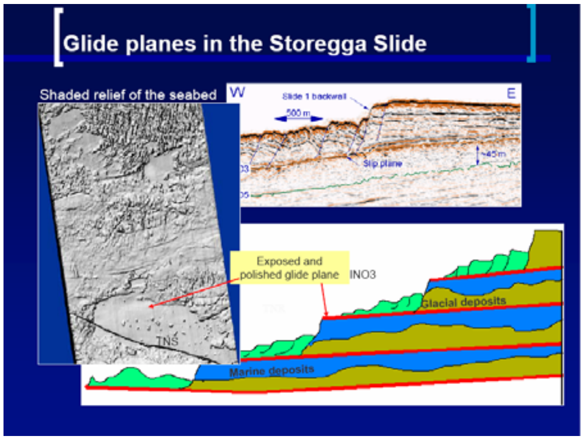
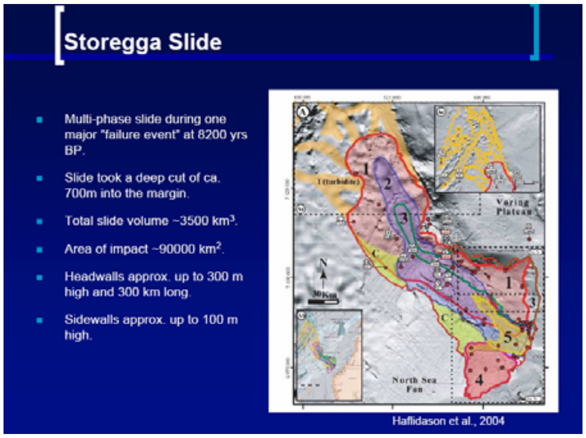


Glide planes in the Storegga Slide

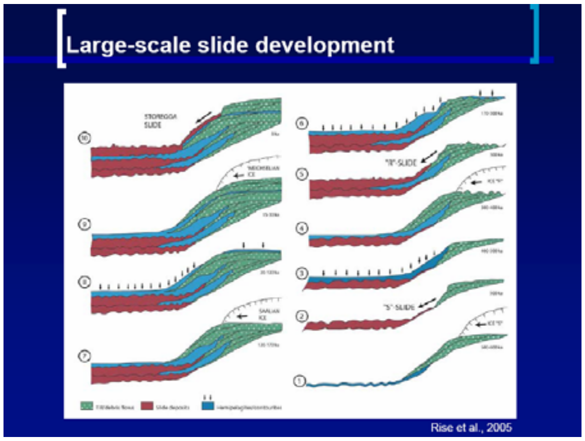
Shaded relief of the seabed



Storegga Slide

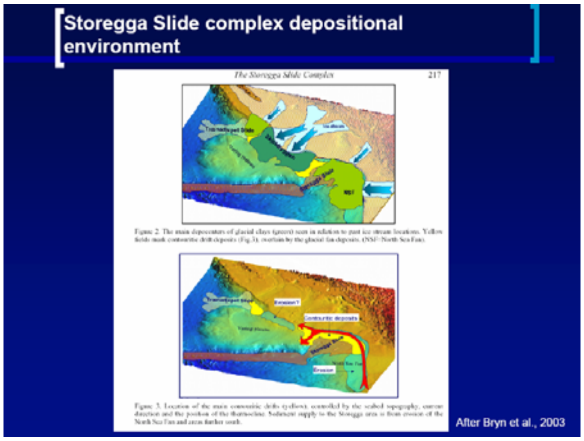
- Multi-phase slide during one major "failure event" at 8200 yrs BP.
- Slide took a deep cut of ca. 700m into the margin.
- Total slide volume ~3500 km^3.
- Area of impact ~90000 km^2.
- Headwalls approx. up to 300 m high and 300 km long.
- Sidewalls approx. up to 100 m high.

Haflidason et al., 2004



Large-scale slide development

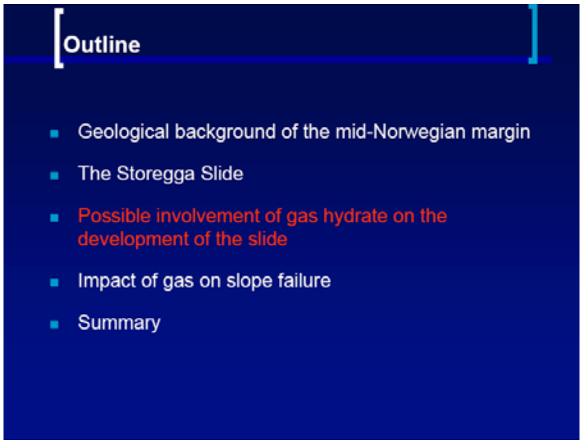
Rise et al., 2005



Storegga Slide complex depositional environment

The Storegga Slide Complex 217

After Bryn et al., 2003



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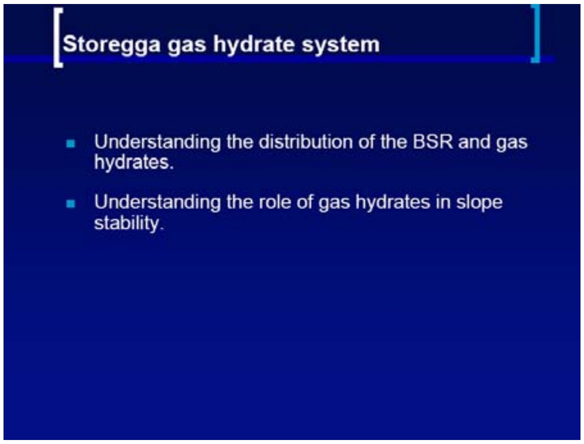
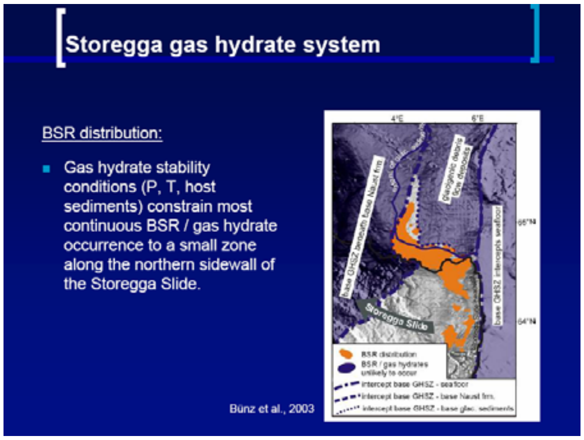


Storegga gas hydrate system

- Understanding the distribution of the BSR and gas hydrates.
- Understanding the role of gas hydrates in slope stability.

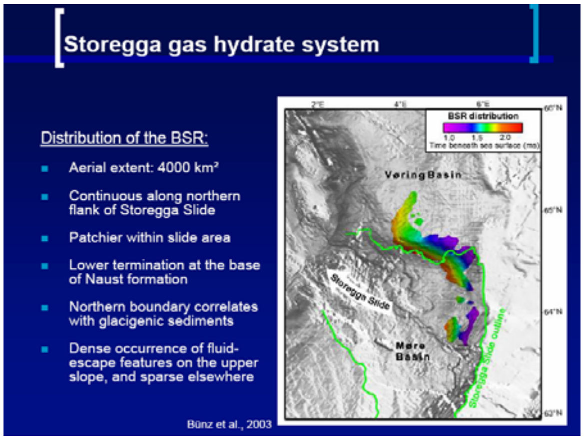


Storegga gas hydrate system

BSR distribution:

- Gas hydrate stability conditions (P, T, host sediments) constrain most continuous BSR / gas hydrate occurrence to a small zone along the northern sidewall of the Storegga Slide.

Bünz et al., 2003

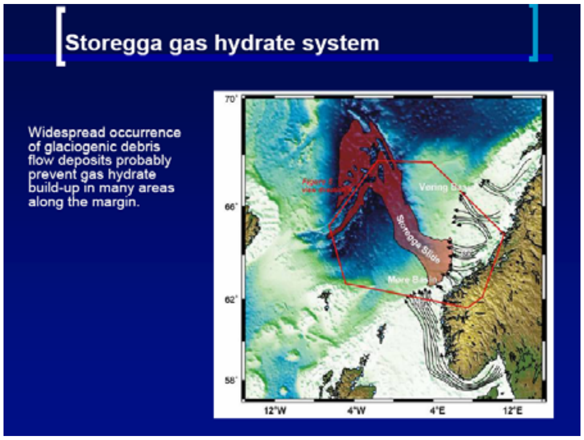


Storegga gas hydrate system

Distribution of the BSR:

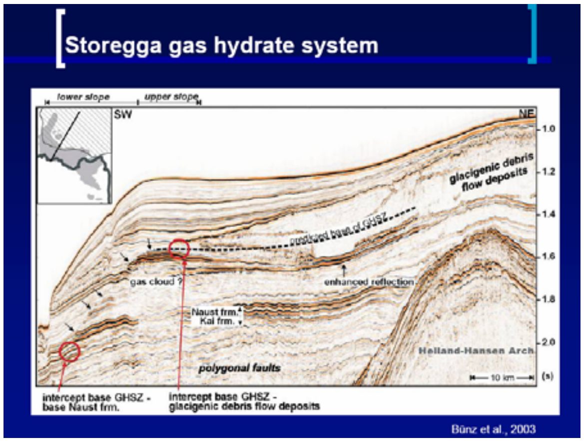
- Aerial extent: 4000 km²
- Continuous along northern flank of Storegga Slide
- Patchier within slide area
- Lower termination at the base of Naust formation
- Northern boundary correlates with glacigenic sediments
- Dense occurrence of fluid-escape features on the upper slope, and sparse elsewhere

Bünz et al., 2003



Storegga gas hydrate system

Widespread occurrence of glaciogenic debris flow deposits probably prevent gas hydrate build-up in many areas along the margin.

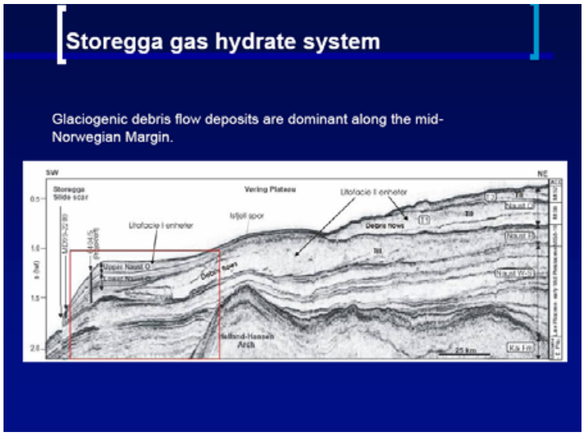


Storegga gas hydrate system

intercept base GHSZ - base Naust frm.

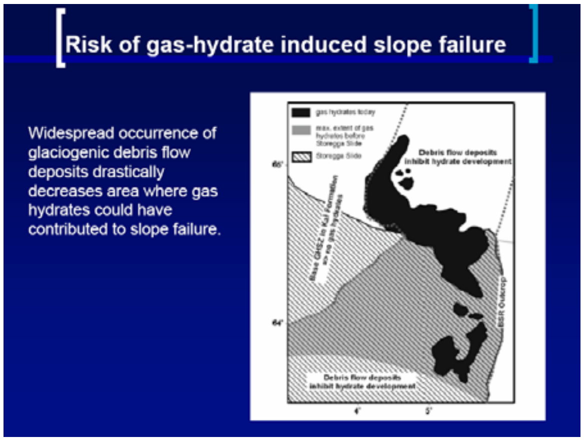
intercept base GHSZ - glacigenic debris flow deposits

Bünz et al., 2003



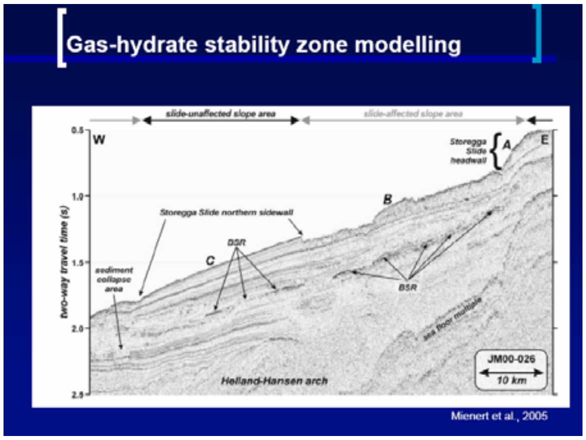
Storegga gas hydrate system

Glaciogenic debris flow deposits are dominant along the mid-Norwegian Margin.



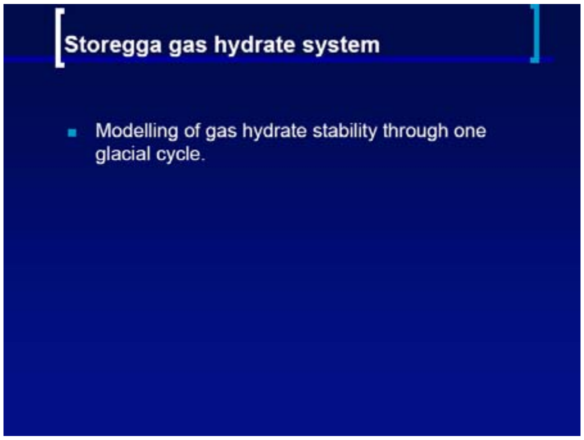
Risk of gas-hydrate induced slope failure

Widespread occurrence of glaciogenic debris flow deposits drastically decreases area where gas hydrates could have contributed to slope failure.



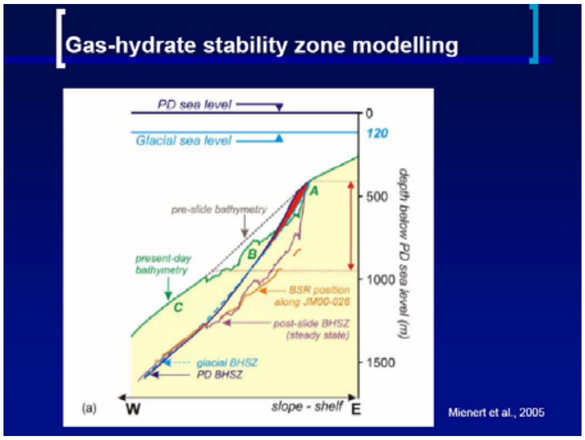
Gas-hydrate stability zone modelling

Mienert et al., 2005



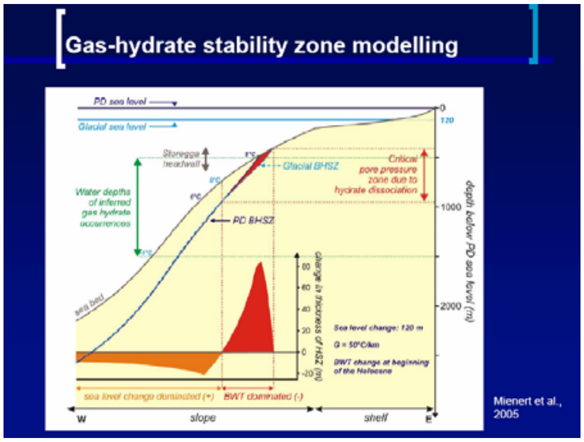
Storegga gas hydrate system

- Modelling of gas hydrate stability through one glacial cycle.



Gas-hydrate stability zone modelling

Mienert et al., 2005



Gas-hydrate stability zone modelling

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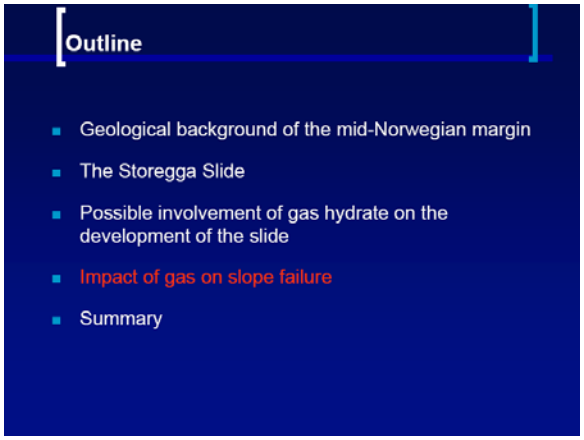

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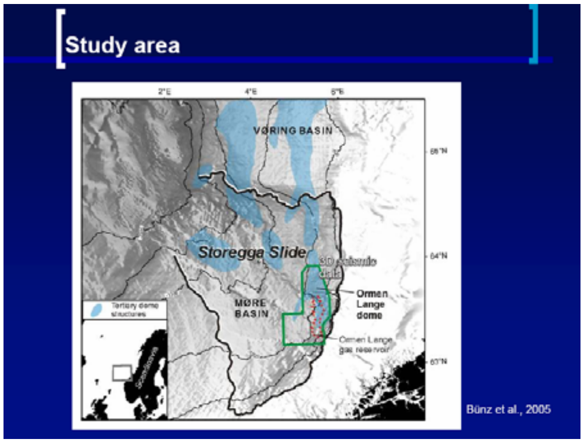
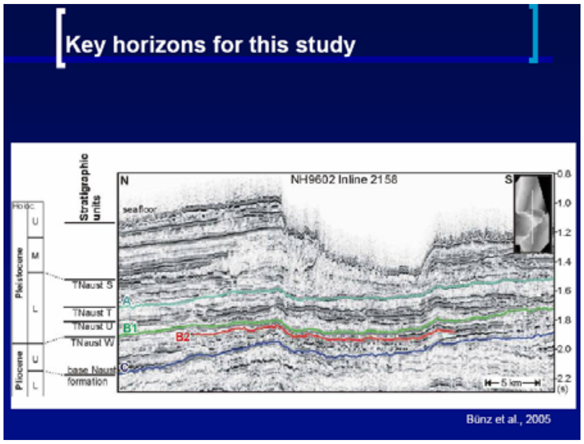


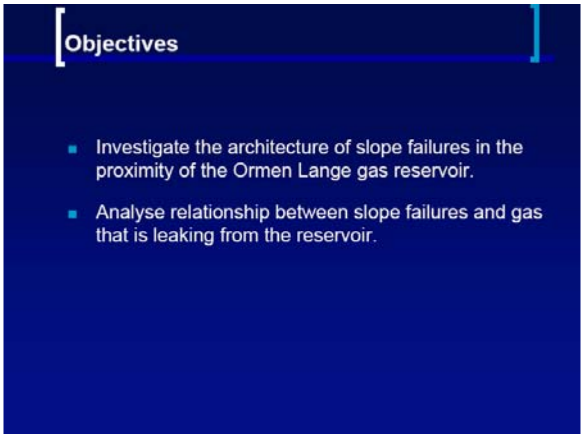
Study area

Bünz et al., 2005



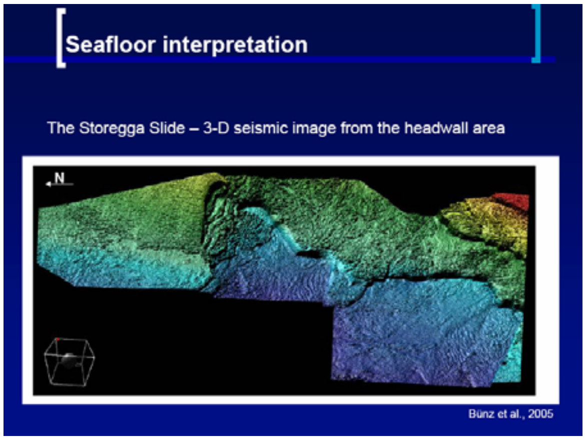
Key horizons for this study

Bünz et al., 2005



Objectives

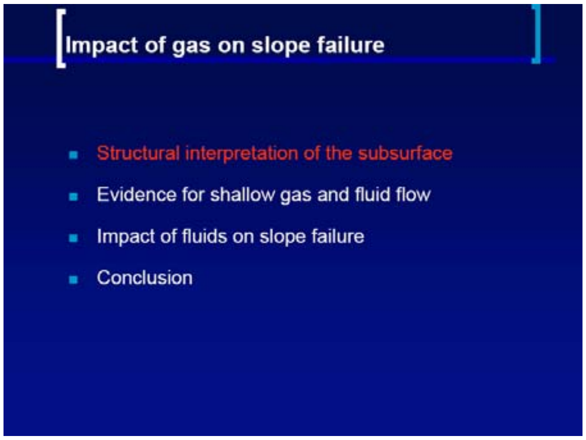
- Investigate the architecture of slope failures in the proximity of the Ormen Lange gas reservoir.
- Analyse relationship between slope failures and gas that is leaking from the reservoir.



Seafloor interpretation

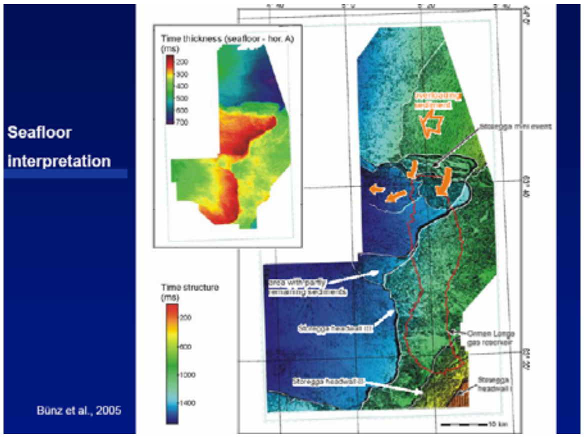
The Storegga Slide – 3-D seismic image from the headwall area

Bünz et al., 2005



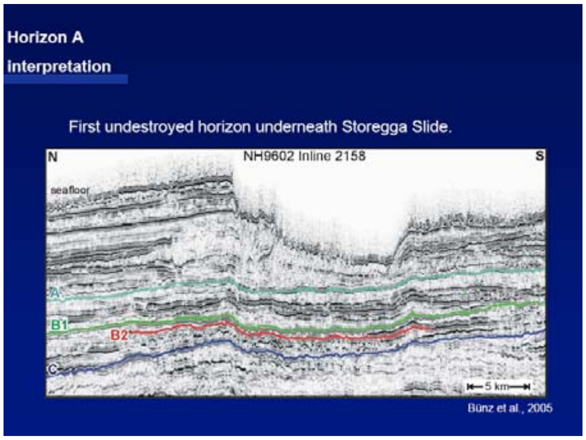
Impact of gas on slope failure

- Structural interpretation of the subsurface
- Evidence for shallow gas and fluid flow
- Impact of fluids on slope failure
- Conclusion



Seafloor interpretation

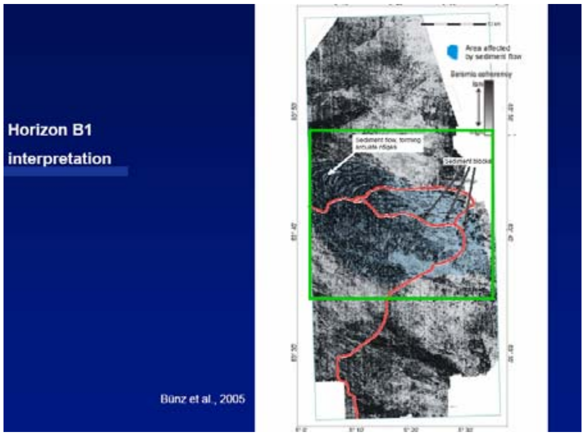
Bünz et al., 2005



Horizon A interpretation

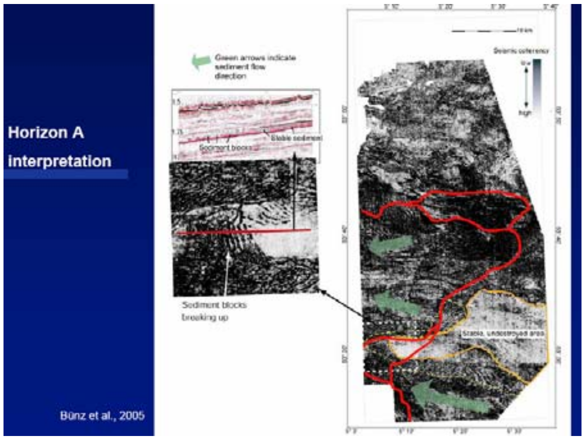
First undestroyed horizon underneath Storegga Slide.

Bünz et al., 2005



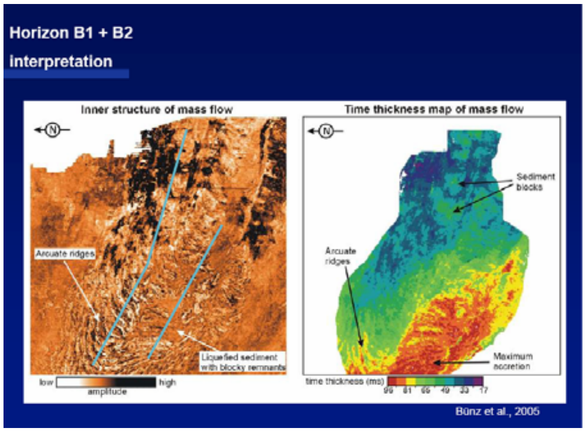
Horizon B1 interpretation

Bünz et al., 2005



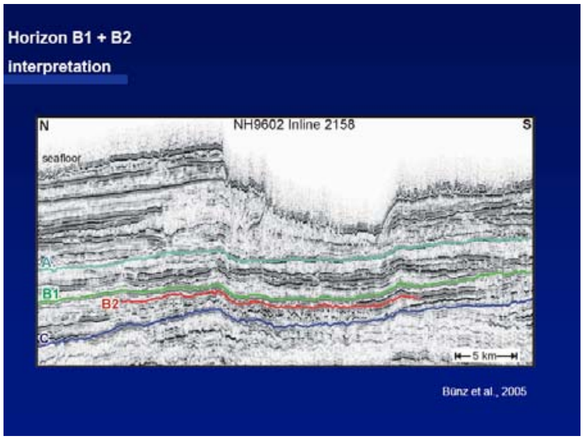
Horizon A interpretation

Bünz et al., 2005



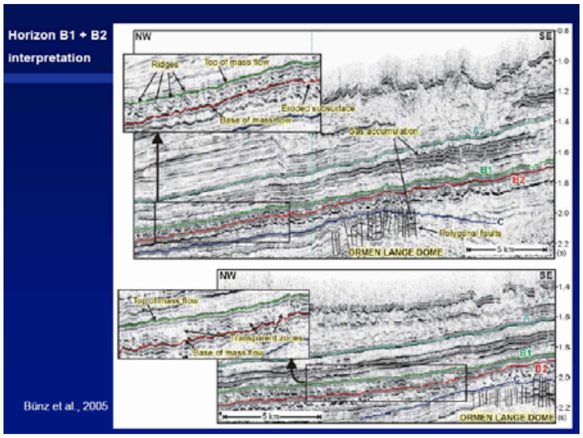
Horizon B1 + B2 interpretation

Bünz et al., 2005



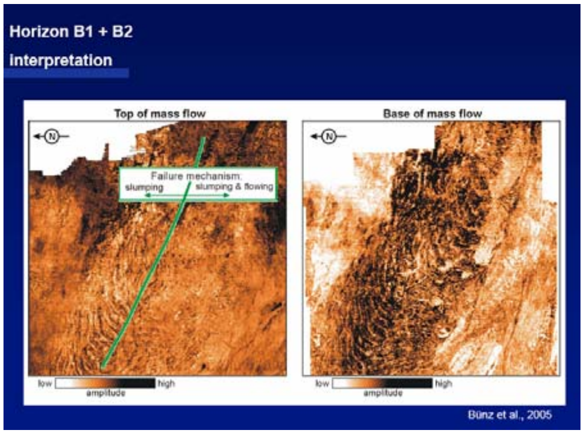
Horizon B1 + B2 interpretation

Bünz et al., 2005



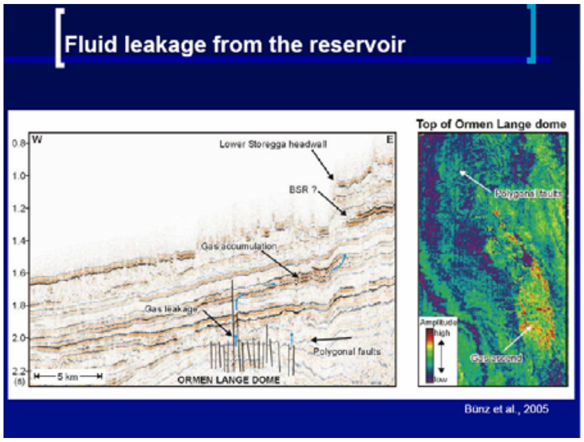
Horizon B1 + B2 interpretation

Bünz et al., 2005



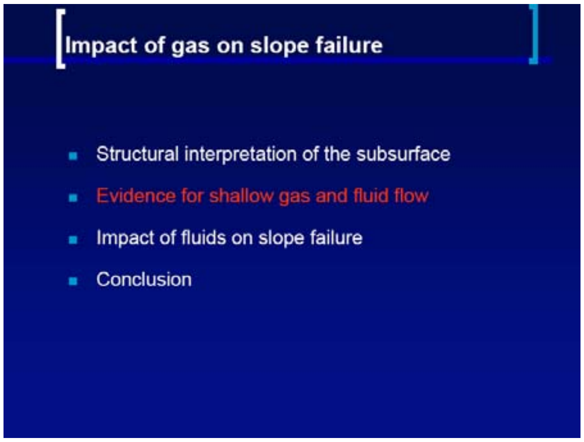
Horizon B1 + B2 interpretation

Bünz et al., 2005



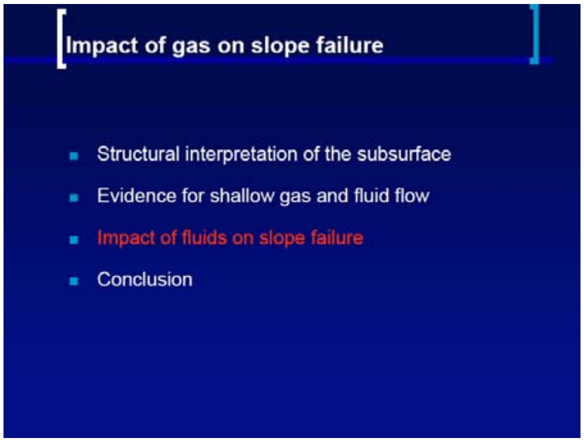
Fluid leakage from the reservoir

Bünz et al., 2005



Impact of gas on slope failure

- Structural interpretation of the subsurface
- Evidence for shallow gas and fluid flow
- Impact of fluids on slope failure
- Conclusion



Impact of gas on slope failure

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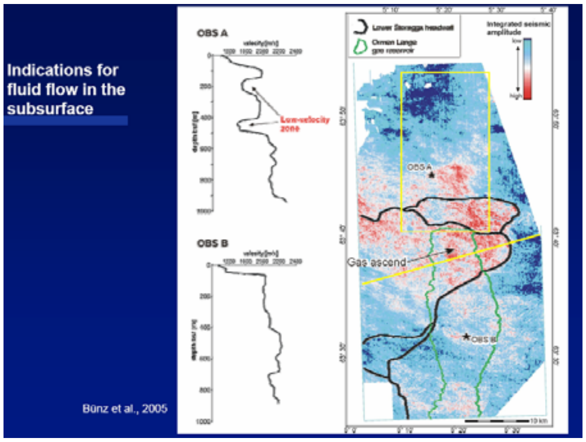
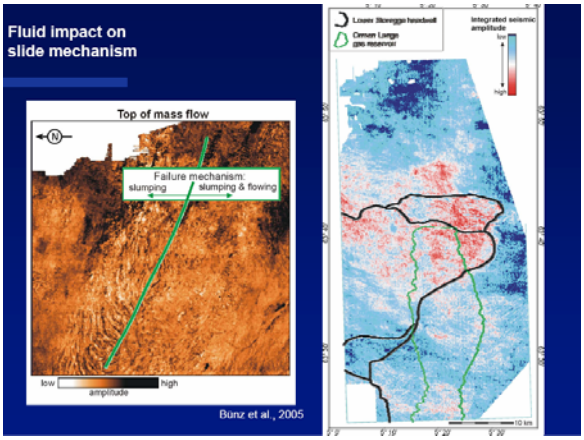


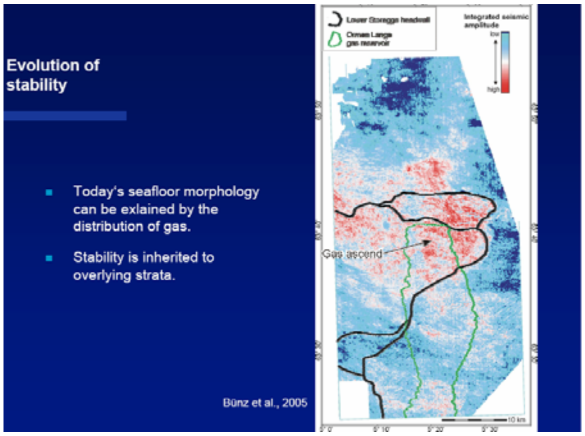
Indications for fluid flow in the subsurface

Bünz et al., 2005



Fluid impact on slide mechanism

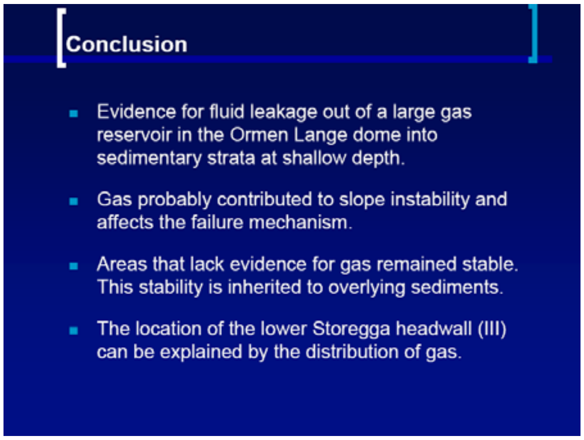
Bünz et al., 2005



Evolution of stability

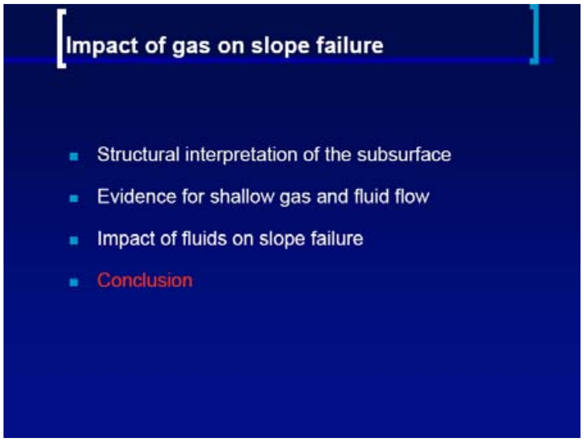
- Today's seafloor morphology can be exlained by the distribution of gas.
- Stability is inherited to overlying strata.

Bünz et al., 2005



Conclusion

- Evidence for fluid leakage out of a large gas reservoir in the Ormen Lange dome into sedimentary strata at shallow depth.
- Gas probably contributed to slope instability and affects the failure mechanism.
- Areas that lack evidence for gas remained stable. This stability is inherited to overlying sediments.
- The location of the lower Storegga headwall (III) can be explained by the distribution of gas.



Impact of gas on slope failure

- Structural interpretation of the subsurface
- Evidence for shallow gas and fluid flow
- Impact of fluids on slope failure
- Conclusion

6. ***Hydrate kinetics.*** Dendy Sloan, Colorado School of Mines.

Hydrate Kinetics

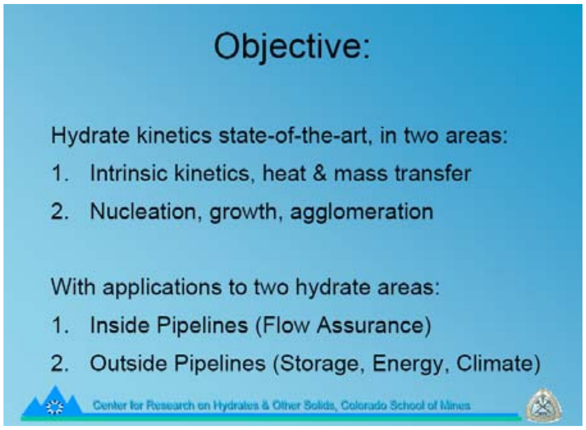
Dendy Sloan, Carolyn Koh, Kelly Miller
4th International Workshop on Methane Hydrate R&D

Victoria, BC, Canada
May 9, 2005

Center for Research on Hydrates & Other Solids, Colorado School of Mines

The CSM Hydrate Team

Center for Research on Hydrates & Other Solids, Colorado School of Mines



Objective:

Hydrate kinetics state-of-the-art, in two areas:

1. Intrinsic kinetics, heat & mass transfer
2. Nucleation, growth, agglomeration

With applications to two hydrate areas:

1. Inside Pipelines (Flow Assurance)
2. Outside Pipelines (Storage, Energy, Climate)

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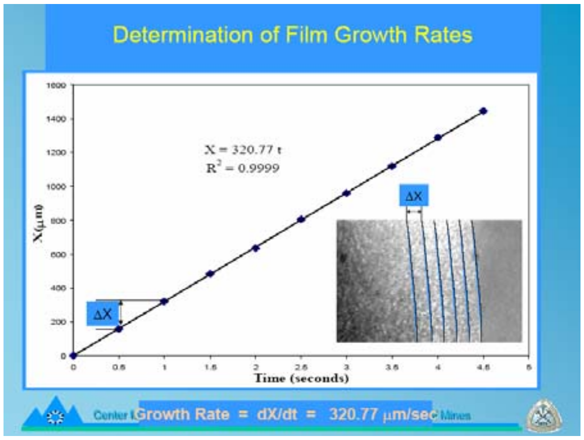
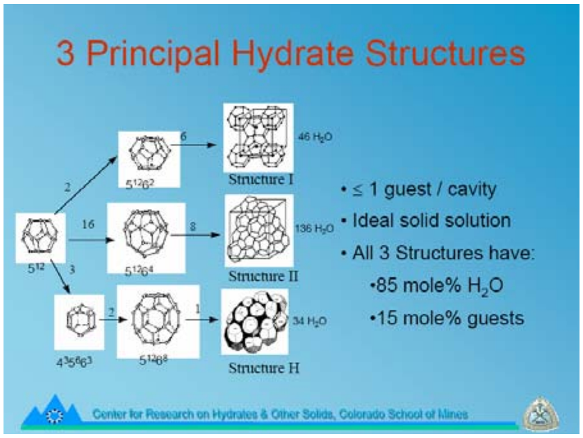


Determination of Film Growth Rates

$X = 320.77\,t$

$R^2 = 0.9999$

Growth Rate = dX/dt = 320.77 μm/sec



3 Principal Hydrate Structures

- ≤ 1 guest / cavity
- Ideal solid solution
- All 3 Structures have:
  - 85 mole% H_2O
  - 15 mole% guests

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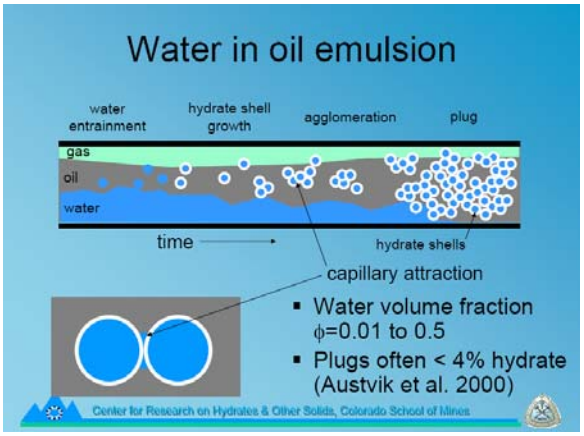

Water in oil emulsion

- Water volume fraction ϕ=0.01 to 0.5
- Plugs often < 4% hydrate (Austvik et al. 2000)

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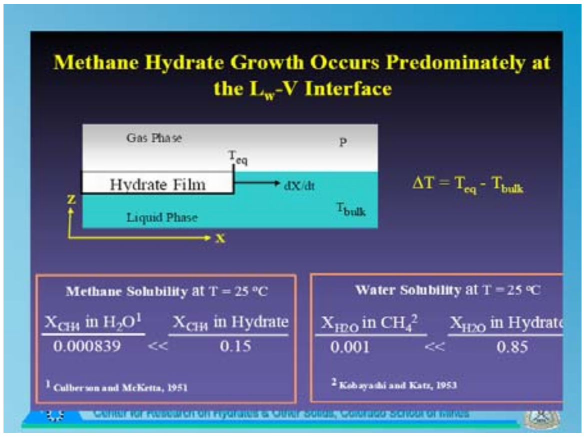

Methane Hydrate Growth Occurs Predominately at the L_w-V Interface

$\Delta T = T_{eq} - T_{bulk}$

Methane Solubility at T = 25 °C

X_{CH4} in H_2O^1		X_{CH4} in Hydrate
0.000839	<<	0.15

[1] Culberson and McKetta, 1951

Water Solubility at T = 25 °C

X_{H2O} in $CH_4{}^2$		X_{H2O} in Hydrat
0.001	<<	0.85

[2] Kobayashi and Katz, 1953

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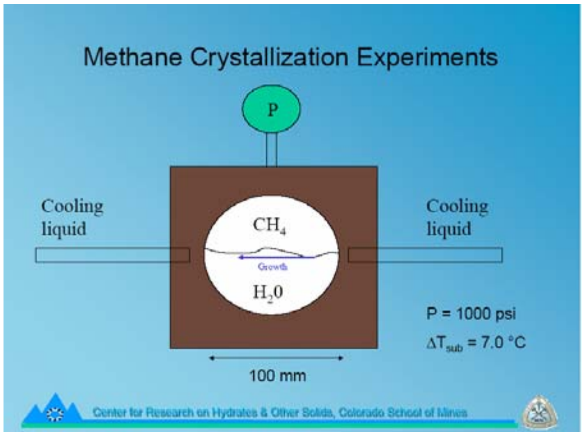

Methane Crystallization Experiments

P = 1000 psi

ΔT_{sub} = 7.0 °C

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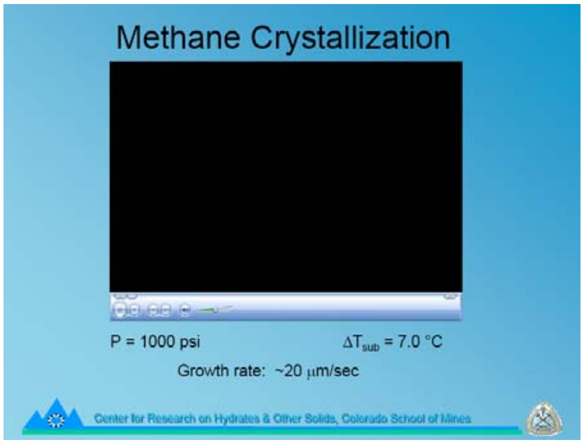
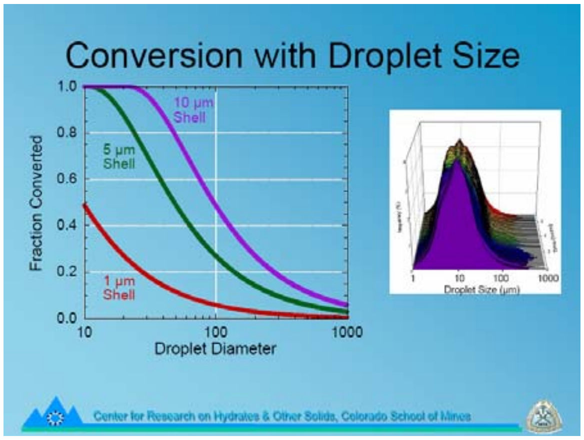


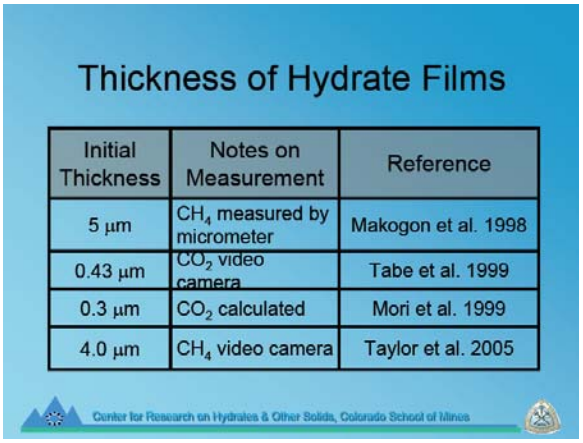
Methane Crystallization

P = 1000 psi ΔT_{sub} = 7.0 °C

Growth rate: ~20 μm/sec

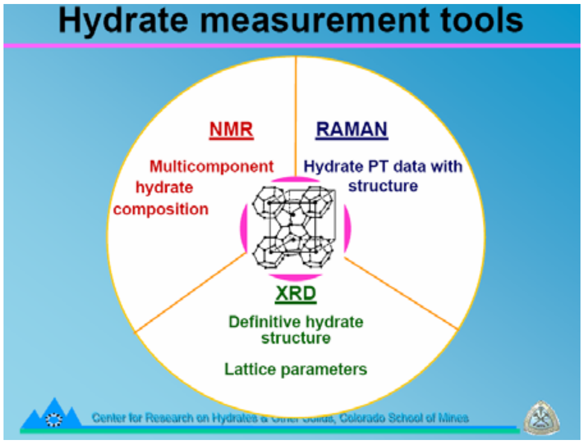


Conversion with Droplet Size



Thickness of Hydrate Films

Initial Thickness	Notes on Measurement	Reference
5 μm	CH_4 measured by micrometer	Makogon et al. 1998
0.43 μm	CO_2 video camera	Tabe et al. 1999
0.3 μm	CO_2 calculated	Mori et al. 1999
4.0 μm	CH_4 video camera	Taylor et al. 2005



Hydrate measurement tools

NMR

Multicomponent hydrate composition

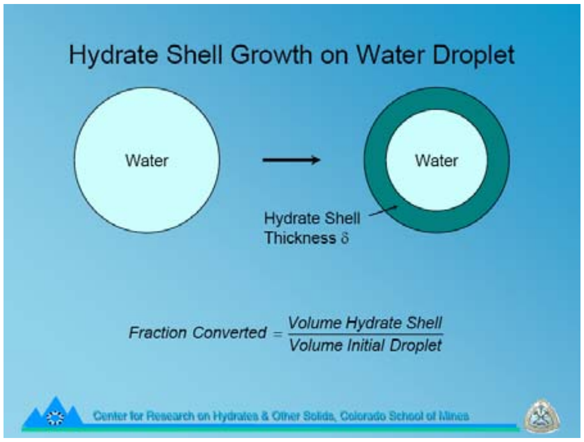
RAMAN

Hydrate PT data with structure

XRD

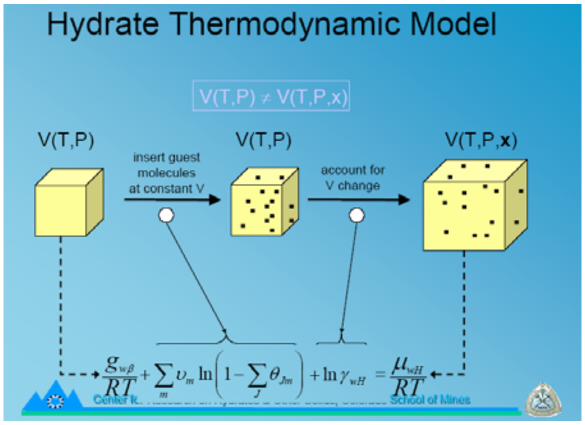
Definitive hydrate structure

Lattice parameters



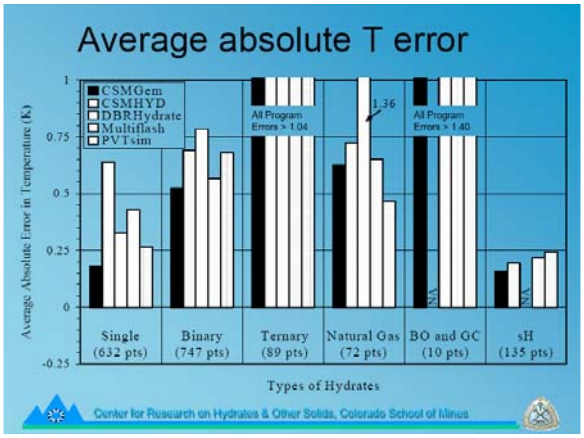
Hydrate Shell Growth on Water Droplet

$$\textit{Fraction Converted} = \frac{\textit{Volume Hydrate Shell}}{\textit{Volume Initial Droplet}}$$



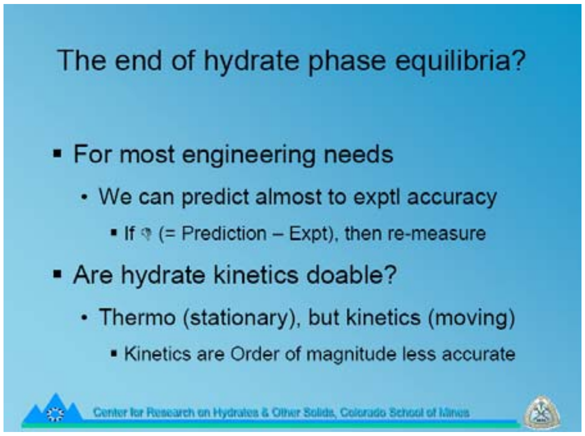
Hydrate Thermodynamic Model

$$\frac{g_{w\beta}}{RT}+\sum_m \upsilon_m \ln\left(1-\sum_J \theta_{Jm}\right)+\ln\gamma_{wH}=\frac{\mu_{wH}}{RT}$$



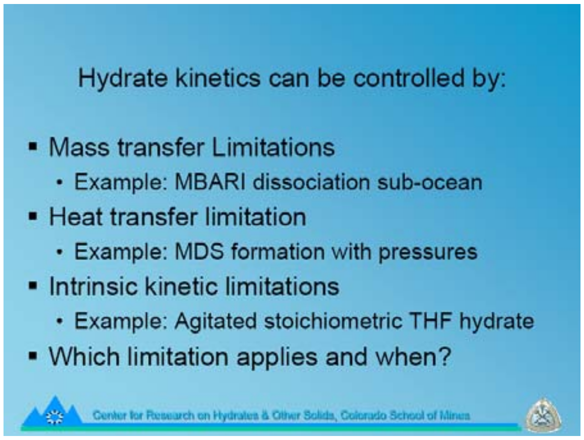
Average absolute T error

Heat and Mass Transfer & Kinetics



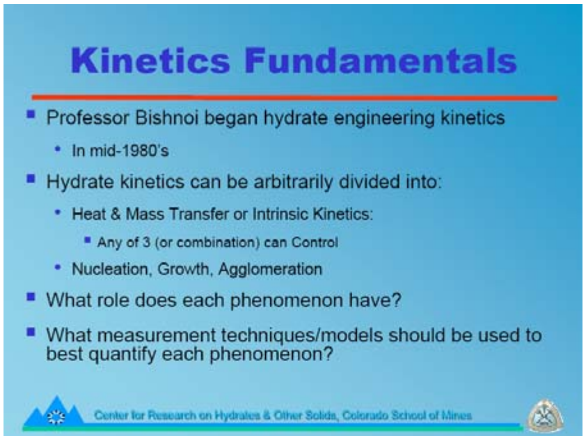
The end of hydrate phase equilibria?

- For most engineering needs
  - We can predict almost to exptl accuracy
    - If 👎 (= Prediction – Expt), then re-measure
- Are hydrate kinetics doable?
  - Thermo (stationary), but kinetics (moving)
    - Kinetics are Order of magnitude less accurate



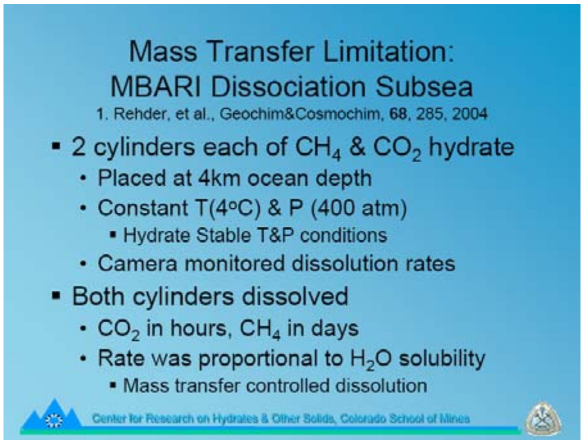
Hydrate kinetics can be controlled by:

- Mass transfer Limitations
  - Example: MBARI dissociation sub-ocean
- Heat transfer limitation
  - Example: MDS formation with pressures
- Intrinsic kinetic limitations
  - Example: Agitated stoichiometric THF hydrate
- Which limitation applies and when?



Kinetics Fundamentals

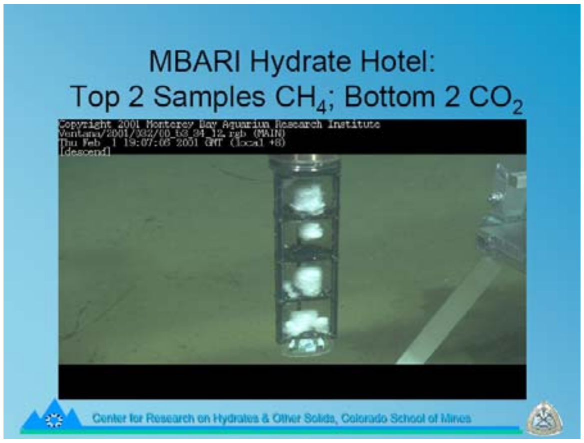
- Professor Bishnoi began hydrate engineering kinetics
  - In mid-1980's
- Hydrate kinetics can be arbitrarily divided into:
  - Heat & Mass Transfer or Intrinsic Kinetics:
    - Any of 3 (or combination) can Control
  - Nucleation, Growth, Agglomeration
- What role does each phenomenon have?
- What measurement techniques/models should be used to best quantify each phenomenon?



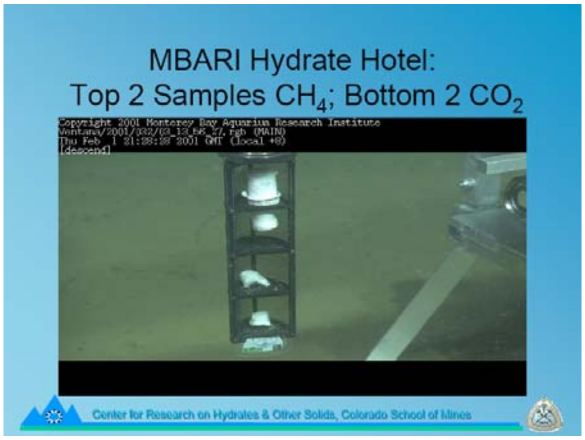
Mass Transfer Limitation: MBARI Dissociation Subsea

1. Rehder, et al., Geochim&Cosmochim, **68**, 285, 2004

- 2 cylinders each of CH_4 & CO_2 hydrate
  - Placed at 4km ocean depth
  - Constant T(4°C) & P (400 atm)
    - Hydrate Stable T&P conditions
  - Camera monitored dissolution rates
- Both cylinders dissolved
  - CO_2 in hours, CH_4 in days
  - Rate was proportional to H_2O solubility
    - Mass transfer controlled dissolution



MBARI Hydrate Hotel: Top 2 Samples CH_4; Bottom 2 CO_2



MBARI Hydrate Hotel: Top 2 Samples CH_4; Bottom 2 CO_2

Heat transfer controlled hydrate growth:

- Note: All *in situ* and core dissociation appears to be heat transfer controlled
- MDS C_2H_6 growth in seawater at 4°C
  - Spherical crystals at 148 psig
  - Became dendritic crystals at 155 psig
- Dendrites: Nature's max of Area/Volume
  - To efficiently dispel heat generation
  - With increase in formation driving force

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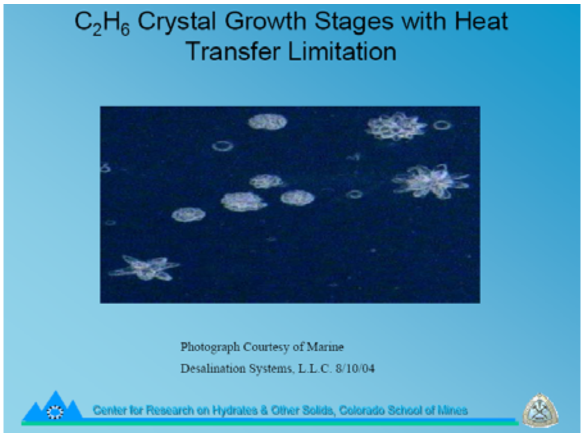

C_2H_6 Crystal Growth Stages with Heat Transfer Limitation

Photograph Courtesy of Marine Desalination Systems, L.L.C. 8/10/04

Intrinsic growth kinetics

- THF single crystal grown
  - Stoichiometric concentration of liquid
    - Eliminated mass transfer resistance
  - Increased shear at crystal surface
    - To minimize heat transfer
    - Never completely eliminated

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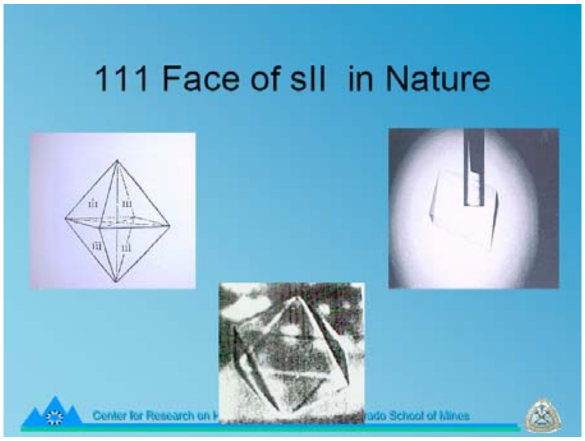
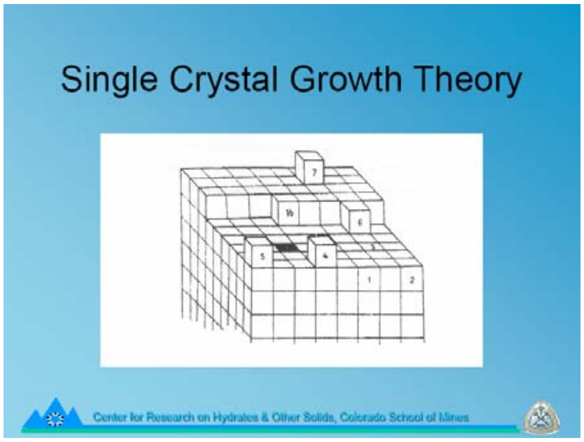


111 Face of sII in Nature



Single Crystal Growth Theory

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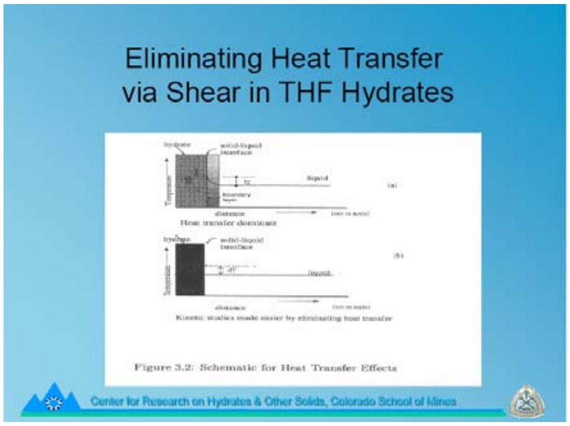

Eliminating Heat Transfer via Shear in THF Hydrates

Heat transfer dominant

Kinetic studies made easier by eliminating heat transfer

Figure 3.2: Schematic for Heat Transfer Effects

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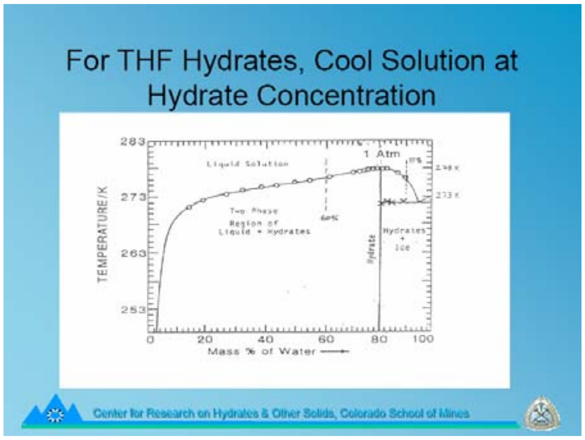

For THF Hydrates, Cool Solution at Hydrate Concentration

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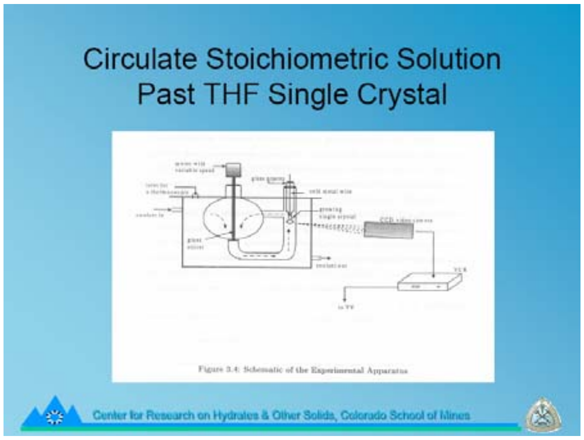

Circulate Stoichiometric Solution Past THF Single Crystal

Figure 3.4: Schematic of the Experimental Apparatus

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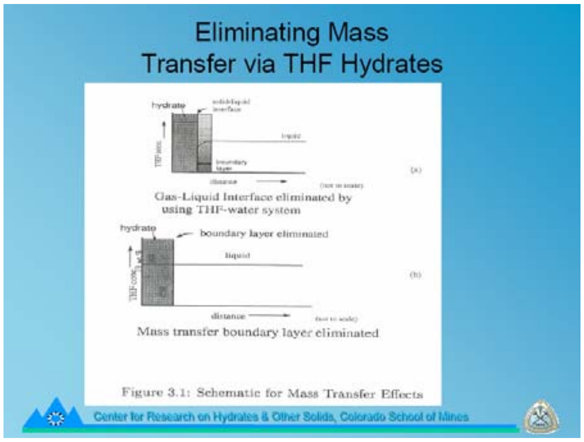

Eliminating Mass Transfer via THF Hydrates

Gas-Liquid Interface eliminated by using THF-water system

Mass transfer boundary layer eliminated

Figure 3.1: Schematic for Mass Transfer Effects

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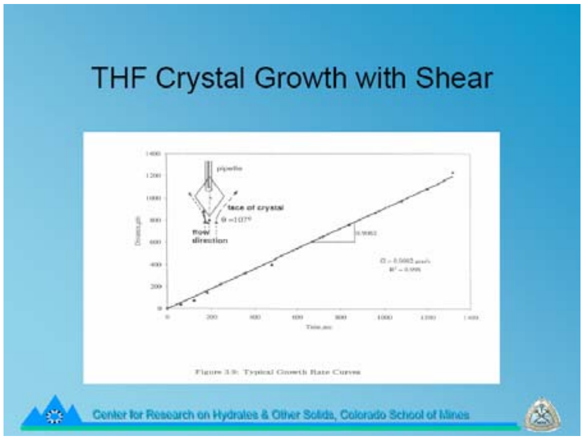

THF Crystal Growth with Shear

Figure 3.9: Typical Growth Rate Curves

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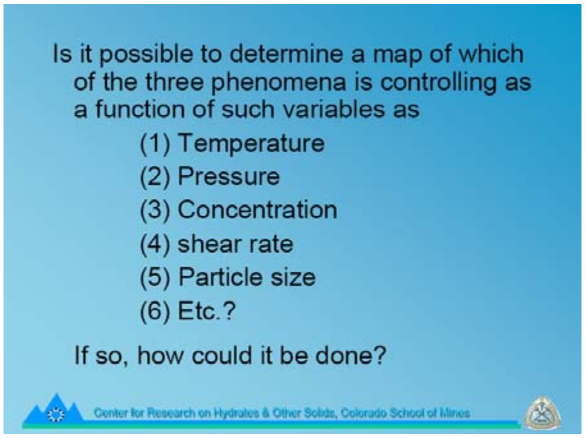
Is it possible to determine a map of which of the three phenomena is controlling as a function of such variables as

(1) Temperature
(2) Pressure
(3) Concentration
(4) shear rate
(5) Particle size
(6) Etc.?

If so, how could it be done?

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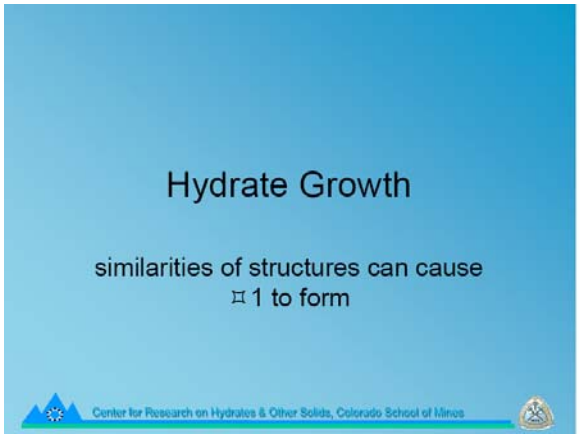
Hydrate Growth

similarities of structures can cause
⌑1 to form

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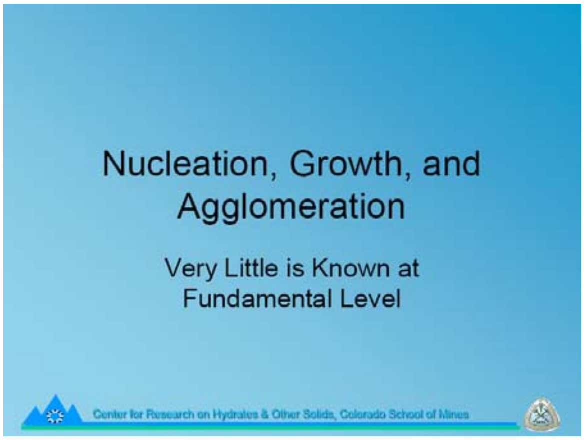
Nucleation, Growth, and Agglomeration

Very Little is Known at
Fundamental Level

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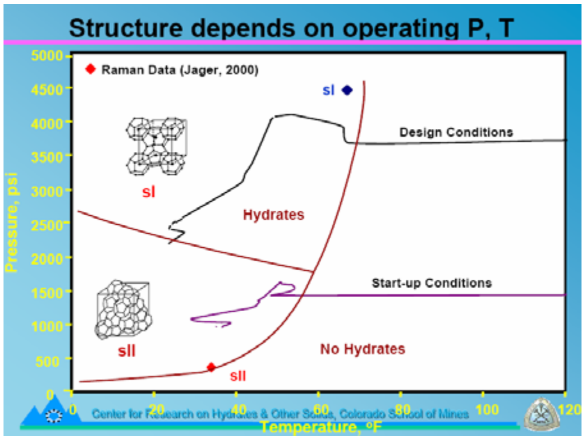
Structure depends on operating P, T

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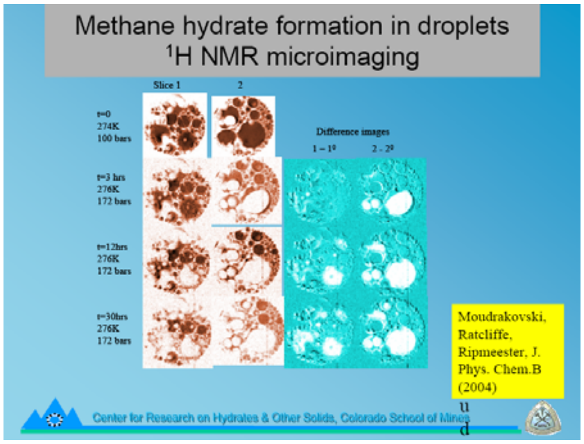
Methane hydrate formation in droplets ^{1}H NMR microimaging

Moudrakovski, Ratcliffe, Ripmeester, J. Phys. Chem.B (2004)

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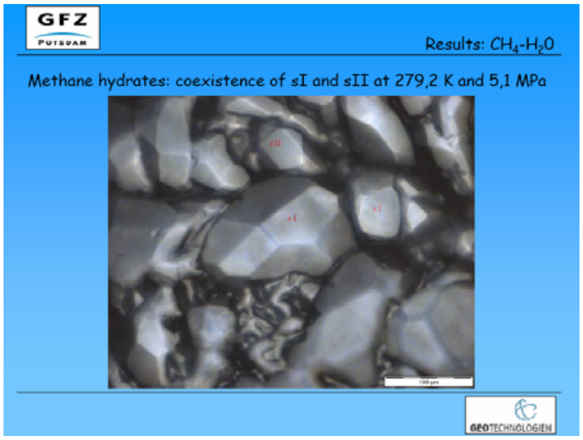
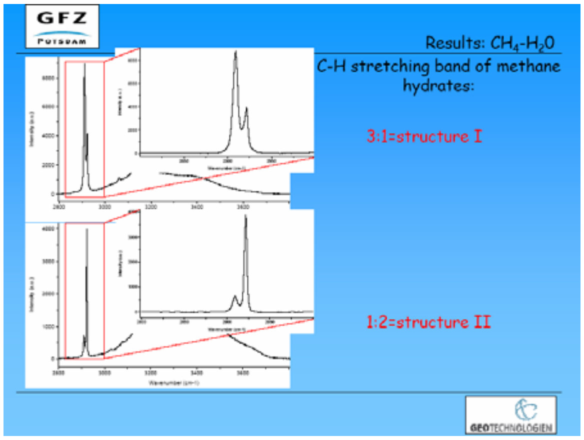

GFZ POTSDAM

Results: CH_4-H_20

Methane hydrates: coexistence of sI and sII at 279,2 K and 5,1 MPa

GEOTECHNOLOGIEN

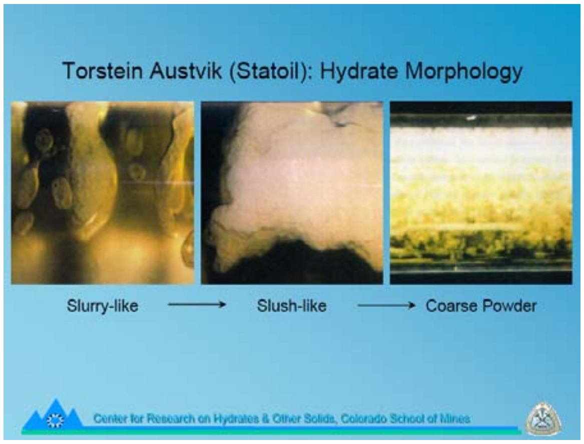


Results: CH_4-H_2O

C-H stretching band of methane hydrates:

3:1=structure I

1:2=structure II



Torstein Austvik (Statoil): Hydrate Morphology

Slurry-like → Slush-like → Coarse Powder

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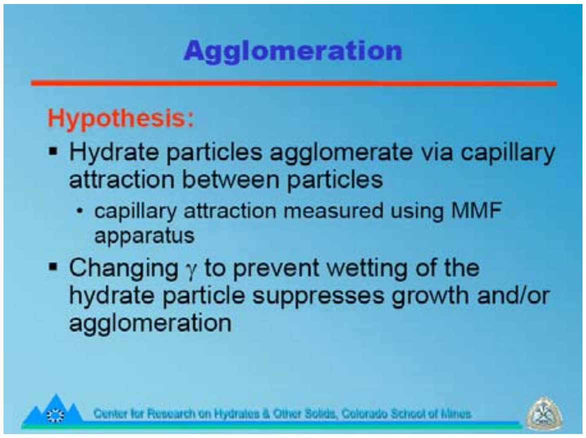

Agglomeration

Hypothesis:

- Hydrate particles agglomerate via capillary attraction between particles
  - capillary attraction measured using MMF apparatus
- Changing γ to prevent wetting of the hydrate particle suppresses growth and/or agglomeration

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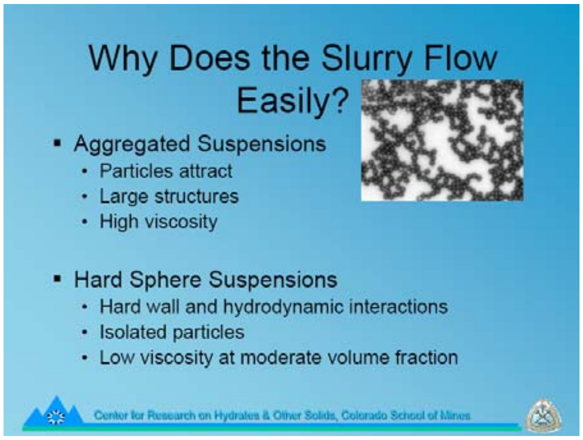

Why Does the Slurry Flow Easily?

- Aggregated Suspensions
  - Particles attract
  - Large structures
  - High viscosity
- Hard Sphere Suspensions
  - Hard wall and hydrodynamic interactions
  - Isolated particles
  - Low viscosity at moderate volume fraction

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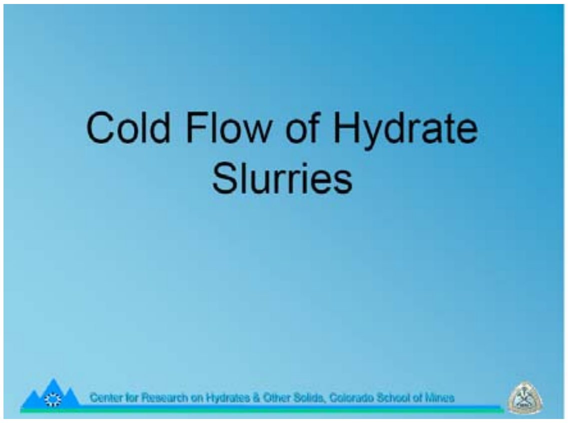
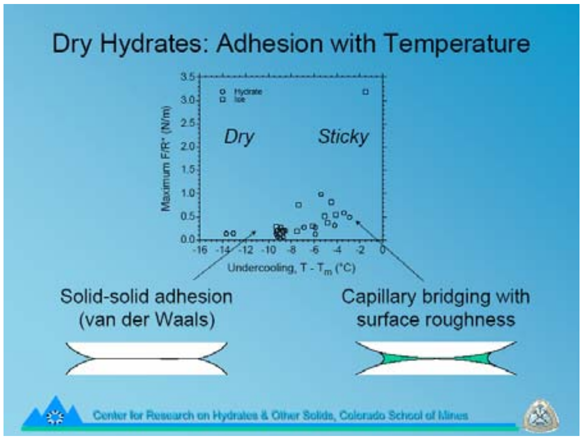


Cold Flow of Hydrate Slurries

Center for Research on Hydrates & Other Solids, Colorado School of Mines



Dry Hydrates: Adhesion with Temperature

Solid-solid adhesion (van der Waals)

Capillary bridging with surface roughness

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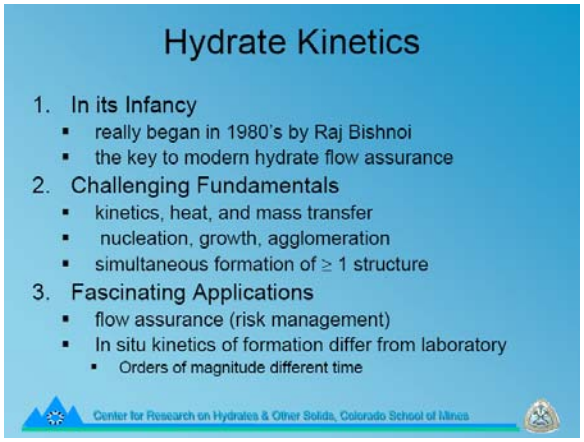

Hydrate Kinetics

1. In its Infancy
   - really began in 1980's by Raj Bishnoi
   - the key to modern hydrate flow assurance
2. Challenging Fundamentals
   - kinetics, heat, and mass transfer
   - nucleation, growth, agglomeration
   - simultaneous formation of ≥ 1 structure
3. Fascinating Applications
   - flow assurance (risk management)
   - In situ kinetics of formation differ from laboratory
     - Orders of magnitude different time

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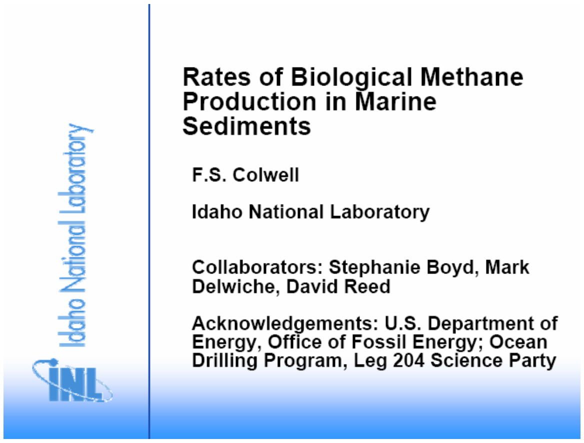
7. ***Rates of biological methane production in marine sediments.*** Frederick Colwell, Idaho National Laboratory.



Idaho National Laboratory

INL

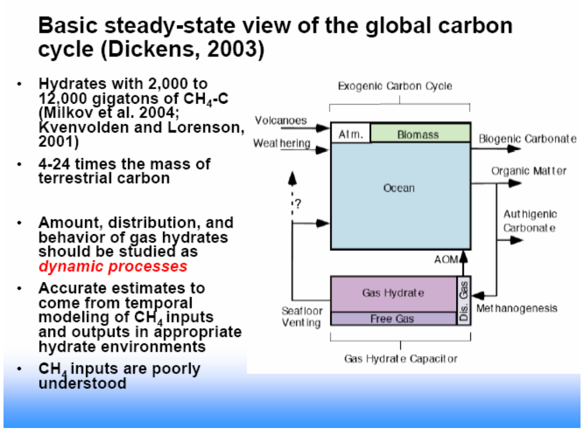
Rates of Biological Methane Production in Marine Sediments

F.S. Colwell

Idaho National Laboratory

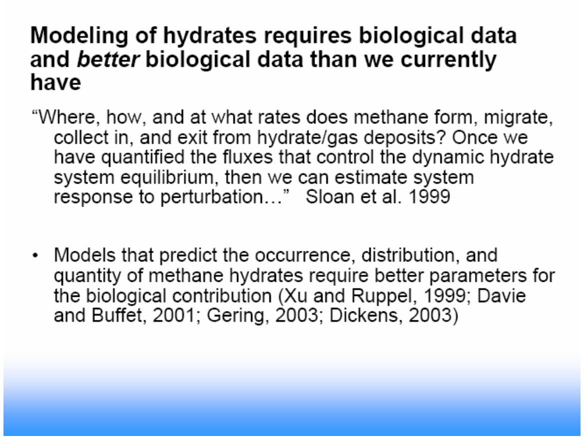
Collaborators: Stephanie Boyd, Mark Delwiche, David Reed

Acknowledgements: U.S. Department of Energy, Office of Fossil Energy; Ocean Drilling Program, Leg 204 Science Party



Basic steady-state view of the global carbon cycle (Dickens, 2003)

- **Hydrates with 2,000 to 12,000 gigatons of CH_4-C (Milkov et al. 2004; Kvenvolden and Lorenson, 2001)**
- **4-24 times the mass of terrestrial carbon**
- **Amount, distribution, and behavior of gas hydrates should be studied as *dynamic processes***
- **Accurate estimates to come from temporal modeling of CH_4 inputs and outputs in appropriate hydrate environments**
- **CH_4 inputs are poorly understood**



Modeling of hydrates requires biological data and *better* biological data than we currently have

"Where, how, and at what rates does methane form, migrate, collect in, and exit from hydrate/gas deposits? Once we have quantified the fluxes that control the dynamic hydrate system equilibrium, then we can estimate system response to perturbation…" Sloan et al. 1999

- Models that predict the occurrence, distribution, and quantity of methane hydrates require better parameters for the biological contribution (Xu and Ruppel, 1999; Davie and Buffet, 2001; Gering, 2003; Dickens, 2003)

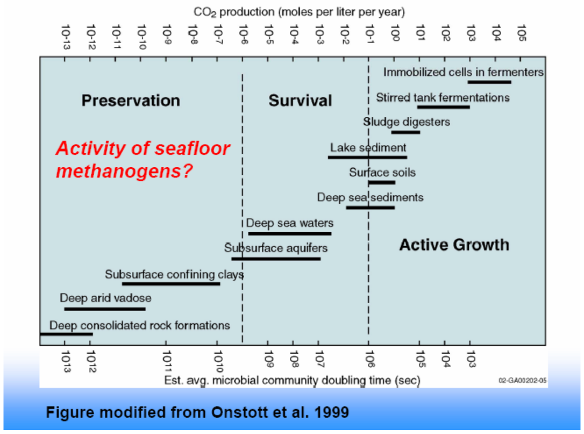
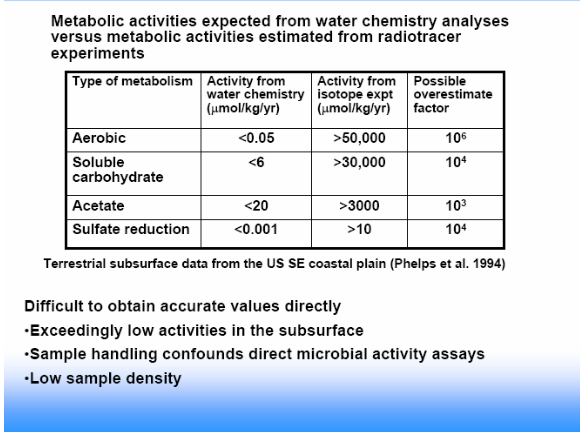


Figure modified from Onstott et al. 1999



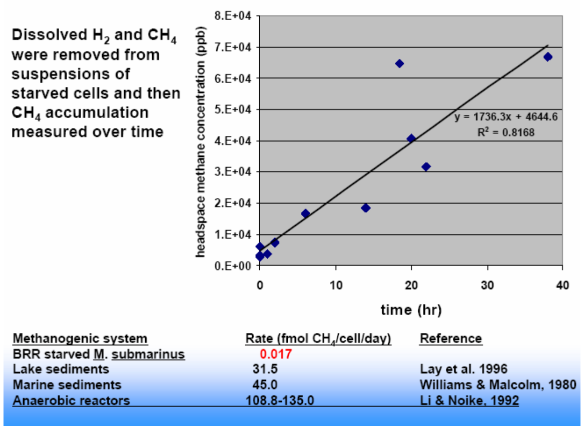
Metabolic activities expected from water chemistry analyses versus metabolic activities estimated from radiotracer experiments

Type of metabolism	Activity from water chemistry (μmol/kg/yr)	Activity from isotope expt (μmol/kg/yr)	Possible overestimate factor
Aerobic	<0.05	>50,000	10^6
Soluble carbohydrate	<6	>30,000	10^4
Acetate	<20	>3000	10^3
Sulfate reduction	<0.001	>10	10^4

Terrestrial subsurface data from the US SE coastal plain (Phelps et al. 1994)

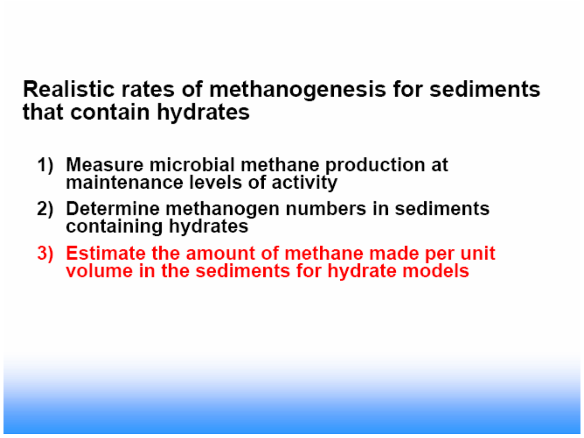
Difficult to obtain accurate values directly

- Exceedingly low activities in the subsurface
- Sample handling confounds direct microbial activity assays
- Low sample density



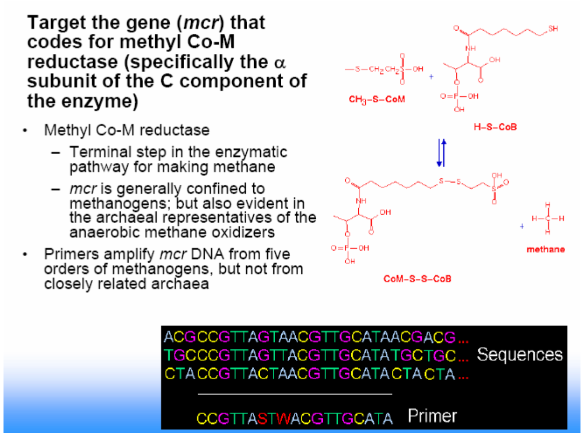
Dissolved H_2 and CH_4 were removed from suspensions of starved cells and then CH_4 accumulation measured over time

Methanogenic system	Rate (fmol CH_4/cell/day)	Reference
BRR starved M. submarinus	0.017	
Lake sediments	31.5	Lay et al. 1996
Marine sediments	45.0	Williams & Malcolm, 1980
Anaerobic reactors	108.8-135.0	Li & Noike, 1992



Realistic rates of methanogenesis for sediments that contain hydrates

1) Measure microbial methane production at maintenance levels of activity
2) Determine methanogen numbers in sediments containing hydrates
3) Estimate the amount of methane made per unit volume in the sediments for hydrate models

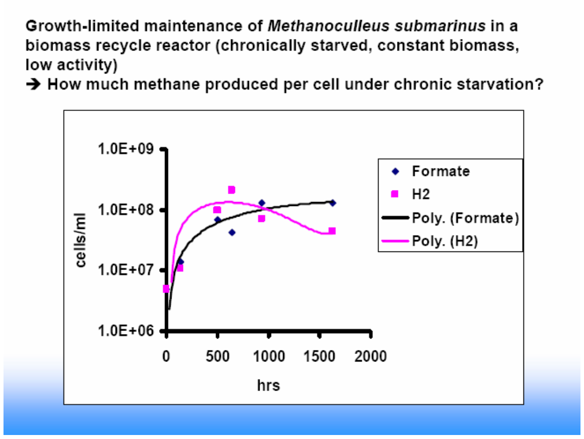


Target the gene (*mcr*) that codes for methyl Co-M reductase (specifically the α subunit of the C component of the enzyme)

- Methyl Co-M reductase
  - Terminal step in the enzymatic pathway for making methane
  - *mcr* is generally confined to methanogens; but also evident in the archaeal representatives of the anaerobic methane oxidizers
- Primers amplify *mcr* DNA from five orders of methanogens, but not from closely related archaea

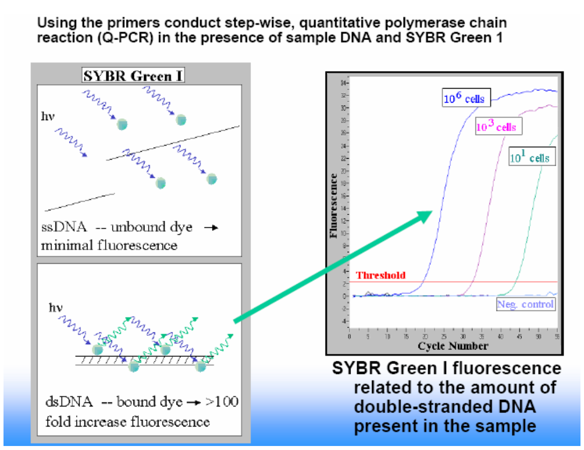
ACGCCGTTAGTAACGTTGCATAACGACG...
TGCCCGTTAGTTACGTTGCATATGCTGC... Sequences
CTACCGTTACTAACGTTGCATACTACTA...

CCGTTASTWACGTTGCATA Primer



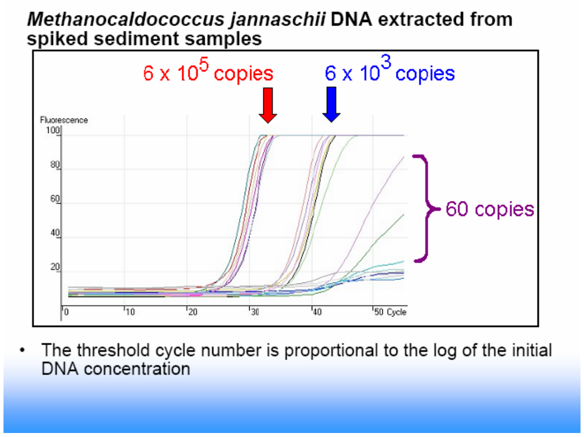
Growth-limited maintenance of ***Methanoculleus submarinus*** in a biomass recycle reactor (chronically starved, constant biomass, low activity)

→ How much methane produced per cell under chronic starvation?



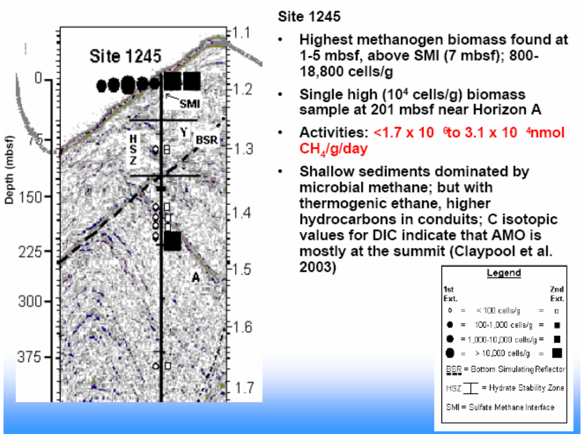
Using the primers conduct step-wise, quantitative polymerase chain reaction (Q-PCR) in the presence of sample DNA and SYBR Green 1

SYBR Green I fluorescence related to the amount of double-stranded DNA present in the sample



Methanocaldococcus jannaschii **DNA extracted from spiked sediment samples**

- The threshold cycle number is proportional to the log of the initial DNA concentration



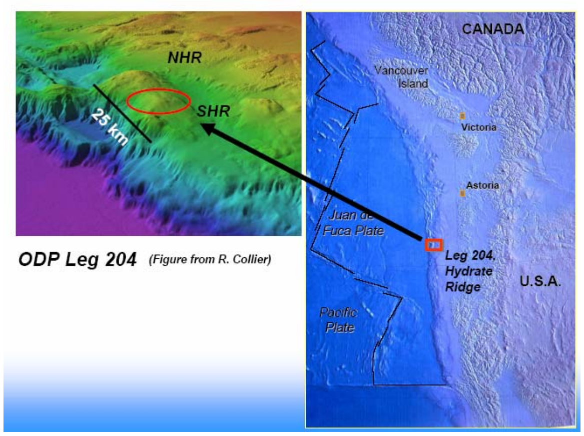
Site 1245

- **Highest methanogen biomass found at 1-5 mbsf, above SMI (7 mbsf); 800-18,800 cells/g**
- **Single high (10^4 cells/g) biomass sample at 201 mbsf near Horizon A**
- **Activities: <1.7 x 10 ^{6}to 3.1 x 10 ^{4}nmol CH_4/g/day**
- **Shallow sediments dominated by microbial methane; but with thermogenic ethane, higher hydrocarbons in conduits; C isotopic values for DIC indicate that AMO is mostly at the summit (Claypool et al. 2003)**

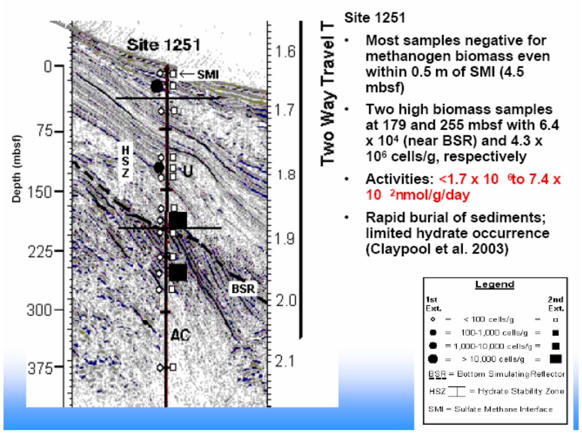
Legend

1st Ext.				2nd Ext.
◇	=	< 100 cells/g	=	□
●	=	100-1,000 cells/g	=	■
●	=	1,000-10,000 cells/g	=	■
●	=	> 10,000 cells/g	=	■

BSR = Bottom Simulating Reflector
HSZ = Hydrate Stability Zone
SMI = Sulfate Methane Interface



ODP Leg 204 *(Figure from R. Collier)*



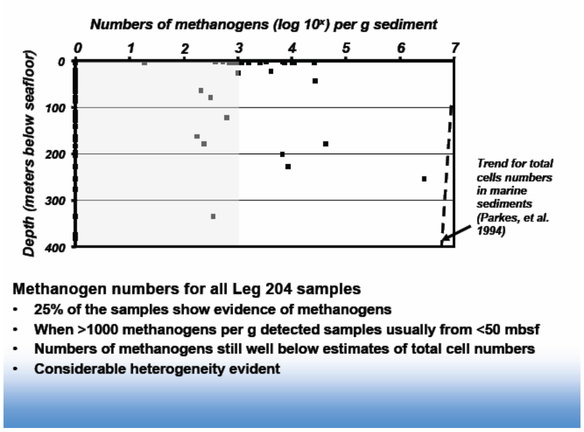
Site 1251

- **Most samples negative for methanogen biomass even within 0.5 m of SMI (4.5 mbsf)**
- **Two high biomass samples at 179 and 255 mbsf with 6.4 x 10^4 (near BSR) and 4.3 x 10^6 cells/g, respectively**
- **Activities: <1.7 x 10 ^{6}to 7.4 x 10 ^{2}nmol/g/day**
- **Rapid burial of sediments; limited hydrate occurrence (Claypool et al. 2003)**

Legend

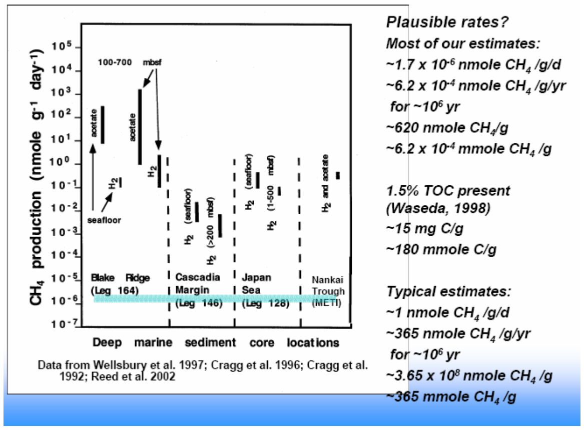
1st Ext.				2nd Ext.
◇	=	< 100 cells/g	=	□
●	=	100-1,000 cells/g	=	■
●	=	1,000-10,000 cells/g	=	■
●	=	> 10,000 cells/g	=	■

BSR = Bottom Simulating Reflector
HSZ = Hydrate Stability Zone
SMI = Sulfate Methane Interface



Methanogen numbers for all Leg 204 samples

- **25% of the samples show evidence of methanogens**
- **When >1000 methanogens per g detected samples usually from <50 mbsf**
- **Numbers of methanogens still well below estimates of total cell numbers**
- **Considerable heterogeneity evident**



Data from Wellsbury et al. 1997; Cragg et al. 1996; Cragg et al. 1992; Reed et al. 2002

Plausible rates?

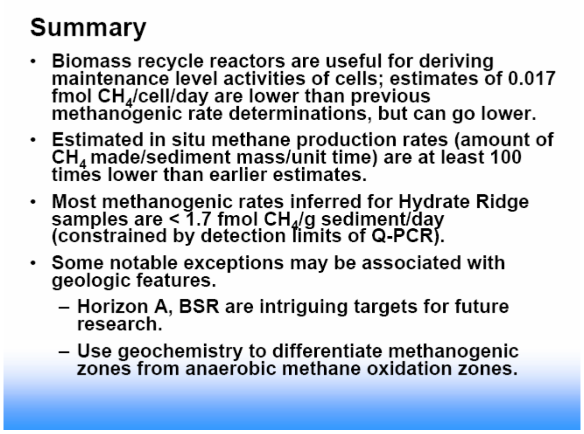
Most of our estimates:

~1.7 x 10^{-6} nmole CH_4 /g/d
~6.2 x 10^{-4} nmole CH_4 /g/yr
for ~10^6 yr
~620 nmole CH_4/g
~6.2 x 10^{-4} mmole CH_4 /g

1.5% TOC present (Waseda, 1998)
~15 mg C/g
~180 mmole C/g

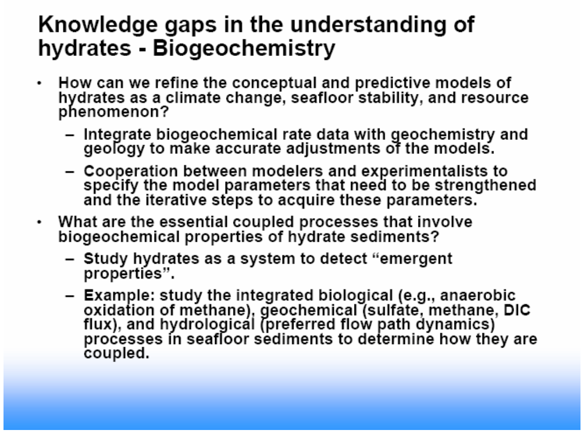
Typical estimates:

~1 nmole CH_4 /g/d
~365 nmole CH_4 /g/yr
for ~10^6 yr
~3.65 x 10^8 nmole CH_4 /g
~365 mmole CH_4 /g



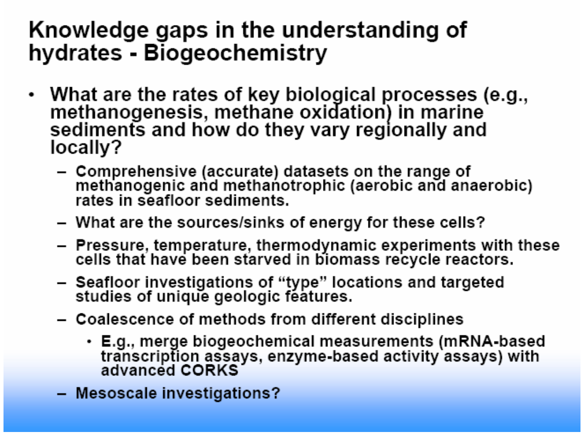
Summary

- Biomass recycle reactors are useful for deriving maintenance level activities of cells; estimates of 0.017 fmol CH_4/cell/day are lower than previous methanogenic rate determinations, but can go lower.
- Estimated in situ methane production rates (amount of CH_4 made/sediment mass/unit time) are at least 100 times lower than earlier estimates.
- Most methanogenic rates inferred for Hydrate Ridge samples are < 1.7 fmol CH_4/g sediment/day (constrained by detection limits of Q-PCR).
- Some notable exceptions may be associated with geologic features.
  - Horizon A, BSR are intriguing targets for future research.
  - Use geochemistry to differentiate methanogenic zones from anaerobic methane oxidation zones.



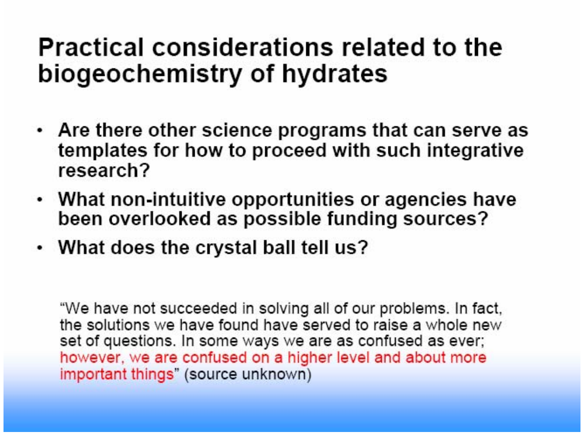
Knowledge gaps in the understanding of hydrates - Biogeochemistry

- How can we refine the conceptual and predictive models of hydrates as a climate change, seafloor stability, and resource phenomenon?
  - Integrate biogeochemical rate data with geochemistry and geology to make accurate adjustments of the models.
  - Cooperation between modelers and experimentalists to specify the model parameters that need to be strengthened and the iterative steps to acquire these parameters.
- What are the essential coupled processes that involve biogeochemical properties of hydrate sediments?
  - Study hydrates as a system to detect “emergent properties”.
  - Example: study the integrated biological (e.g., anaerobic oxidation of methane), geochemical (sulfate, methane, DIC flux), and hydrological (preferred flow path dynamics) processes in seafloor sediments to determine how they are coupled.



Knowledge gaps in the understanding of hydrates - Biogeochemistry

- What are the rates of key biological processes (e.g., methanogenesis, methane oxidation) in marine sediments and how do they vary regionally and locally?
  - Comprehensive (accurate) datasets on the range of methanogenic and methanotrophic (aerobic and anaerobic) rates in seafloor sediments.
  - What are the sources/sinks of energy for these cells?
  - Pressure, temperature, thermodynamic experiments with these cells that have been starved in biomass recycle reactors.
  - Seafloor investigations of “type” locations and targeted studies of unique geologic features.
  - Coalescence of methods from different disciplines
    - E.g., merge biogeochemical measurements (mRNA-based transcription assays, enzyme-based activity assays) with advanced CORKS
  - Mesoscale investigations?



Practical considerations related to the biogeochemistry of hydrates

- Are there other science programs that can serve as templates for how to proceed with such integrative research?
- What non-intuitive opportunities or agencies have been overlooked as possible funding sources?
- What does the crystal ball tell us?

“We have not succeeded in solving all of our problems. In fact, the solutions we have found have served to raise a whole new set of questions. In some ways we are as confused as ever; however, we are confused on a higher level and about more important things” (source unknown)

8. ***Gas hydrate: the paths forward.*** Art Johnson, Hydrate Energy International.

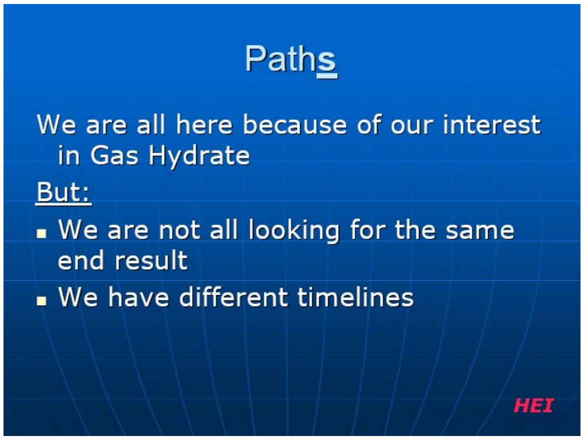
The Paths Forward

(Pulling the Pieces Together)

Art Johnson
Hydrate Energy International

4th International Hydrates Conf., Victoria, BC
May 9-11, 2005

HEI



Path<u>s</u>

We are all here because of our interest in Gas Hydrate

<u>But:</u>

- We are not all looking for the same end result
- We have different timelines

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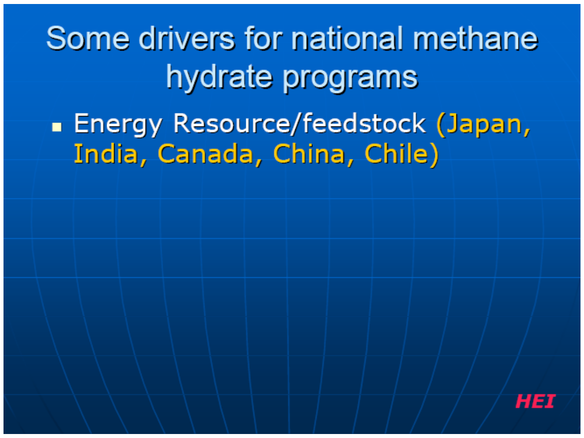
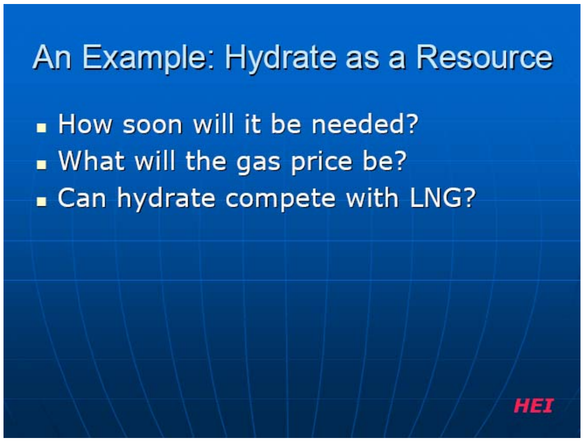


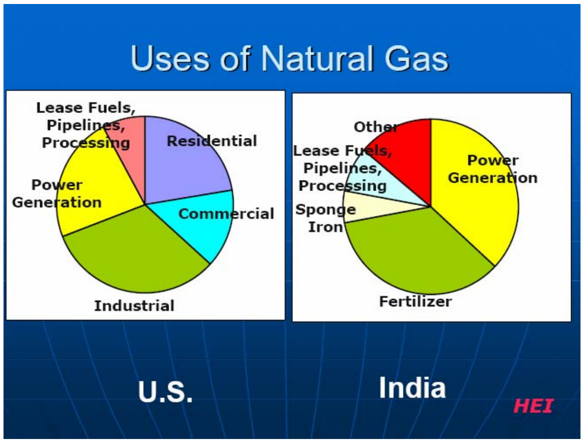
Some drivers for national methane hydrate programs

- Energy Resource/feedstock (Japan, India, Canada, China, Chile)

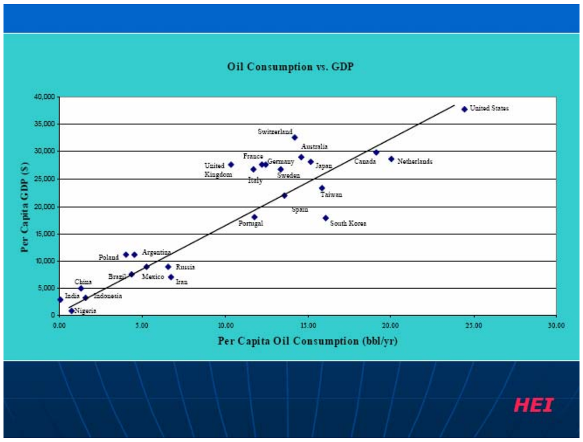


An Example: Hydrate as a Resource

- How soon will it be needed?
- What will the gas price be?
- Can hydrate compete with LNG?



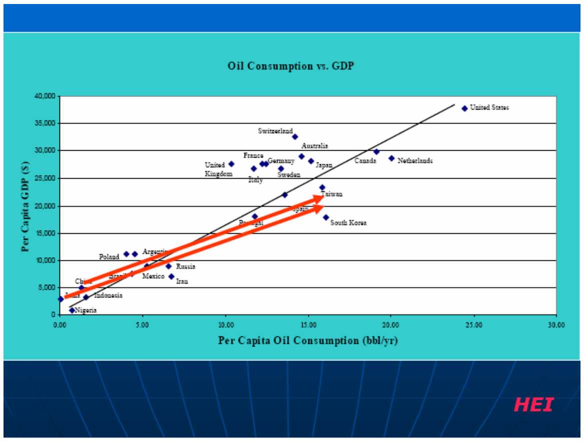
Uses of Natural Gas

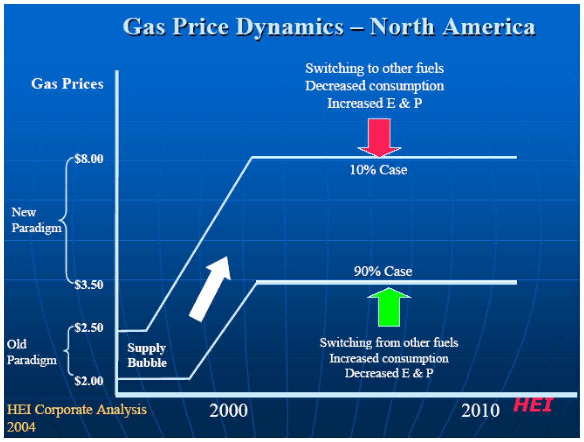


Some drivers for national methane hydrate programs

- Energy Resource/feedstock (Japan, India, Canada, China, Chile)
- Geohazard (EU, esp. Germany & Norway)
- Global Climate (EU)
- Basic Science (EU, esp. Germany)

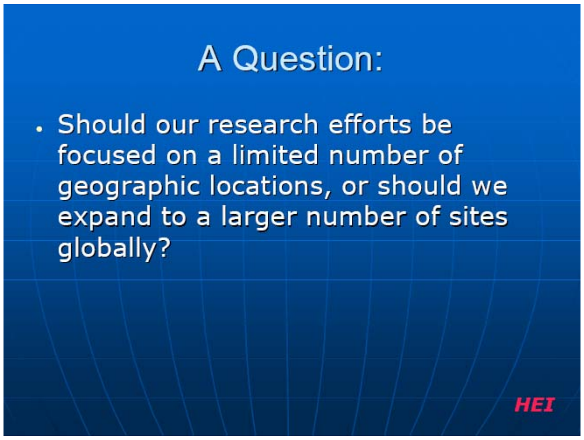
- U.S. – All of the above





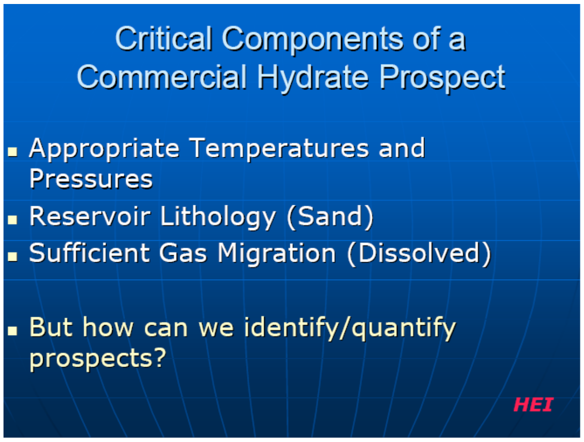
Gas Price Dynamics – North America

HEI Corporate Analysis 2004



A Question:

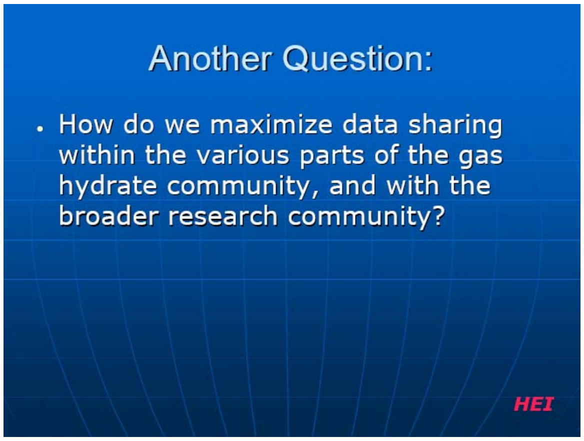
- Should our research efforts be focused on a limited number of geographic locations, or should we expand to a larger number of sites globally?



Critical Components of a Commercial Hydrate Prospect

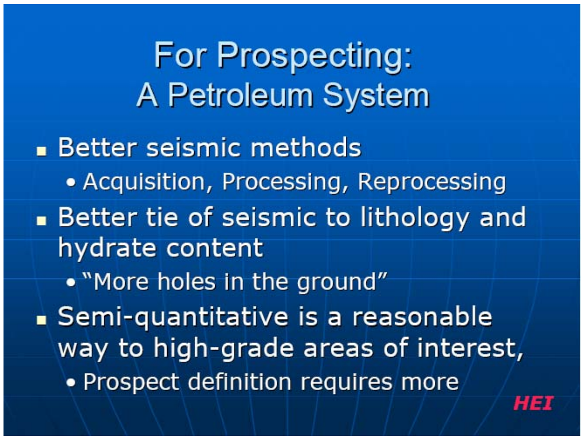
- Appropriate Temperatures and Pressures
- Reservoir Lithology (Sand)
- Sufficient Gas Migration (Dissolved)

- But how can we identify/quantify prospects?



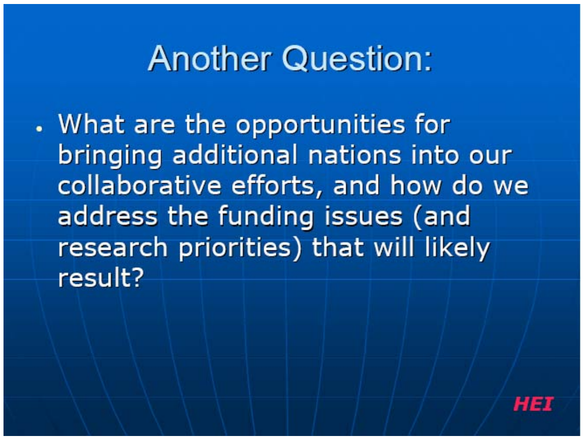
Another Question:

- How do we maximize data sharing within the various parts of the gas hydrate community, and with the broader research community?



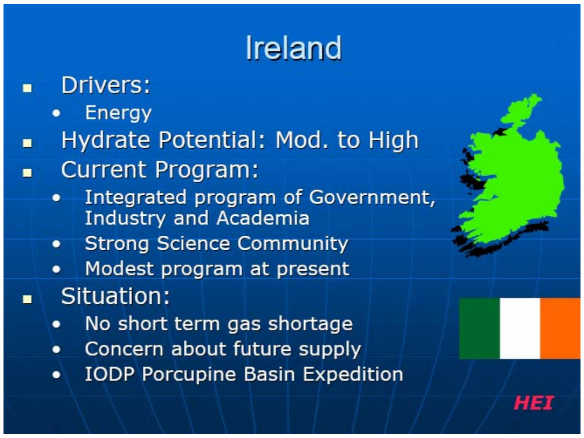
For Prospecting:
A Petroleum System

- Better seismic methods
  - Acquisition, Processing, Reprocessing
- Better tie of seismic to lithology and hydrate content
  - “More holes in the ground”
- Semi-quantitative is a reasonable way to high-grade areas of interest,
  - Prospect definition requires more



Another Question:

- What are the opportunities for bringing additional nations into our collaborative efforts, and how do we address the funding issues (and research priorities) that will likely result?



Ireland

- Drivers:
  - Energy
- Hydrate Potential: Mod. to High
- Current Program:
  - Integrated program of Government, Industry and Academia
  - Strong Science Community
  - Modest program at present
- Situation:
  - No short term gas shortage
  - Concern about future supply
  - IODP Porcupine Basin Expedition

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Ukraine

- Drivers
  - Energy
- Hydrate Potential: High
- Current Program
  - Minor Academic
- Situation
  - Oil and Gas industry dismantled under Soviet direction
  - Strong Academic Community
  - Low funding

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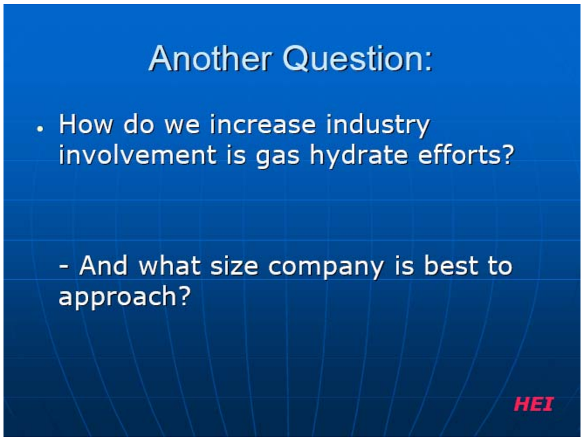

Another Question:

- How do we increase industry involvement is gas hydrate efforts?

  - And what size company is best to approach?

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Russia

- Early Leader on Hydrates
- Hydrate Potential: High
  - Production at Messoyakha
- Current Program:
  - Minor academic
- Situation
  - Large Conventional Gas Resource
  - Strong Academic Interest
  - Low Funding
- Opportunity:
  - Science Drilling at Messoyakha

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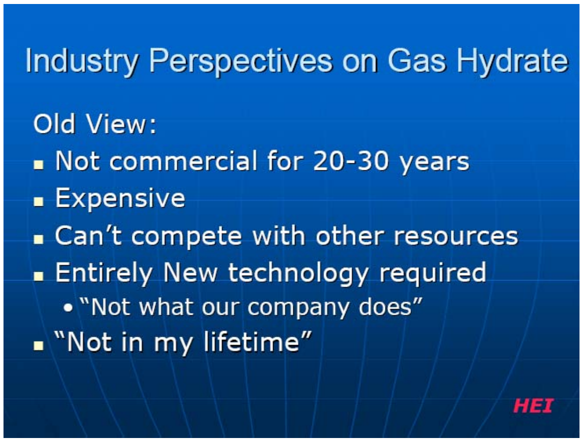
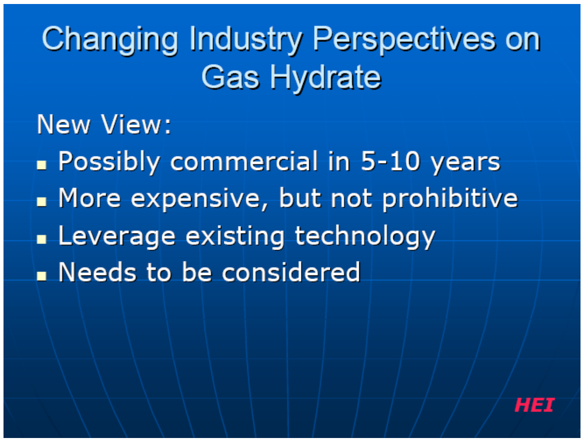


Industry Perspectives on Gas Hydrate

Old View:

- Not commercial for 20-30 years
- Expensive
- Can't compete with other resources
- Entirely New technology required
  - "Not what our company does"
- "Not in my lifetime"

HEI



Changing Industry Perspectives on Gas Hydrate

New View:

- Possibly commercial in 5-10 years
- More expensive, but not prohibitive
- Leverage existing technology
- Needs to be considered

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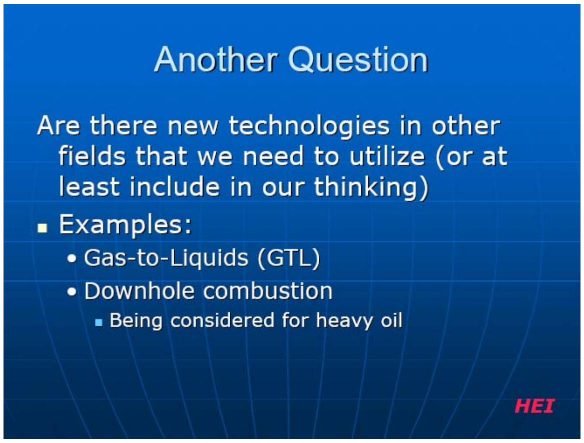
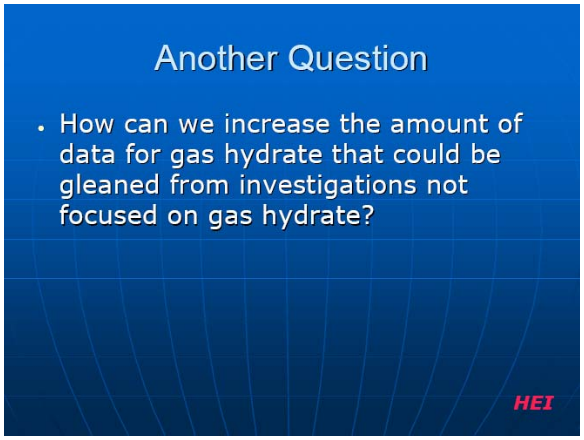


Another Question

Are there new technologies in other fields that we need to utilize (or at least include in our thinking)

- Examples:
  - Gas-to-Liquids (GTL)
  - Downhole combustion
    - Being considered for heavy oil

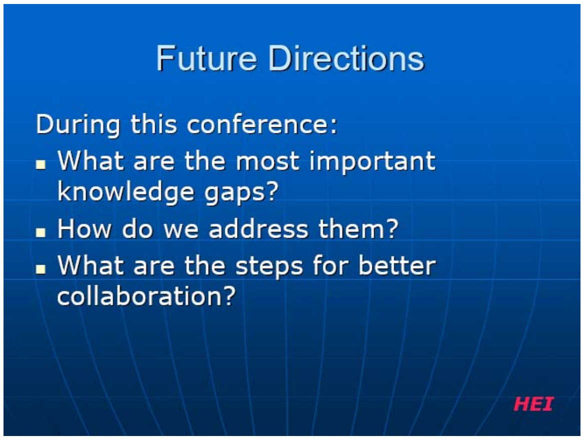
HEI



Another Question

- How can we increase the amount of data for gas hydrate that could be gleaned from investigations not focused on gas hydrate?

HEI



Future Directions

During this conference:

- What are the most important knowledge gaps?
- How do we address them?
- What are the steps for better collaboration?

HEI

IV. BREAKOUT SESSIONS

Workshop sessions were organized for discussion under the four workshop themes. Subsequent to these discussions the breakout sessions were organized for continued discussion between themes in Sessions 1 & 4 and 2 & 3. These four sessions were summarized on the final day of the workshop. The following text is based on the notes that were provided by the session chairs.

A. Session 1 – Chair, Warren Wood (NRL)

Methane Hydrate Resource Characterization and Distribution

Knowledge Gaps and Barriers in Hydrate Research

1. What are the knowledge gaps?

- Paucity of good quality, pertinent field observations, particularly;
    - Spatial and temporal hydrogeology (all scales) of methane hydrate bearing systems, (focused vs. diffuse flux, etc.)
    - Effects on hydrate hydrologic system of a time dependent thermal regime (primarily from seafloor or land surface T changes)
    - Seismic velocity vs. hydrate content in sediment (fine & coarse grain)
    - Electrical resistivity (log) vs. hydrate content in sediment (fine & coarse grain)

- A means of remote identification and quantification of hydrate better than the BSR, especially for permafrost hydrate, i.e. better proxies.
    - Can Electro-Magnetic methods be used more effectively?
    - How do bio-geologic factors affect gas hydrate production/accumulation (e.g. terrestrial vs. marine organic carbon?

- Geotechnical behavior of hydrate bearing sediment, i.e. sediment bearing strength, dynamics, and statics).

- Modeling?

- Laboratory?

2. What are the barriers?

- Cultural:
    - There is a lack of consensus in research focus and priorities
    - Biases are based on individual research goals.
    - We are too focused on BSRs in marine environments.
    - In many Labs there is only one person doing hydrate research, resulting in a lack of a “critical mass”.

- Logistic:
    - FUNDING/COST (lack of industrial involvement)
    - Datasets and knowledge are limited to current sites that are being studied.
    - Industry perspective vs. science (research) perspective. “Language Barriers”.

- Scientific:
    - Lab sample results are frequently not applicable to the in situ environment.
    - Simulating natural gas hydrate in the lab is extremely difficult.
    - It is very difficult to make hydrologic measurements in situ.

3. What are the Solutions?

- Cultural:
    - Investigate importance of local geology in GH formation (e.g. contrast regions that should have BSRs but don’t, vs. regions that do).
    - Integrate laboratory experimental results with models.
    - Link research efforts and activities to resource potential (industry perspective).

- Laboratory:
    - Standardize methodology for creating hydrates in the lab that best simulates the natural environment to more accurate determine the effect of hydrate on sediment physical properties (e.g. crack permeability, velocity and resistivity).

- Numerical:
    - Perform detailed hydrogeologic modeling.
    - Construct and manage central databases, with integration and synthesis.

- Field:
    - Dynamic areas require long term, continuous monitoring stations (e.g. Ole Miss and Neptune systems).
    - Use magnetic imaging to identify regions of gas hydrates.
    - Investigate shear wave properties of hydrate bearing sediments.
    - Investigate anisotropy to identify
    - discreet features for enhanced permeability.
    - Perform hydrologic testing (e.g. tracer injection experiments)
    - Use instrumented pressure core.
    - Use AUV’s for targeted surveys (not wide-areas).

4. Status of specific research programs: This includes a list of comments from briefings on several ongoing projects.

a. HERMES (Angus Best)

- EU 4 year project – Investigation of ecosystem hotspots along European Margin and west coast of Africa
  - Cold Seeps
  - Mud Slides
  - Mud Volcanoes
  - Cold Water Corals
  -
- Focus on benthic ecosystems

- Diverse team of researchers

- Multiple cruises planned
  - Some for Gas Hydrate research
  - Opportunities for international collaboration

- Program is underfunded; need to bring some funding

- General research goals are fairly well established. Flexibility lies with individual Chief Scientists

- Possible opportunities to link with efforts on Cascadia Margin (e.g. exchange of researchers?)

- Opportunities for technology sharing with Cascadia Margin and Gulf of Mexico (GOM)

- Current Capabilities Include:
  - OBS
  - Side-scan Sonar
  - ROV's w. high-resolution imaging
  - 3-D Seismics
  - Lab Facilities (geotechnical resonance column)

b. Jens Greinert - German Efforts (COMET, MUMM2), Cruises planned within HERMES and in New Zealand

- Temporal Methane Studies

- Sediment Samples (for AOM)

- Current Capabilities Include:
  - Side-scan sonar
  - Deep tow streamers
  - Lad facilities for pressurized studies

- Opportunities exist to get samples from cruises and to collaborate with other programs

c. Georgia Tech – Built a device to accept a PCS to do seismic, heat, and resistivity…need opportunities to test.

- Tentative plans exist in IODP areas to calibrate field measurement systems w/ well log data.

- Track 311 HYACE tools for pressure core transfers w/ Geaorgia Tech devices to be employed on Track 311.

d. NRL Capabilities (Warren Wood)

- Deep-tow seismics
    - DTAGS

- Detailed Temperature
    - Thermal Probes

- NMR

- Microbiology

- Stable isotopes
    - $\delta^{13}C$

- X-Ray CT

- Computer Simulations
    - Heat flow
    - Methane
    - Carbon flux

e. EU collaboration w/ Russia (80% Russia, 20% EU money) – INTAS

- Multiple research priorities including
    - Hydrate nucleation and growth
    - Study of hydrate accumulation
    - Kinetics

- Examples of joint research program:
    - ECOSSE –
    - Wellbore Stability w/ CSIRO in Australia

    - Effect of Repeated Formation and Dissociation of GH on Sediment Strength w/ NZ
    - TSEC – Towards Sustainable Energy Economy – CO_2 Hydrates

- *Capabilities* –
    - Extensive lab facilities for hydrate formation and dissociation simulations
    - Microglass formations micro-model
    - Porous media rig
    - Ultrasonic rig

f. IRELAND – Padraic MacAodha

- What is required for a Hydrate prospect?
    - Hydrocarbon Source
    - Timing
    - Migration
    - Reservoir Rock
    - Seal
    - Trap

- Resource risk assessment model based on seismic data, sediment type, and known reservoirs

- Capabilities:
    - Multi-beam and sub-bottom profiling
    - New (~46m) research vessel
    - ROV with deep tow and multi-beam

B. Session 2 – Chair, J. Ripmeester (NRC-Ottawa); Secretary – D. Sloan (CSM)

Methane Hydrates Kinetics, Dissociation and Biogeochemistry

1. Major Questions

- Decomposition of natural hydrate (production)
    - What are we decomposing?
        - Is it methane hydrate or a more complicated material?
        - What are the minor components? Will they need to be removed before utilization of gas?
        - How do they affect the P, T stability conditions? If the hydrate is more complex, will the degree of destabilization need to be increased over that for pure methane hydrate?
    - Decomposing the hydrate system – that is hydrate in sediment.
        - Can this be treated as an intrinsic hydrate decomposition (eg as defined by Bishnoi) plus the effect of heat transfer plus the effect of mass transfer?

        - How does permeability change with decomposition of hydrate in sediment?

Note: There was no general agreement on whether such a thing as "intrinsic hydrate kinetics" exists. First of all, we need to agree on a definition that can be tested by both experimentalists and modelers. Once a general approach has been agreed upon, the data generated can be used in developing predictive reservoir models.

- Formation kinetics (flow assurance, CO_2 sequestration)
    - Nucleation statistics (or induction times) – we need information that is independent of the experimental apparatus used.
    - Growth - data is needed to link growth (from the smallest observable particles) to formation conditions eg driving force, mass and heat flow limited conditions
    - We need to know the mechanism of hydrate inhibition.

Note: Very little work has been done, so the knowledge gaps are many. Modelers need information on nucleation statistics, the connection between hydrate morphology and formation conditions, etc. in order to compare their models with experiment. As well, the interaction of hydrate inhibitors with hydrates needs to be understood at a molecular level (modeling and experiment).

- Biogeochemistry
    - The methane cycle
        - We need to understand the role of microbial oxidation and the consumption of methane in the overall picture of the methane cycle.
        - Models are needed to identify the impact of the methane cycle on global climate and its effect on ecosystems; where does the methane released end up?
        - More extensive piston core, push core, and seismic analysis are needed to locate and understand the role of biogeochemistry in producing the deep hydrate resource.
        - As these measurements are very complex, there is a need for interactions to determine which parameters are the key ones and how to measure them.
        - Everything needs to be brought together, T profile, cores, seismic data, etc.

2. Session recorder (Tom Smith, ONR) offered a few observations on data availability, data sharing, and interdisciplinary and group collaboration and proposed a solution to the problem.

- Because of the great diversity of disciplines there are few opportunities for open discussion (different disciplines seldom meet in the same location).
    - Solution: set up a website (eg. hydrate@cineplex.org) that will allow open discussions of hydrate issues, listing recent research results, opportunities for

  - collaboration, funding opportunities, research infrastructure that is available or under development.
  - List serve is easy to set up, it will include e-mail addresses of all attendees,
  - Links will be added to other hydrate websites as well as the CODATA website for accessing archived data.

Note: Further plans on the nature and governance of the website were made at the plenary session on Wednesday.

3. Discussion around collaborations (also summarized in table produced by group chaired by Rick Colwell)

- IODP – 6 group members indicated an interest in joining the program – largely to obtain core samples or to go to PGC to carry out experiments
- Neptune – 1 group member indicated an interest in participating – geochemical data pertaining to methane flux in the water column
- Mallik 3 – likely to be mainly a prolonged production test (piggybacking science?)
  - Very expensive as an experimental site (~$60M) – indicated need for a reliable reservoir simulator with good predictive properties
  - As input, requires verification of fundamental concepts of hydrate decomposition (lab + microscopic modeling) before adding effects of heat and mass transfer, permeability. An excellent opportunity for the microscopic and reservoir modelers and experimentalists working at a variety of length scales to contribute.

C. Session 3 – Chair, Rick Colwell (INL)

Environmental Concerns: Seabed Stability and Ecosystem Health

1. Seabed Stability: In the area of seabed stability, knowledge gaps exist in recognizing the locations that are prone to destabilization, in sensor development and in the environmental effects of methane release on marine biota. Causes of seabed slips, whether or not connected to gas hydrates, are not well understood. Seabed slips can occur either as a single event, multiple progressive discrete events, or as a long-term continuous movement.

- The following knowledge gaps and barriers were indicated as impeding our understanding of the processes that control seafloor stability in locations where methane hydrates are present:

  - There is a general lack of data on pore pressure and temperatures in the sediments that might become destabilized and in sediments at control sites where destabilization is unlikely. This hampers the ability to model these systems.
  - There are new 3-D seismic tools that detect overpressure conditions (consider the presentation by Stefan Bunz); however, these tools appear to require calibration (i.e., careful measurements of the actual conditions in the sediments where the geophysical tools are used).
  - There is a lack of understanding of the temporal aspects of stability. For example, does slow creep occur in unstable areas yet are we unable to detect this slow motion? The events that initiate large slope failures are not known.
  - We do not understand how physical properties of gas hydrates change during formation and decomposition of hydrates in sediments. These events may impact seafloor stability.
  - The impact of biological processes on slope failure (e.g., the conditions or rates that permit microbial activities to cause an increase in sediment pore pressures) is unknown.

- The following experiments were discussed as ways in which some of the knowledge gaps might be addressed:
  - Arrayed systems, fitted with appropriate temperature and pore pressure sensors, may be able to detect conditions that precede slope failure. In addition to locations that are considered candidates for slope failure, sites that are considered control or background locations are important to instrument in this fashion as well although it is acknowledged that such efforts are expensive.
  - New versions (less expensive on a unit basis, more accurate than the currently used CORKS [circulation obviation retrofit kits]) of downhole tools or wellhead systems located on the seafloor would enable better experimental design and more accurate data to be collected in order to understand seafloor conditions that might initiate slope failure. An example of such a system is the Simple Cone Instrument for Measuring Parameters In-situ (SCIMPI).
  - The tools required to obtain 4-D bathymetry data are available; however these tools have not yet been used.

2. Ecosystem Health

- The following knowledge gaps and barriers were identified with respect to ecosystem health in hydrate-rich areas. After some discussion this topic area was broadly defined as referring to ecosystem health issues that range from local (e.g., ecosystems that develop on seafloor equipment or simply in the sediments) and global (e.g., the biome affected by large-scale releases of methane from seafloor sediments).
  - In addition to a general lack of knowledge regarding the size of the methane hydrate reservoir there is perhaps an even more severe absence of data regarding the size of the dissolved gas reservoir in marine sediments.

  - The impact of gas emitted as bubbles and from seeps is unknown. The fate of methane-C has not been traced through the biota to determine its impact on the local ecosystem and the biosphere when released.
  - We do not understand in any detail the temporal and spatial distribution of methane in the water column.

- The following experiments were discussed as ways in which some of the knowledge gaps might be addressed:
  - Uniform sampling of sediments and waters for dissolved methane needs to be conducted. In order to be attained this experimental need is dependent upon the development of better methane sensors. To achieve the necessary advancements these methane sensors must be more sensitive, robust, and inexpensive than existing sensors so that they can be deployed in a dense array where the data are required. Such sensors should have real-time data collection capabilities and should have cable tie-in options.
  - Corresponding sampling and characterization of the structural and functional attributes of microbial communities that exist in the sediments and waters needs to occur in order to tie the geochemical conditions (e.g., dissolved methane concentrations) to the biological community dependent upon this source of energy. Eventually, it will also be important to tie the responsiveness of the microbial community (i.e., methanotrophic activity) to these methane fluxes allowing a more thorough understanding of the dynamics of relevant microbial activities to this abiotic parameter.
  - Collaborative research in any of the knowledge gaps identified would be of value to the community. Specific note was made of efforts to build shallow water observatories like the Canadian VENUS project as well as cabled monitoring programs like the NEPTUNE and MARS programs. Additional programs where collaborative R&D might be possible towards addressing the key knowledge gaps include the U. Mississippi gas hydrate observatory, the Rhone Delta, and the Japanese cabled observation system. The establishment of undersea monitoring laboratories with nodes for attaching instrumentation using a remotely operated vehicle would be invaluable for testing of newly designed pressure, temperature, and methane concentration instrumentation. There may be worldwide opportunities for seafloor monitoring projects, although the overarching programs may not be specific to methane hydrates. None of these systems except VENUS will be placed in a location where seafloor stability may be an issue as typically, cable safety is integral to the equipment design. Nonetheless, these systems could be used for instrumentation development and measuring baselines for pressure perturbation studies.
  - ***Table 1*** was developed to identify near-term collaboration opportunities for international parties. The table identifies field sites (at least 12 listed) that will permit some level of collaboration in the sampling and characterization of hydrate formations. Some of these entries require careful editing by the responsible cruise organizers to determine the accuracy of the details that are noted in the table. As yet uncompleted, but deemed worthy of consideration

were “idealized sites” that might permit the description of the perfect location for investigating a particular process or problem. It was also proposed that the table include pending hydrate lab experiments that may include outside participants, experimental facilities for pressure studies, vehicles designed for seafloor investigations, tools, and sensors. As the table is developed to include tools or sensors it should include statements that indicate the objective, readiness, availability, contact, and web address pertinent to the equipment in question. A link to the NSF oceanographic sensors site will be important to prevent duplication of effort. Significantly, a web-based forum for cross-disciplinary discussions was proposed.

Table 1: Overview of near-term collaboration opportunities for international collaborations.

Site	**Topic Area**	**Objective**	**Ongoing Effort**	**Needs-Opportunities**	**Archiving Options**	**Contacts**	**Poster**	**Connected efforts**
Chile Jan-Feb 2006		Further exploration of gas hydrate seismic profiles and coring of a specfic mound with significant biological activity. Personnel development and training, geomechanical studies, economics	Seismic studies, piston coring, heat flow	Water column flux, 10 spaces available, open to suggestions if space is available, potential for newer research vessel, side scan sonar, understand origin of BSR and presence of methane, temporary on-site assignments (~ 1 year)		Rick Coffin, Juan Diaz-Naveas (idiaz@ucv.cl)	Yes	Lisa Levans, Chris German, World University Network (WUN), Census of Marine Life; INSPIRE (www.soc.soton.ac.uk/chess/se-pacific.html); UK Deep Oceans
Gulf of Mexico-microbial observatory (MC118) - June 2005 CFP due date	Microbial processes and products	5-10 years of monitoring (physical, biological, chemical) a known hydrate mound	Understanding biological systems in an active hydrate mound-microbial research	June 2005 CFP	All data/meetings open to public	Ray Highsmith, NIUST (ray@olemiss.edu)		
New Zealand-July 2006	Resource	Sediment recovery from seep sites, piston coring, seismic studies, dredging for carbonates		Open space for a large number of people				
New Zealand-2007		Biogeochemical cycling of methane of entire water column	(see also hydrate ridge rock drilling)	Ship is full, but data analysis opportunities available		Jens Greinert		
New Zealand-2008		DTAGS						
Hydrate Ridge			Rock drilling chemoherm (this technology may be available for other projects)			Jens Greinert		

Site	**Topic Area**	**Objective**	**Ongoing Effort**	**Needs-Opportunities**	**Archiving Options**	**Contacts**	**Poster**	**Connected efforts**
Cascadia-IODP						Michael Riedel (GSC)		
Cascadia-thermogenic (Barkley Cany)	ecosystem health	Characterization of hydrocarbon seeps; geochm, microbial and geophys	Past geophysical, geochem studies, some microbial	on submersible dives, possible remote participation; data and sample sharing; some berths possible		Ross Chapman (Uvic)	Sept 04 EOS paper	connected with IODP Cascadia
Japan						Hideo Narita		
MARS		Bore hole test facility	Test instruments and sensors, hydrology, geomicrobiology studies at well head, dispersal around sensors, seismic borehole	Borehole installation and engineering collaboration, technology development		Charlie Paull (MBARI)		
Venus - Fraser River delta	slope stability	understanding sediment dynamics, effect of gas in sediments, deltaic processes	multi-yr seabed cable infrastructure program	Data is fully web-accessible; possible new experiments can be added to the node but there are constraints (you have to pay)		Phil Hill (GSC)	Venus web site	Neptune-Canada
HERMES; Haakon Mosby, Storegga, Gulf Cadiz; started April 2005..for 4 yrs	seafloor stability	"Hot spot" ecosystems; habitat mapping driven by marine biology, find methane seeps, microbiologists	Continuation of work on continental margins; subjects: hydrates, seeps, cold water communities, stabilities	Numerous opportunties through contact with Phil Weaver; sample sharing and shipboard opportunities available with contact		Angus Best/Phil Weaver (Southampton)		
NRL						Warren Wood		

D. Session 4 – Chair, Art Johnson (HEI)

Methane Hydrate Future Development

The intent of this breakout session was to delineate a "roadmap" for the various themes of gas hydrate research and identify the critical barriers to achieving the respective goals. The themes considered were:

1. Resources
2. Hazard: (Seafloor and Slope Stability; Drilling and Production Effects; Flow Assurance)
3. Industrial Processes (Nanotechnology); (Sequestration of Substances)
4. Climate/Global Change
5. Material Storage and Transport Media

Due to time constraints, Climate/Global Change and Material Storage and Transport Media were not discussed, other than to define goals. The critical barriers identified for Resources, Hazard, and Industrial Processes are listed below, along with opportunities for moving the research forward. A more complete description of the components of each roadmap is included in the attached spreadsheet.

1. Resource

- Goal:
    - Delivery of natural gas, liquids from GTL (gas-to-liquids) process, or hydrogen

- Barriers:
    - There is a need to create a new gas hydrate exploration paradigm that goes beyond hunting for BSRs.
    - This will require more multidisciplinary prospect identification and characterization, using diverse geophysical and geological methods (cross-validation of interpretations).
    - There is a need for better models of reservoir performance and reserve characterization.
    - Except for settings like the GOM, Gas hydrates are affected by lack of transportation to market and competition from the co-located conventional resource.
    - In North America Gas Hydrate has to compete against other, more favorably located, non-conventional resources.
    - There is a need for development of a tailor-made hydrate technology (drilling, completion, etc.). The use of conventional approaches is unnecessarily expensive.
    - Technical and engineering innovations need to be explored that would improve the competitiveness of Gas Hydrate.

    - There are unrealistic community and industry expectations for immediate success.
    - There is a need for a better understanding of the detailed response of the reservoir to production (reservoir geotechnical stability, etc.).

- Opportunities:
    - Technology transfer from and to other non-conventional resources.
    - Employ new technologies and tools such as Autonomous Underwater Vehicles (AUV's) etc. to improve prospect identification and characterization.
    - This is an opportunity for a very big R&D win by improving reservoir performance (new reservoir paradigm).
    - Fracturing can be used to create a larger artificial surface area of dissociation.
    - Other unconventional resources (such as heavy oil) face some issues similar to those of gas hydrate. There is an opportunity for effective communication of barriers to these other potential solution providers.

2. Hazards (Seafloor and Slope Stability; Drilling and Production Effects; Flow Assurance)

- Seafloor and Slope Stability
    - Goals:
        - Safe and Sustainable Marine and Polar Operations
        - Enhanced Coastal Zone Security.
        - Minimize Environment Impact.
    - Barriers:
        - Identifying hydrate occurrence and concentration, as a function of lithological characteristics.
        - Potential interactions with natural processes (forcing functions).

- Drilling and Production Effects
    - Goals:
        - Minimize Environment Impact.
        - Minimize Cost Impacts.
        - Safe operations.
    - Barriers:
        - Identifying hydrate occurrence and concentration, as a function of lithological characteristics.
        - Potential interactions with anthropogenic processes (forcing functions).
        - Inability to distinguish the hazard attributed to gas hydrate versus free gas trapped below gas hydrate.
        - There is a reporting and perception gap, with possible incidents either unrecognized as being hydrate-related and/or unreported as such.

- Flow Assurance

        - Goals:
        - Minimize Environment Impact.
        - Reduce cost and lost time.
    - Barriers:
        - In the managed risk approach are there barriers (material interactions, regulations)?
        - The lack of kinetic models is a barrier to managed risk.
        - There needs to be a paradigm shift from remediation to data collection and prevention.

3. Industrial Processes (including Nanotechnology and Sequestration of Substances)

- Desalination and Water Treatment
    - Goal:
        - More cost effective and environmentally competitive desalination processes
    - Barrier:
        - Business Goals may not be compatible with collaboration.

- Dewatering
    - Goal:
        - More cost effective and environmentally completive dewatering processes
    - Barrier:
        - Business Goals may not be compatible with collaboration.

- Gas Separation
    - Goal:
        - More cost effective and environmentally completive gas separation processes
    - Barrier:
        - Business Goals may not be compatible with collaboration.

- Sequestration
    - Goal:
        - Reduction of Point Source CO_2 emissions to the atmosphere.
    - Barriers:
        - There are special challenges to porous media sequestration.
        - Kinetics
        - Business Goals may not be compatible with collaboration.
        - Regulatory Hurdles.

- New Materials
    - Goal:
        - New materials-based products and processes
    - Barriers:

        - Undefined Applications
        - Lack of Business Sense by Scientists

4. Climate/Global Change

- Goal:
    - Understand the Mechanisms and Impacts of gas hydrate on Global Change.

5. Material Storage and Transport Media

- Goal:
    - Cost-Effective and Safe transportation of materials

Note: All participants provided valuable contributions in the breakout session. In particular, the efforts of rapporteur Brian Rehard (LMI Government Consulting) and Kirk Osadetz (Geological Survey of Canada) are especially appreciated.

E. Discussions Between Sessions 1 & 4 – Chairs W. Wood (NRL) and A. Johnson (HEI)

1. Theme 1 Summary of identified knowledge gaps, barriers, and priorities for research and collaboration in Methane Hydrate Resource Characterization and Distribution (Warren Wood).

- Gaps:
    - Paucity of good quality, pertinent field observations
    - A means of remote identification and quantification for gas hydrate other than a BSR
    - Modeling?
    - Laboratory?
    - Geotechnical behavior of hydrate bearing sediments

- Barriers:
    - Cultural
        - BSR's
        - Individual Research goals
        - Lack of critical mass
        - Lack of consensus
    - Logistics
        - Funding/Cost
        - Datasets and knowledge are limited to current sites being studied
        - Lack of industrial involvement
        - "Language barriers" between science and industry
    - Scientific
        - Lab samples are frequently not applicable to the in situ environment
        - Simulating natural gas hydrates in the lab is extremely difficult.

        - Very difficult to make hydrologic measurements in situ

- Solutions:
    - Cultural
        - Investigate local geology in gas hydrate formation
        - Integrate lab experiments with models
        - Link research efforts and activities to resource potential
    - Laboratory
        - Standardize methodology for creating hydrates in the lab that best simulates the natural environment.
    - Numerical
        - Perform detailed hydrological modeling
        - Construct and manage central databases, with integration and synthesis
    - Field
        - Dynamic areas require long-term, continuous monitoring stations
        - Use magnetic imaging to identify regions of gas hydrate
        - Investigate sheer wave properties of hydrate bearing sediments
        - Investigate anisotropy to identify discreet features for enhanced permeability
        - Perform hydrologic testing
        - Use instrumented pressure cores
        - Use AUV's for targeted surveys

- Capabilities presented in Theme 1, Day 2 Session 1
- Use Roadmapping to identify gaps, and implement solutions

2. Theme 4 Gas Hydrate Futures Roadmap Summary (Art Johnson):

- Futures Broken down into Themes
    - Resources
    - Hazard
    - Industrial Processes
    - Climate Change
    - Material Storage and Transport Media

- Goals/ Deliverables Identified

- Each Theme Broken down into categories
    - Category of accumulation
    - Prospect of opportunity
    - Valuation
    - Exploration and development
    - Transportation/Logistics
    - Linkages (between Scientific Community and Industry)
    - Barriers

    - Opportunities
        - In most cases, barriers and opportunities are the same

- Examples of barriers/opportunities identified in Roadmap:
    - Cannot image hydrate bearing sands
    - Low hydrate bearing substrates

- General Comments:
    - Can we create a new gas hydrate exploration paradigm?
    - Can knowledge gaps identified Theme 1 be addressed through research and "plugged into" Roadmap to remove barriers?
    - Different approaches to hydrate bearing sands vs. mud mounds, vents, and other marine gas hydrates (Fisheries/Forestries Models)

F. Discussions Between Sessions 2 & 3 – Chairs, J. Ripmeester (NRC-Ottawa) and R. Colwell (INL).

1. Identification Matrix for Field Studies and Projects (that might be opportunities for collaborations) (MS Excel, ***Table 1***)

- Includes:
    - Site
    - Topic Area
    - Objectives
    - Ongoing Efforts
    - Needs/Opportunities
    - Archiving Options
    - Contact(s)
    - Poster Presented?
    - Connected Efforts

- Examples of Upcoming Efforts (with varying opportunities for collaboration):
    - Chile –Jan-Feb 2006
    - GOM Microbial Observatory RFP – June 2005
    - New Zealand 2006
    - New Zealand 2007
    - New Zealand 2008
    - Hydrate Ridge – Partially funded; needs a ship
    - Cascadia IODP – Sept-Oct 2005
    - Cascadia thermogenic (Barkley Canyon) – Ongoing 2006
    - Japan?
    - MARS – Monterey Canyon; IODP (MBARI) effort; Bore hole test facility
    - VENUS – Late 2006; Fraser River delta

  - HERMES – EU (Cadiz Canyon, Storegga, Haakon Mosby Mud Slide, Mediterranean, Nile Delta, Black Sea, and others); Started April 2005; 4 year project

- Idealized Sites (Wish List)
  - Seafloor Stability
  - Resource Characterization and Distribution
  - Ecosystem Health
  - Kinetics, Dissociation
  - Biogeochemistry

- Theme 2 identified ongoing efforts for kinetics/biogeochemistry studies
  - IODP Efforts
  - MALIK Effort – Makenzie Delta; Winter 2006-2007
    - A further study of Malik would be a good opportunity for supporting modeling opportunities, including hydrate production at the micro and macro level. Modelers should feed data needs into experimental program.

- Other future sites?

- Antarctica?

- Additional tables might include:
  - Technology, tools, sensors:
    - Technology
    - Objective
    - Readiness
    - Availability
    - Contact
    - Cost?
  - Specially designed experimental facilities
  - Information technologies, databases
  - Models

2. Linked discussion (data) forum.

- Information, literature

- New results, ideas
  - Woods Hole has a large on-line database that can be used for data sharing.

- Experimental design
  - It is important to get engineer input on data needs to sensor developers.

- Collaborative opportunities
    - ***Forum for cross-disciplinary discussions is missing. A web-base discussion group and list server should be designed to facilitate this communication.***

- Funding opportunities

3. Sensor Development

- Critical to development of sensors are:
    - Spatial constraints
    - Required measurements
    - Measuring environment

- For power usage reasons, sensor arrays are best optimized if they only turn on based on a need to take data.

- Distributed sensors arrays for continuous pressure and temperature would be useful.

- Wood's hole presented information on underwater in-situ chemical sensing and imaging (e.g., mass spec units that could measure concentrations of methane (μmoles/liter)).

V. WORKSHOP SUMMARY

A. Summary of the Breakout Topic Discussions.

The 4th Workshop on International Collaboration on Methane Hydrate Research and Development was intended to facilitate the organization of field and laboratory research collaborations among international partners. Workshop presentations and discussions through all sessions were organized to enhance the discussion of knowledge gaps in gas hydrate research, integrate global perspectives on methane hydrate research themes in different nations, and initiate plans to integrate field exploration, laboratory experiments, and theoretical modeling. Discussions and planning were conducted on the basis that new funding will not develop for this program but cost and technology sharing, associated with database development under the different national focuses could enhance each interested researcher's program activity. There were four general topics: 1.) methane hydrate resource characterization and distribution; 2.) methane hydrate kinetics, dissociation and biogeochemistry; 3.) environmental concerns including seabed stability and ecosystem health, and 4.) future development of methane in hydrates as an energy source. Sharing in this effort during the discussions included available data, international expertise, methods and technology, results and models. The workshop format was initial discussion of the four themes, individual theme breakout discussions, and integration of the themes for concluding remarks.

The open discussions during the breakout sessions introduced detailed information about several current and planned hydrate research programs that was shared with all the participants. This information provides the basis for establishing new collaborations. The concluding plenary session focused on establishing an effective mechanism to sustain the interactions that were developed at the workshop, and provide a means for disseminating new information. The active projects discussed are listed below with lead scientists to contact for further discussion. This summary is not intended to provide an overview of research by all scientists in this field and working in the regions mentioned. Instead, it is intended to provide the potential for researchers that participated in the workshop to expand collaborations, share technology and platform support. Regions discussed for potential collaboration include, the Texas-Louisiana Shelf in the Gulf of Mexico, Cascadia Margin along southwestern Canada, the mid Chilean Margin, several regions off western Europe and the coast of New Zealand.

The general consensus for future development of international methane hydrate research was that the priorities includes resource assessment, environment and platform hazards, industrial processes, climate change, material storage and media transport. The potential for success in this effort is sharing the current activities, knowledge and opportunities in scientific, industrial, political, social and economic contexts. The international plan for the goals of the developing program needs to include integration of the national deliverables, sharing opportunities, sharing the exploration data base, forming stronger linkages between the scientific and industrial communities. An international broadcast of this activity could provide effective lobbying with government and industry in different nations. Success of this international effort would result in the formation of a new gas hydrate exploration paradigm.

With the development of an international program there is a broad base of shared knowledge gaps on scientific, financial, cultural and political topics. In terms of science and exploration technology there is paucity of quality, pertinent field observations. There is a limited data base on the spatial and temporal hydrogeology of methane hydrate bearing systems. While seismic surveys for BSR distributions are the primary approach for preliminary hydrate surveys it has been well established that hydrates are present in sediments where the BSR is not detected. There is a strong need for a more thorough survey of the diffusive vs. advective flux in sediments. Surveys need to address the changes in hydrate systems through time dependent thermal regimes. Models for seismic velocity to predict hydrate content in sediments need evaluation for application to fine and coarse grain variation. Further development of electric resistivity coupled with the seismic surveys could enhance the capability to quantify hydrate distributions. Biogeochemical influence on the methane hydrate formation, stability and cage occupancy needs more basic research. Further development also needs to include understanding of the geotechnical behavior of hydrate bearing sediment in terms of sediment strength, dynamics and statics. There is also a need for interaction between field programs and laboratory research, since the results from laboratory experiments are not always applicable to natural environments. This occurs because simulation of natural gas hydrate in the lab is extremely difficult, and hydrologic measurements are difficult to obtain *in situ.* Standardized laboratory methods will help to compare the experimental data base.

A major limitation in the field program for methane hydrate exploration is the sampling techniques for in situ data acquisition. In situ pressure cores would provide samples for thorough physical, chemical and biological parameters. Analytical instruments on the pressure cores would further advance the in situ data base. There is a need to test and calibrate new seismic survey tools. This effort could provide better 3-D mapping and initiation of 4-D mapping of hydrate distributions. A need stated during discussions included investigation of shear wave properties of hydrate bearing sediments, as a means to determine anisotropic variation in the sediment permeability. Long term surveys at monitoring stations in dynamic regions with in situ data acquisition will start to access variations in methane fluxes and hydrate bed stability.

Many programs in methane research are undermanned and do not have a critical mass to address multidisciplinary research questions. There are strong "language barriers" between the science and industrial communities. Biases on individual national goals will impede the international development. The international development of this topic needs to combine consensus in the research focus and priorities. An increase in the international collaboration will increase the necessary critical mass. Specific approaches for enhancement of the international collaboration that were presented during the discussions included comparisons of local geology in the gas hydrate formation, an integration of laboratory experiments with models, and a combination of the applied methane hydrate exploration with basic science topics. Experiments and field sampling needs to be designed to obtain data that addresses the temporal aspects of hydrate stability, hydrate physical property parameter changes during formation and destabilization, biological cycling of methane and the result of methane flux into the water column and atmosphere.

B. Current and Future Sites for Methane Hydrate Collaboration.

1. Cascadia Margin:

The region off Vancouver Island is one of the most comprehensively studied gas hydrate occurrences in the world. The presence of gas hydrates at depth in the sediment and at the sea floor is well established from previous research over the past 15 years at the northern Cascadia Margin. Seismic surveys have shown the general distribution of hydrates over the area, as indicated by the presence of a bottom simulating reflector (BSR). The vertical distribution has also been studied at selected sites of high-density survey grids, and at locations of drilling sites of the Ocean Drilling Program Leg 146. Other geophysical studies were carried out including piston coring and related physical property and geochemistry studies, heat-flow studies, and bottom video observations. The occurrence of hydrates is related to the hydrothermal fluid flow in the accretionary prism, and to the geological structure of the sediments within the hydrate stability zone.

There are two areas within the margin where extensive collaborative research is being done at present. The Barkley Canyon hydrate site was discovered and studied during a series of three collaborative research cruises between UVic (R. Chapman) and NRL (R. Coffin) that used the ROPOS submersible to survey the site and characterize the geochemistry of the hydrocarbons. The site is a small plateau about 1 square km and 850 m deep on the north wall of Barkley Canyon, a submarine canyon about 100 km off the west coast of Vancouver Island. The site consists of several hydrate outcrops clustered within a few 10s of metres of the central location. The hydrate is exposed as sheets up to 8 m long on the sea floor, and on the flanks of thinly-sedimented mounds about 2-3 m high. The sediment is primarily very fine grain silty mud. Near the mounds the sediment contains gas, quantities of light oil, and small hydrate fragments, and there is evidence of episodic gas emission. The seep supports extensive colonies of chemosynthetic communities consisting of several species of vesicomyid clams clustered around the hydrate mounds. Thin bacterial mats cover large portions of the hydrates and sediment on most of the mounds.

Our results from the initial survey and a subsequent visit in 2003 indicate that the site is a highly localized thermogenic gas and hydrocarbon seep. The Barkley Canyon hydrates are unique compared to hydrates recovered from shallow (8 m) piston cores at other sites nearby in the northern Cascadia Margin and from Hydrate Ridge farther south off Oregon, which are primarily of microbial origin.

In addition, the Barkley Canyon site is one of the nodes for the Neptune Canada sea floor cable program. The site will be instrumented for long term study of the hydrate system. NEPTUNE provides the opportunity to investigate two fundamental research hypotheses about the formation of hydrates in this region:

- Hydrates form at the seafloor in areas of high fluid or gas flux, which implies that local high-permeability conduits focus the methane supply.
- In regions of low diffuse fluid and gas flux, hydrate is concentrated near the BSR and decreases toward the seafloor.

These hypotheses are expanded into science questions:

- What factors control the formation and dissociation of hydrate at depth in the sediment and at the sea floor?
- What is the response of the hydrate system to periodic temporal variations in the bottom environment, and to episodic events caused by tectonic forces?
- What is the flux of methane and other hydrocarbons at the sea floor?
- What are the relationships with microbial processes in the sediment and in the water column?

The other area of interest is near ODP site 889 that was drilled in 1992. Most recently, the IODP drilling program supported Expedition 311 to further constrain the models for the formation of marine gas hydrate in subduction zone accretionary prisms. The objectives included characterizing the deep origin of the methane, its upward transport, its incorporation in gas hydrate, and its subsequent loss to the seafloor. The main attention of this expedition was on the widespread seafloor-parallel layer of dispersed gas hydrate located just above the base of the predicted stability field.

The expedition included coring and downhole measurements along a transect of four sites across the Northern Cascadia accretionary prism. The sites will track the history of methane in an accretionary prism from (1) its production by mainly microbiological processes, (2) its upward transport through regional or locally focused fluid flow, (3) its incorporation in the regional hydrate layer above the BSR or in local concentrations at or near the seafloor, (4) methane loss from the hydrate by upward diffusion, and (5) methane oxidation and incorporation in seafloor carbonate, or expulsion to the ocean. An additional Site is planned within an active cold vent, near former ODP Site 889, to characterize an environment of focused fluid flow associated with near-seafloor massive gas hydrate deposits and seafloor carbonate formations.

This expedition builds on the previous Cascadia gas hydrate drilling of ODP Leg 146 and on more recent ODP Leg 204 off Oregon. Important experiments for this expedition include, (1) logging-while-drilling (LWD), (2) wire-line logging, (3) intensive coring and subsampling, and (4) pressure core sampling (PCS/HYACINTH) of gas hydrate, and fluid recovery under in situ conditions.

Point of contacts for further information on this activity include Ross Chapman (University of Victoria, chapman@uvic.ca), and Richard Coffin (NRL, rcoffin@ccs.nrl.navy.mil).

2. Mid Chilean Margin:

An international collaboration for hydrate exploration has been further developed through planning at previous workshops. During 2003 and 2004 two methane hydrates surveys were accomplished along the mid Chilean coast. For this research there was participation by scientists from 5 nations. Scientists from The Catholic University of Valparaiso, Naval Research Laboratory, Canadian Geological Survey, University of Toronto, University of Tokyo, AIST Tskuba, Virginia Institute of Marine Science Rice Unviresity, Milbar Hydrotest, Inc., University of Concepción and University of Bremen participated in the two expeditions. Geophyscial, geochemical and biological parameters were integrated on the two cruises. This research is focused on the NRL objectives to develop international collaboration on methane hydrate exploration and Chile-FONDEF goals to locate hydrates along the Chilean coast in terms of distribution and methane content for understanding the available energy and geological hazards. This effort integrates future energy exploration with ocean and climate research topics.

Piston coring, heat flow and biological sample sites were selected in two regions on the basis of previous seismic surveys during April 2003 and work conducted by scientists at the University of Concepción. The coring and heat flow, along the previous NRL seismic line (DTAGS), was run between 36’10.38S, 73’35.72W and 36’12.50S, 73’3976W. Sulfate, sulfide, methane, chloride, and DIC profiles in piston core pore water samples, heat flow data and seismic profiles were combined to confirm the presence of hydrates in this region. An additional sample region was selected at the base of a 40 meter sub-sea mound located at 36’22S, 73’43W where biologists from University of Concepción had located large concentrations of benthic organisms.

Along the previous DTAGS line, the selection of piston coring and heat flow sites was based on a review of previously collected seismic data. Selection included regions with strong shallow and deep BSRs and regions through gas wipe out zones. There was a strong correlation between the heat flow and piston core data. In the gas wipe out regions, high heat flow values were observed. The piston core profiles through these regions were found to have extremely shallow slopes for the methane and sulfate profiles with minimum values measured between 25 and 250 cm. The deepest geochemical profile was measured at the top of the BSR with transition to minimum values observed at approximately 700 cm. The combination of the heat flow and piston core data suggest a strong vertical migration of methane from deep sediments at site where seismic data indicate a gas wipe out and possible perturbation of the BSR.

Another objective in during this cruise was the integration of geochemical data with the biological communities over the methane hydrate sediment regions. Recent benthic surveys in the bathyal area off Concepción revealed important clues indicating the existence of methane seepage and related biological chemosynthetic communities (Sellanes et al. in press). Shell fragments of two species of bivalves of the genus *Calyptogena* (VESICOMYIDAE) and one species of *Acharax* (SOLEMYIDAE) were retrieved in two dredge hauls off Concepción

(36°21.46’S 73°44.08’W, water depth 934 m, and 36°16.40’S, 73°40.70’, 651 m). An important quantity of carbonate crusts were also collected, indicating that anaerobic oxidation of methane is occurring. The accompanying, non-obligate chemosynthetic fauna from one of the hauls was very diverse, containing several species apparently new to science. The geochemical data collected from this region found shallow profiles for methane and sulfate. Hydrate samples were obtained through one of the cores at the base of this mound. On board hydrate gas analysis resulted in a conclusion that the hydrates are from biogenic origin. Again there were no large sulfide profiles in this region.

Final data interpretation will be completed with a survey of additional parameters in the laboratory. Geochemical and biogeochemical parameters will include stable carbon and radiocarbon isotope analysis of a variety of carbon pools to address the biological cycling of methane. Microbial community diversity and analysis of low molecular weight acids will assist in this study. With regard to organisms collected in trawls at the sediment water column interface, it is expected that the species assemblages associated with cold seepage off Chile are similar in structure to others reported elsewhere, but should bear an important number of endemic species, many of them still unknown to science. Stable C and N isotopic signatures of the fauna will also be analyzed in order to determine the extent of the reliance of heterotrophic benthos in primary production derived from chemosynthesis.

Data collected from this survey will be used to stage subsequent research topics and focus areas in this region. The next research cruise is planned for January-February 2007. Points of contact for collaborative research plans are Dr. Juan Diaz (jdiaz@ucv.cl).

3. Coast of New Zealand:

The Hikurangi Margin offshore of New Zealand’s east coast is an active continental margin where the Pacific Plate is being subducted beneath the Australian Plate. Its geologic similarity to the Nankai Trough, Japan’s focus area for future production of gas from hydrates, combined with its proximity to major population centers (Auckland, Wellington), make this margin the most promising gas hydrate province off New Zealand for possible future gas extraction. Ubiquitous BSRs indicate wide-spread presence of gas hydrates over a large area. The strong variability of BSR strength suggests locations of focusing of gas supplied into the gas hydrate zone, a key requirement for the formation of gas hydrate “sweet spots”, areas of highly concentrated hydrate. A state-of-the-art seismic transect was acquired by GNS in 2005 with the M/V “Pacific Titan” across several candidates for such “sweet spots”.

The current plan is for June 2006, during which an interdisciplinary field exploration will be carried out in the region 176° 30’E – 39°30’S S to 178°30’E – 41°00’S off the north-eastern coast of New Zealand on the Hikurangi Margin. In this effort different geophysical and geochemical methods will be applied for the detection and characterization of gas hydrates. Technical capability for this project will be mixed with expertise from New Zealand, UK, Germany, Australia and the US. The result of this experiment, together with the compilation of previous information will initiate characterization of gas hydrates in this region. The fact that this project depends on the collaboration of foreign research centers and experts, means an invaluable exchange of technological information useful for the resource exploration in the New Zealand coast. This collaborative study will focus on several “sweet spot” candidates along the PT05 transect. During these cruises geochemical methods and heatflow probing will be applied for the detection and characterization of gas hydrates. Geochemical analysis will include the sediment carbon content, porewater methane concentrations, vertical pore water sulfur speciation gradients, and carbon isotope analysis of carbon pools related to the hydrate formation, lattice saturation and content. In addition to the work in the sediment methane and hydrocarbon leakages from hydrate reservoirs that are exposed towards the ocean floor and consequences for the ocean carbon balance, including chemical and biological conversion will be studied. This will be compared to corresponding rates of methane leakage to the atmosphere. Heatflow will be conducted for prediction of the vertical fluid flow. Preliminary exploration is Research objectives for the Hikurangi Margin include:

- Quantify heat, fluid, and solute flux in and around possible concentrated gas hydrate deposits using a combination, thermal measurements, and geochemical analyses of sediment cores.
- Determine the source and migration paths of gas for gas hydrate formation via seismic imaging combined with elemental isotope analysis on sediments, geotechnical laboratory studies, and reservoir-style modeling.
- Initiate genetic characterization of the microbial assemblage in hydrate-laden sediments.

Current participants in research off Hikurangi Margin include:

- Institute of Geological and Nuclear Sciences (Lower Hutt, New Zealand),
- Naval Research Laboratory (Washington, DC, Stennis Space Center, USA)
- Commonwealth Scientific and Industrial Research Organisation (Perth, Australia)
- University of Hawaii (Honolulu, USA)
- University of Otago (Dunedin, New Zealand)

Point of contacts for further information on this activity include: Ingo Pecher (GNZ, i.pecher@gnz.nz), Richard Coffin (NRL, rcoffin@ccs.nrl.navy.mil) and Warren Wood (NRL, warren.wood@nrl.navy.mil).

4. **Texas-Louisiana Shelf:**

The northern Gulf of Mexico contains conditions suitable for gas hydrate: appropriate pressures from continental slope water depths, moderate thermal gradients typical of continental margins, and abundant methane from a well-known leaky petroleum system. Two sites have been surveyed for methane hydrate distribution and intensity, Atwater Valley and Keathley Canyon. In support of the Chevron-Texaco JIP (CT) for methane hydrate exploration two research cruises, lead by NRL and USGS, were designed to assist in selection of the deep drilling test site. These cruises integrated seismic surveys by USGS (D. Hutchinson) with heatflow probing and geochemical analysis of shallow pore waters to predict deep sediment hydrate distribution. A multidisciplinary study involving government agencies, industry, and academia, has collected 2D and 3D multichannel seismic reflection data, made heat flow measurements, and analyzed geochemical constituents in piston cores in order to understand the subsurface distribution, behavior, and seismo-stratigraphic indicators of gas hydrate.

The research outlined in this proposal is designed to enhance the geochemical and heatflow analysis of Atwater Valley and Keathley Canyon, contribute to basic research on the biogeochemical influence on methane cycling and provide background data for the CT drilling in this region. Development of the geochemical and heatflow data set and comparison with the deep well drilling is designed to provide a thorough approach for preliminary site surveys, prior to site selection of drilling sites. Research is planned to accomplish:

1. Further calibration of piston coring, heat flow and seismic data for prediction of deep sediment methane hydrate beds. Data from previous cruises and work outlined in the proposal will be compared with the Chevron-Texaco deep drilling to assist in understanding the variation in the seismic and geochemical data.

2. Increase data set for interpretation of the Chevron-Texaco deep drilling on Atwater Valley and Keathley Canyon.

3. Provide geochemical interpretation of data collected in bathymetric mapping and DTAGS surveys during February 2005 (Gardner, Gettrust and Wood, NRL DC and Stennis).

4. Contribute to the understanding of biogeochemical influence on methane cycling (production and oxidation).

Future plans for subsequent research at this location are underway and open for sharing collaborative research plans. Researchers interested in collaborating in research at this location should contact Dr. Richard Coffin (rcoffin@ccs.nrl.navy.mil) or Dr. Warren Wood (warren.wood@nrlssc.navy.mil).

C. Overview of International Field Research and Survey Integration Approaches.

Assessment of the gas hydrate bearing sediment volume has been made using various techniques including seismic surveys, well logging, electromagnetic surveys, geochemical investigations, and vertical fluid flow predictions using temperature gradients. Chloride anomalies in interstitial water are believed to be a reliable method of estimating gas hydrate amounts on small geographic scales, as documented during Ocean Drilling Program (ODP) leg 164. Broad site evaluations are accomplished with seismic surveys. Seismic surveys have developed over the last 40 years for observation of bottom simulating reflector (BSR) and the corresponding methane hydrate distribution. Subsequently, single and multichannel seismic measurements have been performed to elucidate the relationship between BSR and hydrate reservoirs and to estimate the extent of these reservoirs.

Vertical seismic profiling in areas including the Cascadia Margin and Blake Ridge, have been supported by deep sea drilling activity. Recent integration of geophysical and geochemical data for coastal methane hydrate exploration demonstrate an inconsistency in data sets for the identification of hydrates in sediments. Regions with strong “wipe out” zones do not correspond with shallow sulfate-methane interfaces and shallow sulfate-methane interfaces are found in regions that the BSR is not found. These data sets show the need for more thorough geophysical and geochemical parameter integration for hydrate exploration. The following text is an overview of current approaches that is being conducted by the workshop attendees:

1. Seismic Survey Approaches – Seismic approach in this summary are presented in terms of the NRL Advanced Research Initiative in methane hydrate exploration. The existence of seafloor seeps has been known for many decades because their seafloor manifestations can be easily identified on a variety of acoustic and seismic mapping systems. However, to determine the importance (acoustically, chemically, and biologically) of these methane conduits and reservoirs to the local and global environment requires an understanding of 1) the quantities of methane present; 2) how it is distributed around the seep; 3) the magnitude of methane flux through the seafloor; and 4) how quickly the quantities, distribution, and flux may change in the event of stimuli such as changes in temperature, pressure, or hydrologic head gradient.

Historically, obtaining accurate observations has been difficult due to 1) the remote nature of the hydrate seeps, (typically in water deeper than 500m), 2) the strong lateral variability of the seeps, which is frequently larger than the uncertainty in the position of the observing platform (ship or ROV); and 3) the large and complex affect of gas and precipitate on acoustic signals. Further, because the hydrology, chemistry and physics of these systems are so inter-related, there does not yet exist a single, comprehensive, numerical model that is sufficient to predict the distribution of methane and methane hydrate at seafloor seeps.

Summary of NRL Science Objectives

We seek to understand the mechanisms and habits of methane emplacement at seafloor seeps through detailed seismic, thermal, chemical and biological constraints on numerical simulations of methane flux. Because of the strong affect of gas on acoustic wave propagation, DTAGS seismic imaging constrains the spatial extent of gas with an accuracy of 1-2m over scales of 100s of meters vertically and laterally. In a methane hydrate system, the gas/no-gas boundary can frequently be used to infer the broad scale (10s to 100s of meters) thermal regime within the sediment. Individual thermometry measurements not only aid the constraint of the thermal regime but also constrain the fluid flux. The thermal gradients over the seep constrain the heat flux that, with knowledge of the fluid temperature and heat capacity, can be used to determine the overall fluid flux. Combining the temperature, pressure, and fluid flux throughout the system with methane solubility yields constraints on methane transport from the sediment to the ocean. The methane flux is also constrained by direct chemical measurements of methane in cores, or more frequently, sulfate gradients that indicate the depth to methane in the system. Measurements of the micro-biota within local reservoirs of methane gas and hydrate will constrain the styles and rates of production and consumption of methane in its various stages of flux and residence in the seep system. The NMR measurements, by detecting the amount of liquid water in a given sample (and how that changes as any hydrate in the sample dissociates) constrain the hydrate concentration within a sample, and where the hydrate is forming within the sediment pores, (important for how the hydrate affects the sediment acoustics)

Although several seep sites have been studied in detail with many techniques, some similar to the ones we have used and plan to use, we know of no sites where measurements of such detail have been brought together comprehensively with the hydrology to quantify the methane emplacement and flux through the seafloor.

NRL Approach: Observations as Constraints on Numerical Models

The development of a completely new model was considered beyond the scope of the current ARI. Therefore, we intend to achieve the modeling objectives by breaking the problem into smaller, tractable problems Two approaches to modeling are currently being used, a more standard, finite element package, and a more developmental technique based on lattice gas. The finite element code SUTRA, developed by the USGS has been used in preliminary modeling of fluid conduits to determine the extent to which heat transport via fluid advection perturbs the methane hydrate stability zone. In this work the seismic image, due to its acute sensitivity to gas, is used to constrain the extent of gas below the seafloor. In some cases this gas boundary marks the interface between free gas and methane hydrate, and can be used to identify the PT boundary associated with the base of methane hydrate stability. The lattice gas technique generates 3-D simulations of methane-pore water flux through complex, micro-scale media, thus modeling the faults and conduits observed in sediments.

Time Dependence – There is a great deal of evidence to suggest that nearly every measurable quantity at seeps is time dependent on one or more time scales. The timing of our measurements is intended to mitigate the time dependence, but time dependence but be considered in the final interpretation. The low thermal diffusivity of saturated sediment works to smooth out the decadal and shorter scale temporal variations in the isotherms affecting the base of gas hydrate stability. Only small (<10s of meters) perturbations may occur over short (years) time intervals. The highly localized thermal and chemical measurements should be acquired as close in time as possible to mitigate the temporal variability. A series of measurements at a single site would certainly aid our understanding of emplacement mechanisms, but because the ARI was proposed with a single field effort, no attempt has been made to include a series of measurements (requiring multiple mobilizations) at a single site over a period of time.

Contribution from High Resolution Seismic (DTAGS) - For almost two decades NRL has maintained a unique deep-tow seismic capability. The Deep-Towed acoustics/Geophysics System (DTAGS) provides high resolution (~2-3 m) images of the seafloor that provide outstanding constraints for modeling. The high vertical resolution results from the 200-1000 Hz source (whose signature remains constant in any water depth) and the high lateral resolution results from towing the system only a few hundred meters off the seafloor, even in water depths of several km.

The value of the seismic data in studying gas hydrate is several fold. Seismic images show faults (identifiable by disjoint layering), where fluid, heat, and methane flux are most likely, as well as free gas accumulations within the sediments, constraining the equilibrium hydrate stability boundary. The image can also shows features in the section such as basement highs or buried relict conduits that may have significant effects on the interpretation (and modeling) of the chemistry and temperatures measured at the seafloor. Further, the image can provide information on the seafloor reflectivity (within the wavelengths used) constraining the extent of such phenomena as carbonate pavements or debris fields. In addition to the image the multichannel nature of the DTAGS data can be used to constrain sediment sound speed velocities, diagnostic indicators of gas and gas hydrate.

2. Geochemical Evaluation - Although seismic surveys are a common approach for evaluation of marine hydrate distribution, the target phase (solid hydrate) is not sensed directly, but is inferred by the presence of a BSR. Complementary analysis of biogeochemical and seismic data is being evaluated to assist in the survey of sediment gas hydrate deposits. Ninety percent of methane generated in anoxic marine sediments is removed through the anaerobic oxidation of methane (AOM) in shallow sediments (3-15 m) by a syntrophic consortium of methanogenic *archaea* and sulfate reducing bacteria (SRB). Evaluation of subsurface gas hydrate based on shallow sediment geochemical gradients of AOM metabolites (i.e., sulphate and methane profiles) is based on the assumption that the gradients are related to migration of gas from a deep seated (200-400m) gas hydrate reservoir. For this approach sulfate profiles from piston core porewater samples are surveyed to determine AOM in shallow sediments. The AOM occurs through the following reaction:

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^{-} + HS^{-}$$

This process occurs in sediments at the SMI where downward diffusing seawater sulfate encounters dissolved methane diffusing or advecting upward. Above this location, sulfate concentrations increase to seawater concentrations at the sediment-water interface, while below, methane concentrations increase due to on-site methanogenesis or diffusion and advection from deeper microbial or thermogenic sources. The vertical methane diffusioin through piston core profiles is calculated with measurements of sulfate gradients. Sulfate is conservative during the core sampling and provides a 1:1 ratio during the oxidation of methane with the reduction of sulfate to sulfide. Diffusive flux calculations from the linear sulfate porewater profiles are applied according to Fick’s first law assuming steady state conditions,

$$J = -\phi \cdot D_s \cdot \frac{dc}{dx}$$

where J represents the sulfate flux (mmol m^{-2} a^{-1}), ϕ is the sediment porosity, Ds is the sediment diffusion coefficient, c is the range in sulfate concentration and x is the range of the linear section of the sulfate profile in the piston core. Ds is calculated assuming a tracer diffusion coefficient for sulfate where,

$$D_s = \frac{D_0}{1 + n(1 - \phi)}$$

as D0 is assumed to be 8.7 x 10-5 cm2 s-1, n varies between 1 and 3 depending on the sediement composition, and ϕ, the sediment porosity, can be measured through the sediment cores.

3. Biogeochemical Evaluation – Biogeochemical parameters are incorporated in the sediment core and porewater profiles to understand the methane source and biological cycling. Geochemical and molecular biological analysis of piston core porewaters and sediments addresses the hydrate content, lattice saturation and stability; methane source and biological influence on the methane concentrations. Topics addressed in current research projects include:

- Refined geophysical, geochemical and microbiological technologies for prospecting hydrate content and distribution.

- Contribution to definition of high-priority geographical areas of prospective interest.

- Diagnoses of the possible environmental effects and geologic risks at the continental margin associated with the natural resource occurrence and resource exploitation.

- Contribution to understanding the biogeochemical parameters and associated microbial community diversity in shallow sediments that influences the porewater methane and sulfate cycling and resulting sulfate gradient observed through anaerobic methane oxidation.

4. Heatflow - Thermal data collected in the upper fewer meters of the seafloor using a heatflow instrument has proven to be a reliable provide a proxy for fluid flow and helps define the limits of active flows around methane seeps and mud volcanoes associated with methane seeps and hydrates. The heat flow instrument used is a 3.5-meter-long "violin bow" or "Lister-type" instrument (Hyndman et al., 1979). Eleven thermistors are arranged 30 centimeters apart in a 1-cm-diameter tube held in tension parallel to a solid steel strength member. There is also a temperature sensor mounted on the top of the weightstand which records the water temperature near the sediment-water interface. The system measures both temperature gradient and thermal conductivity in-situ. Sediment temperatures are calculated from the decay of the frictional heat caused by penetration of the instrument into the sediment. Thermal conductivity is determined from the decay of a calibrated thermal pulse applied after a preset period of time (Villinger and Davis, 1987). Heat flow values were determined at each station by computing thermal resistance values at each thermistor,

$$R = \int (1/\lambda)\, dz,$$

where λ is the thermal conductivity. In a situation of steady-state conductivity the heat flow is equal to the slope of the line on a Bullard Plot, a plot of temperature vs. thermal resistance. For each station, any non-linear data that might be attributed to bottom water warming or cooling affects, is removed so as not to bias the statistics. A heat flow value is determined from the slope of the best-fitting linear least-squares line through the remaining data. All heat flow values are corrected for instrument tilt.

High resolution transects are done over the seeps and mounds in order to get an accurate sampling of where elevated thermal signatures. Stations are typically stationed no more than 100 meters apart since it has been our experience that the fluid flow associated with seafloor seeps is relatively distinct and confined in lateral extent. Data typically show clear anomalies in sediment temperature and heat flow associated with the mounds and seeps.

5. Electromagnetics - Electrical conductivity of the oceanic crust and overlying sediments is mainly controlled by the presence of conductive fluids. The presence of gas hydrates and free gas within the hydrate stability zone is known to change physical parameters such as electrical conductivity and shear modulus. In hydrated zones the salt water is replaced by insulating gas hydrate or free gas and the bulk resistivity rises. Hydrocarbon vent sites, such as the Bullseye vent on the Cascadia Margin, are associated with significant resistivity anomalies.

Electrical conductivity in the hydrated zone can be measured using a controlled-source electromagnetic (CSEM) system. The system consists of an EM dipole source, and an array of 2-component electrometers. The array aperture controls the depth of penetration of the electromagnetic signal beneath the sea floor. CSEM arrays can examine both the region above the BSR, in the hydrate zone, and the underlying plumping and methane transport, as well as its evolution in time.

6. Laboratory Approaches to Enhance Field Studies - This section is based on the example provided from the Materials Structure and Function Group at the National Research Council in Ottawa, Canada. For some years now, the Materials Structure and Function Group at NRC has made an effort towards establishing a protocol for the analysis of natural hydrate samples, and to help establish a database on natural gas hydrate properties. Since the science of natural gas hydrates is a complex multidisciplinary area of research, the group establishes connections with field researchers that have recovered natural gas hydrates or plan to do so. The protocol has now developed to a stage where application of the compete suite of techniques now gives a good picture of natural hydrate as a complex mineral, which of course also leads to the possibility of carrying out experiments to model hydrate formation processes in nature. Along with the work on natural samples, the Group does fundamental work on hydrate structures as well as development work to establish new techniques to study hydrate structure, morphology and processes, including methane and hydrogen storage. .

The work is highly collaborative in nature and depends on receiving properly preserved hydrate samples from the field. In the past we have received samples from both Mallik exercises, Gulf of Mexico, Hydrate Ridge, Cascadia (Barkley Canyon and IODP 311). This year we expect to receive samples from offshore India, the South China Sea and the Sea of Japan.

A. Characterization of natural gas hydrates; the idea is to carry out the measurements under controlled conditions to eliminate possible contamination with all measurements taken by subsampling the same recovered material. New techniques are incorporated as necessary to provide new information.

(1) Structural determination: using instrumental methods to determine the structure type of natural gas hydrate and the distribution of hydrocarbons over the guest sites in recovered hydrate samples
(2) Measurement of total gas, water and sediment to establish the degrees of saturation and conversion to hydrate.
(3) Gas composition measurements: to analyze the compositions of uncontaminated gas of natural gas hydrate with high resolution GC/MS.
(4) Isotope analysis – to establish source of hydrocarbons
(5) Sediment characterization – to understand gas hydrate accumulation in nature
(6) Measurement of P,T stability conditions on recovered hydrate.

B. Dissociation of gas hydrate; a variety of issues need to addresses, preferably on intact recovered samples.
(1) To establish the relationship between the physical properties of gas hydrate containing sediments and the amount of gas hydrate. Dissociation properties: to investigate the stability condition and dissociation kinetics of natural gas hydrate in sediments
(2) To determine the kinetics of gas hydrate dissociation under a variety of controlled conditions to simulate natural gas hydrate in reservoirs;
(3) To determine connection between thermal input into hydrate formations, hydrate dissociation and the behavior of water and gas released
(4) To examine the presently available methods available to destabilize gas hydrate by evaluating the efficiency of various methods;
(5) To develop new methods for the efficient destabilization of gas hydrate.

7. Data Access and Sharing: A major goal for this program is the laboratory and field information sharing. In response to this program goal a proposal, presented by Jan Boon, Natural Resources, Canada, was adopted to establish a dynamic web-based communication mechanism for hydrate researchers within the context of the International Methane Hydrate Research and Development Committee:

Proposal: Gas Hydrate Research and Development Communication System (presented by Jan Boone – Natural Resources, Canada)

- Vision:
  - Develop an effective, engaged international gas hydrate research community
- Facilitate information exchange of:
  - Current research activities, knowledge and opportunities
  - Key Priorities in research
  - Political, social, and economic context
  - Funding opportunities
  - Communicate successes and the impact of gas hydrate research

- Act as an effective lobbying force for hydrate research with government and industry
- Goal is to foster effective international collaboration:
    - Key Technologies and Equipment
    - Priorities/Needs
    - OpportunitiesFunding
    - Data/Information Sharing

A steering committee consisting of members of the International Methane Hydrate Research and Development Committee will oversee the establishment and operation of the system. Initially, the web site will be set up and maintained on the CEOR web site. Researchers are encouraged to use the web site to share new information about their research activities.

C. Plans for Future International Collaboration.

This series of workshops has developed strong international collaboration in the a variety of coastal regions; including the Cascadia Margin, Texas-Louisiana Shelf, Blake Ridge, Gulf of Cadiz and Mid Chilean coast. Near-term collaborations are being planned for the coasts of New Zealand and Norway. Participating scientists are from laboratories in the US, Canada, New Zealand, Australia, Chile, Japan, and Germany. Continued research plans are open for collaboration of other regions with scientists from different nations that are interested in sharing costs for field work, field technology and data. Particular attention should be given to developing new collaborations with research focusing on the Norwegian coast and other sites off the western coasts of Europe. These collaborations will be addressed at subsequent workshops in Edinburgh Scotland (October 2006) and Bergen Norway (2007).

An important issue is information storage as well as exchange. Dendy Sloan reported on a new opportunity to establish an information data base on natural gas hydrates within CODATA, the Committee on Data for Science and Technology. A natural gas hydrates working group was set up to interact with CODATA to establish the information site.

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APPENDIX B

POSTER PRESENTATIONS AND ABSTRACTS

Quantifying the Methane Content and Distribution of Natural Gas Hydrate Accumulations in the Deep-Water Basins of the Bering Sea

Ginger A. Barth, David W. Scholl and Jonathan R. Childs

Seismic reflection images from the Aleutian and Bowers Basins of the Bering Sea reveal the abundant presence of natural gas and gas hydrate in this truly deep-water (>3500 m) setting. Distinctive velocity–amplitude anomalies, or VAMPs, stand out as both velocity pseudostructures and gas bright spots within the otherwise horizontal and uniform sedimentary reflection sequences. These are interpreted as methane chimneys overlain by concentrated gas hydrate caps. Hundreds of VAMPs have been imaged throughout the Bering Sea; several thousand are inferred to exist. We have estimated the size and methane content of representative large VAMP structures, based on seismic reflection time anomalies. The VAMPs studied contain 20–40 m cumulative thickness of gas hydrate within ~450 m of sediment above the hydrate BSR. These VAMP features have lateral extents of 4–9 km. Hydrate distribution appears to be lithologically controlled within a section of alternating turbidite and diatomaceous sediments. Free gas is present in the section to well below 1 km bsf. Each individual large VAMP is estimated to contain an equivalent free gas volume (primarily in the form of gas hydrate) similar to that of an economic gas field, >1 Tcf at standard conditions. The basin-wide occurrence of a horizontal, laterally persistent hydrate BSR overlying thousands of gas chimneys associated with VAMP and VAMP-like structures testifies to a high basin-wide flux of methane toward the seafloor. Ongoing USGS development of an interpretive seismic database presents a new opportunity to explore the geometry and distribution of Bering Sea VAMPs relative to basement topography, ancient subduction boundary structures and sediment sources.

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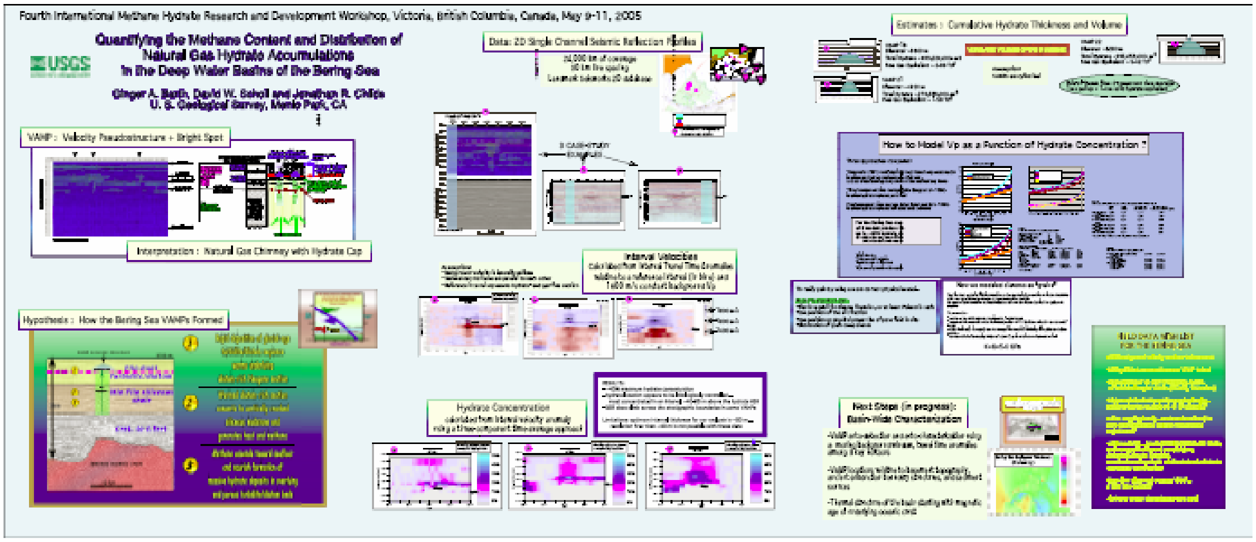

Fourth International Methane Hydrate Research and Development Workshop, Victoria, British Columbia, Canada, May 9-11, 2005

Quantifying the Methane Content and Distribution of Natural Gas Hydrate Accumulations in the Deep Water Basins of the Bering Sea

Ginger A. Barth, David W. Scholl and Jonathan R. Childs
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VAMP: Velocity Pseudostructure + Bright Spot

Interpretation: Natural Gas Chimney with Hydrate Cap

Hypothesis: How the Bering Sea VAMPs Formed

Data: 2D Single Channel Seismic Reflection Profiles

Interval Velocities

Hydrate Concentration

Estimates: Cumulative Hydrate Thickness and Volume

How to Model Vp as a Function of Hydrate Concentration?

Next Steps (in progress): Basin-Wide Characterization

APPENDIX B

Laboratory Seismic Properties of Methane Gas Hydrate-bearing Sand

A. I. Best, J. A. Priest and C. R. I. Clayton

We developed a laboratory resonant column and associated pressure-tempera-ture control systems for creating methane gas hydrates in sediment specimens during the EU HYDRATECH project (2001–2004). The resonant column allows 7 cm diameter, 14 cm-long cylindrical sediment specimens to be excited into resonance in either torsional or longitudinal flexural modes. Measurement of mode resonance frequency and free vibration amplitude decay curves enables P- and S-wave velocity (Vp & Vs, respectively) and attenuation (1/Qp & 1/Qs, respectively) to be calculated. Resonance frequency typically falls below 500 Hz and strain amplitudes are kept below 10-6, thus reducing ambiguity in applying the measured frequency- and strain-dependent elastic wave parameters to the interpretation of seafloor seismic data.

The following range of methane hydrate concentrations were formed in sand specimens using an excess-gas method: 0, 1, 2, 3, 4, 5, 10, 18 & 35% by volume of the pore space (porosity 40%). The remaining pore space was occupied by methane gas. The P- and S-wave velocities measured at 500 kPa effective pressure increased rapidly up to hydrate concentrations of 3–5%, then increased at a lower rate up to 35%. Vp/Vs changed from >5.0 to 2.2 with hydrate concentrations between 0–5%, indicating that the hydrate acted as an effective grain cementing agent. Both 1/Qp and 1/Qs were higher in the hydrate-bearing sand than in the moist sand specimens (both before hydrate formation and after hydrate dissociation) and showed an attenuation maximum at hydrate concentrations between 3–5%. The attenuation results imply a damping mechanism associated with the hydrate. Although the velocity results can be applied to water saturated hydrate-bearing sediments using fluid substitution models, it is difficult to know how the attenuation results relate to water saturated sediments at this stage.

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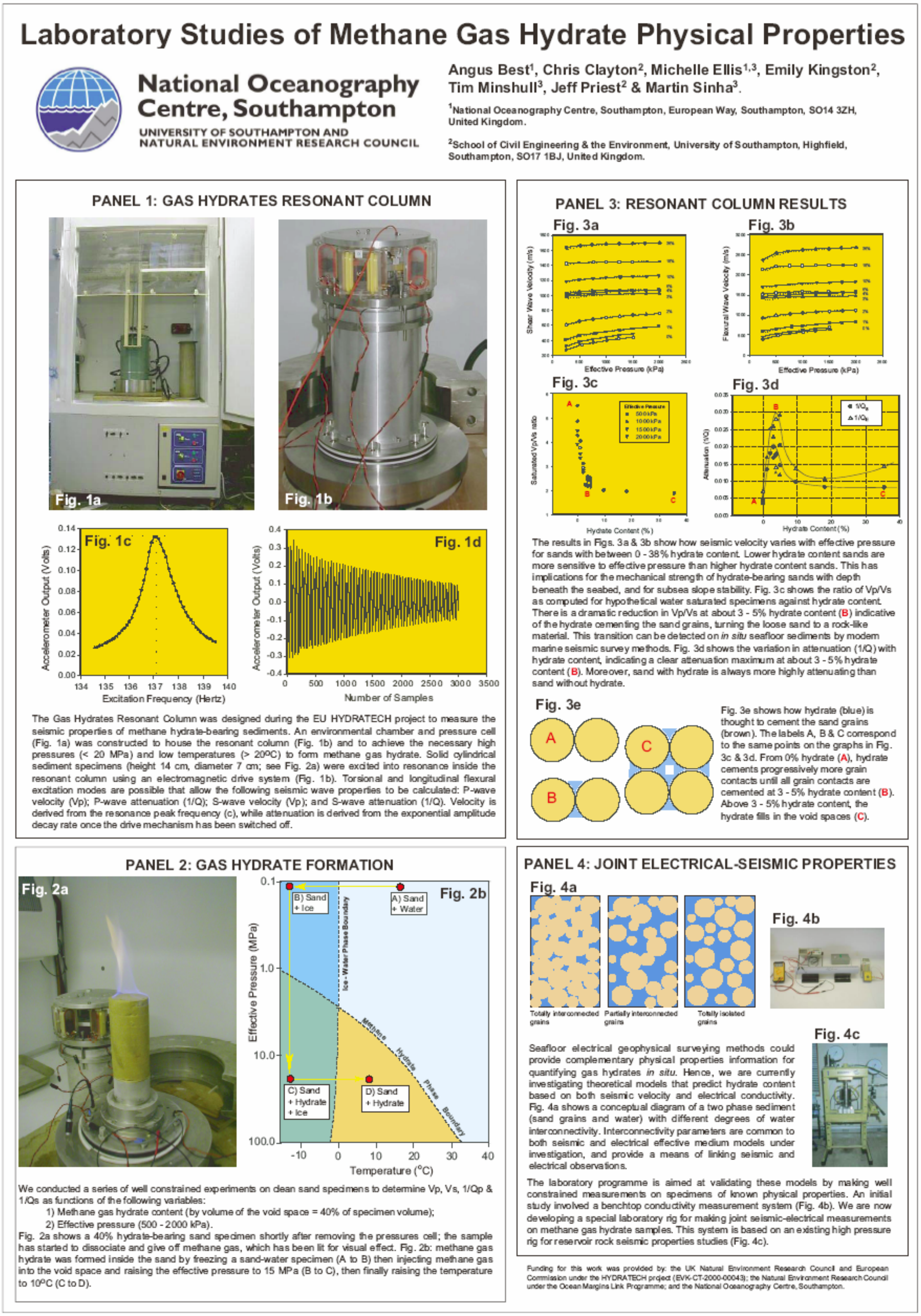

Laboratory Studies of Methane Gas Hydrate Physical Properties

National Oceanography Centre, Southampton
UNIVERSITY OF SOUTHAMPTON AND
NATURAL ENVIRONMENT RESEARCH COUNCIL

Angus Best[1], Chris Clayton[2], Michelle Ellis[1,3], Emily Kingston[2], Tim Minshull[3], Jeff Priest[2] & Martin Sinha[3].

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PANEL 1: GAS HYDRATES RESONANT COLUMN

The Gas Hydrates Resonant Column was designed during the EU HYDRATECH project to measure the seismic properties of methane hydrate-bearing sediments. An environmental chamber and pressure cell (Fig. 1a) was constructed to house the resonant column (Fig. 1b) and to achieve the necessary high pressures (< 20 MPa) and low temperatures (> 20°C) to form methane gas hydrate. Solid cylindrical sediment specimens (height 14 cm, diameter 7 cm; see Fig. 2a) were excited into resonance inside the resonant column using an electromagnetic drive system (Fig. 1b). Torsional and longitudinal flexural excitation modes are possible that allow the following seismic wave properties to be calculated: P-wave velocity (Vp); P-wave attenuation (1/Q); S-wave velocity (Vp); and S-wave attenuation (1/Q). Velocity is derived from the resonance peak frequency (c), while attenuation is derived from the exponential amplitude decay rate once the drive mechanism has been switched off.

PANEL 2: GAS HYDRATE FORMATION

We conducted a series of well constrained experiments on clean sand specimens to determine Vp, Vs, 1/Qp & 1/Qs as functions of the following variables:

1) Methane gas hydrate content (by volume of the void space = 40% of specimen volume);
2) Effective pressure (500 - 2000 kPa).

Fig. 2a shows a 40% hydrate-bearing sand specimen shortly after removing the pressures cell; the sample has started to dissociate and give off methane gas, which has been lit for visual effect. Fig. 2b: methane gas hydrate was formed inside the sand by freezing a sand-water specimen (A to B) then injecting methane gas into the void space and raising the effective pressure to 15 MPa (B to C), then finally raising the temperature to 10°C (C to D).

PANEL 3: RESONANT COLUMN RESULTS

The results in Figs. 3a & 3b show how seismic velocity varies with effective pressure for sands with between 0 - 38% hydrate content. Lower hydrate content sands are more sensitive to effective pressure than higher hydrate content sands. This has implications for the mechanical strength of hydrate-bearing sands with depth beneath the seabed, and for subsea slope stability. Fig. 3c shows the ratio of Vp/Vs as computed for hypothetical water saturated specimens against hydrate content. There is a dramatic reduction in Vp/Vs at about 3 - 5% hydrate content (B) indicative of the hydrate cementing the sand grains, turning the loose sand to a rock-like material. This transition can be detected on *in situ* seafloor sediments by modern marine seismic survey methods. Fig. 3d shows the variation in attenuation (1/Q) with hydrate content, indicating a clear attenuation maximum at about 3 - 5% hydrate content (B). Moreover, sand with hydrate is always more highly attenuating than sand without hydrate.

Fig. 3e shows how hydrate (blue) is thought to cement the sand grains (brown). The labels A, B & C correspond to the same points on the graphs in Fig. 3c & 3d. From 0% hydrate (A), hydrate cements progressively more grain contacts until all grain contacts are cemented at 3 - 5% hydrate content (B). Above 3 - 5% hydrate content, the hydrate fills in the void spaces (C).

PANEL 4: JOINT ELECTRICAL-SEISMIC PROPERTIES

Totally interconnected grains
Partially interconnected grains
Totally isolated grains

Seafloor electrical geophysical surveying methods could provide complementary physical properties information for quantifying gas hydrates *in situ*. Hence, we are currently investigating theoretical models that predict hydrate content based on both seismic velocity and electrical conductivity. Fig. 4a shows a conceptual diagram of a two phase sediment (sand grains and water) with different degrees of water interconnectivity. Interconnectivity parameters are common to both seismic and electrical effective medium models under investigation, and provide a means of linking seismic and electrical observations.

The laboratory programme is aimed at validating these models by making well constrained measurements on specimens of known physical properties. An initial study involved a benchtop conductivity measurement system (Fig. 4b). We are now developing a special laboratory rig for making joint seismic-electrical measurements on methane gas hydrate samples. This system is based on an existing high pressure rig for reservoir rock seismic properties studies (Fig. 4c).

Funding for this work was provided by: the UK Natural Environment Research Council and European Commission under the HYDRATECH project (EVK-CT-2000-00043); the Natural Environment Research Council under the Ocean Margins Link Programme; and the National Oceanography Centre, Southampton.

APPENDIX B

From Multicomponent Seismic Data to Hydrate Saturation

Shyam Chand

The presence of gas hydrate in marine sediments alters their physical properties and fluid flow. Gas hydrate may cement the sediment grains together, and dramatically increase the seismic P and S wave velocities of the composite. Hydrate may also form a load-bearing structure, within the sediment microstructure but with different seismic wave attenuation characteristics to that of the host sediment. It has been observed that the attenuation increases with hydrate saturation at higher frequencies for both P and S waves.

Now it is possible to detect both P and S waves in marine environment using Ocean Bottom Seismograph (OBS) systems. Usually the S waves recorded are those generated from P to S conversion within the sedimentary column. Since S wave behaviour through hydrate-saturated marine sediments also changes with hydrate saturation, we extract this additional information from the horizontal component data. This is done through waveform inversion of vertical component data to derive detailed P wave velocity structure followed by waveform inversion of horizontal component data to derive the detailed S wave velocity structure. We relate these changes in physical parameters of hydrate-bearing sediments to their hydrate content using an effective medium model, which is based on self consistent approximation (SCA) and differential effective medium (DEM) theories and, Biot and squirt flow mechanisms of fluid flow.

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APPENDIX B

FROM MULTI COMPONENT SEISMIC DATA TO HYDRATE SATURATION

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ABSTRACT

The presence of gas hydrate in marine sediments alters their physical properties and fluid flow. Gas hydrate may cement the sediment grains together and dramatically increase the seismic P and S wave velocities of the composite (Chand et al, 2004).Hydrate may also form a load-bearing structure, within the sediment microstructure but with different seismic wave attenuation characteristics to that of the host sediment (Chand and Minshull, 2004). It has been observed that the attenuation increases with hydrate saturation at higher frequencies for both P and S waves (Guerin and Goldberg, 2002).

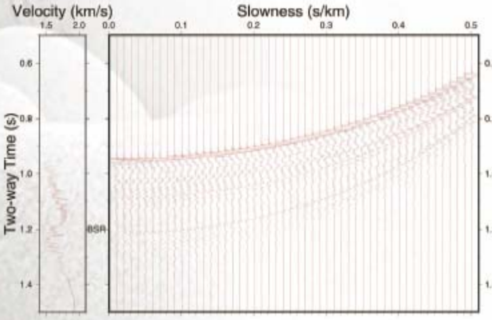

Fig 2a. Synthetic (red) and observed (black) seismograms in the Tau-P domain. The synthetic seismogram is obtained using waveform inversion of the OBS vertical component data. The data is inverted for velocity (red) and velocity & density (black).

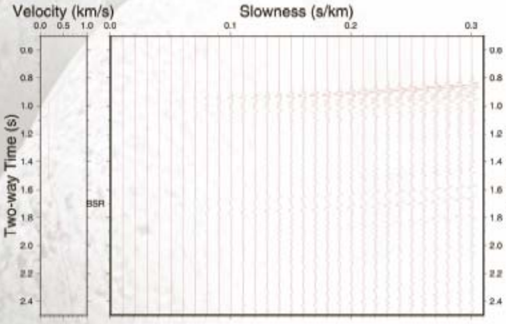

Fig 2b. Synthetic (red) and observed (black) seismograms in the Tau-P domain. The synthetic seismogram is obtained using waveform inversion of the OBS horizontal component data. The data is inverted for velocity.

Acknowledgements:
This work was funded under HYDRATECH Project.

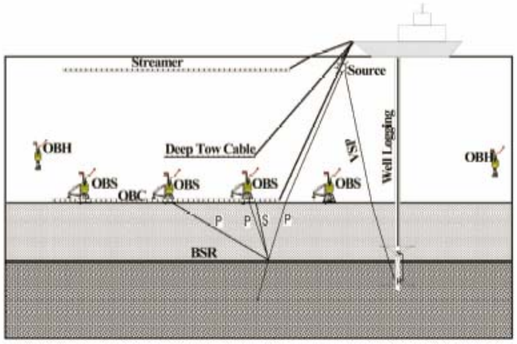

Fig 1. Seismic data collection using different methods. The resolution of the methods differ depending on the proximity to the seafloor and on the source frequency.

Now it is possible to detect both P and S waves in marine environment using multi-component Ocean Bottom Seismograph (OBS) systems (Fig. 1). Usually the S waves recorded are those generated from P to S conversion within the sedimentary column. Since S wave behaviour through hydrate saturated marine sediments also changes with hydrate saturation, we can extract the detailed S wave velocity structure from the horizontal component data using waveform inversion. This invloves a two step process with waveform inversion of vertical component data to derive the detailed P wave velocity structure (Fig. 2a), followed by waveform inversion of the horizontal component data to derive the detailed S wave velocity structure (Fig. 2b). We can then relate these changes in velocities of hydrate-bearing sediments to their hydrate content using an effective medium model. It has been suggested that the self consistent approximation (SCA) and differential effective medium (DEM) model with hydrate cementing morphology can best explain the amount of hydrate present in pore space (Chand et al, 2004). Additional information on the attenuation of P and S waves if available can be modeled using Biot and squirt flow mechanisms of fluid flow in a multi-structural framework (Chand and Minshull,2004).

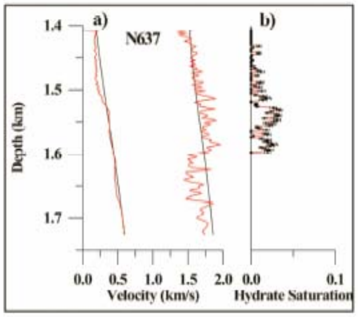

Fig 3. Hydrate saturation estimated using P and S wave velocities and sediment physical properties using the SCA/DEM cemented inversion algorithm

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APPENDIX B

Methane Hydrate Exploration, Atwater Valley, Texas–Louisiana Shelf: Geophysical and Geochemical Profiles

Richard Coffin, Joan Gardner, John Pohlman, Ross Downer and Warren Wood

From May 14 to May 20, 2004 piston core and heat flow measurements were collected across two mound structures, (designated D and F), in as the Atwater Valley offshore lease area. The mounds lie in the floor of the Mississippi Canyon, directly south of the mouth of the Mississippi River, at 1300 meters water depth. Several small mound structures occur in the canyon floor, rising less than 50 meters above the surrounding seafloor. The USGS collected several multichannel seismic lines in this area in 2003. During four days on site we acquired 15 piston cores and 23 thermal profiles on a transect from mound F to mound D. A previous USGS seismic line (AV65) and a 3.5 kHz echosounder profile collected during the cruise were used to guide operations. All attempts at thermal probing resulted in full penetration except for one instance where the instrument laid horizontal on the seafloor.

The sulfate–methane interface (SMI) estimated from pore water sulfate profiles indicated a range in the vertical flux of methane. Sulfate and methane pore water profiles from piston cores on mound F indicated the greatest vertical methane flux in this region of the transect. Sulfate was completely depleted in surface core samples and methane concentrations were elevated suggesting a flow of methane into the water column. Overall the SMI on the transect ranged from 45 to 410 cm. Stable carbon isotope ratios and speciation of gases sampled from the piston cores indicated a microbial source of methane. Chloride data from piston cores did not indicate hydrates were sampled and dissociated during transport from the sediment and deck processing. However, high chloride concentrations were measured on mound F. It is expected that the chloride originated from the deep salt diapir underlying the mounds. DIC concentrations and stable carbon isotope analysis confirmed anaerobic methane oxidation in the pore water profiles. Mound F sites showed shallower DIC concentration peaks and more ^{13}C depletion in the DIC. These data are consistent with increased vertical methane flux in this region.

Thermal probing was conducted at each of the piston coring sites; additional thermal sites were included for more resolution. The data show clear anomalies in sediment temperature and heat flow associated with the mounds. Measurements collected on the top of mound F show elevated sediment temperatures, and heat flow values of around 160 mW/m^2. Sediment temperatures decrease away from the summit of the mound, and heat flow values drop to a background level of 40 to 50 mW/m^2. Sediment temperatures at the summit of Mound D are similar to what was observed at Mound F, and heat flow values are slightly lower at around 132 mW/m^2, partly as a result of the slightly higher bottom water temperature and thus reduced thermal gradient. Away from the summit of Mound D the thermal gradient decreases and heat flow values drop to around 50 mW/m^2. High heat flow measurements coincide with estimates of a high vertical methane flux.

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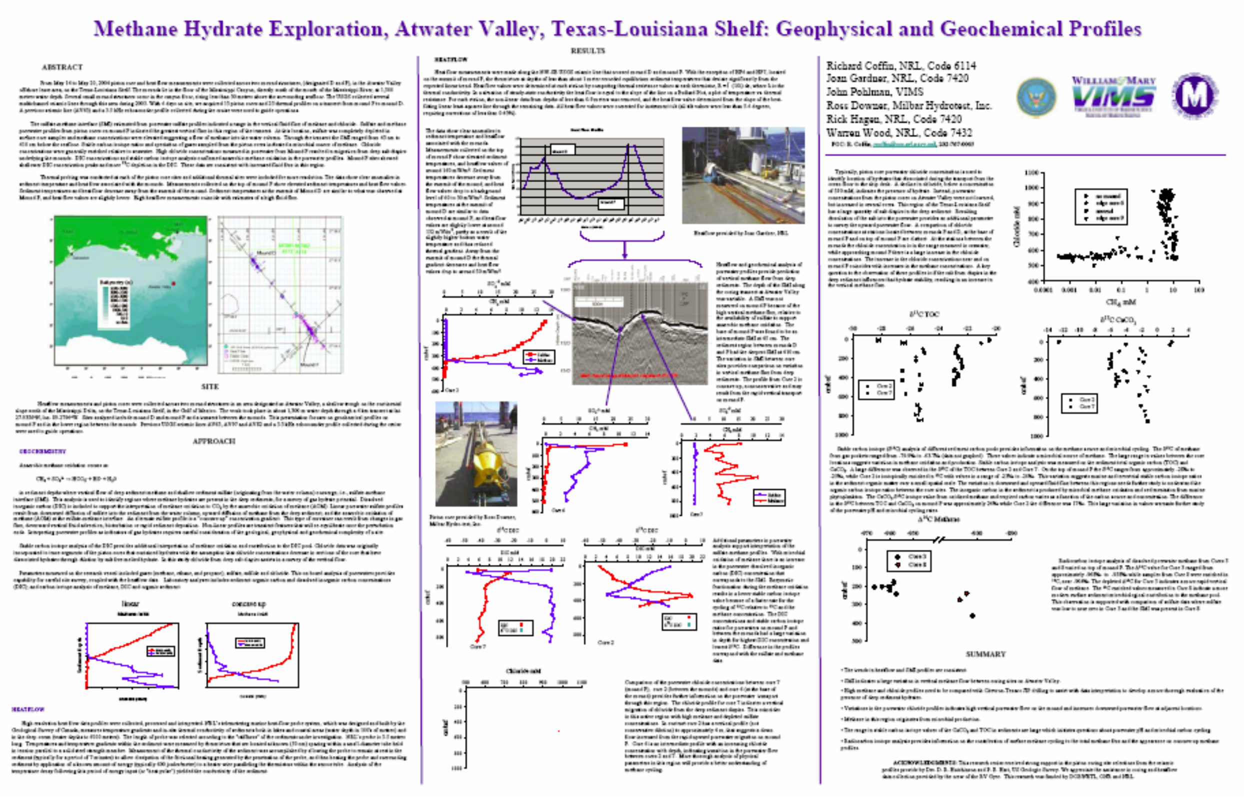

Methane Hydrate Exploration, Atwater Valley, Texas-Louisiana Shelf: Geophysical and Geochemical Profiles

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ABSTRACT

SITE

APPROACH

GEOCHEMISTRY

HEATFLOW

RESULTS

SUMMARY

APPENDIX B

Methane Hydrates and Fluid Flow along the Chilean Margin

Joan M. Gardner, Juan Diaz-Naveas, John W. Pohlman, Rick A. Hagen, Richard Coffin, and Warren T. Wood

POSTER NOT AVAILABLE

An international collaboration between the Naval Research Laboratory and Pontificia Universidad Catolica de Valparaiso (Chile) was developed to investigate methane hydrate distribution along sections of the Chilean margin. Preliminary data collected along the Chilean margin in 2003 by researchers from Chile and the Universities of Bremen and Kiel (GEOMAR) found a clear discrepancy between estimated heat flow inferred from the depth of the bottom simulating reflector (BSR) and direct measurement using a heat flow probe. The data indicated that fluid migration enhanced heat flow in the upper section of the sedimentary column. We conducted a more extensive and higher resolution survey in October 2004 to evaluate this discrepancy and determine if the phenomenon is a local or regional phenomenon. Multichannel seismic data collected in the region, suggest the BSR is shallower than expected. It is possible that tectonic movements present that shifted the BSR upward but did not immediately destabilize the hydrates.

Complimentary pore water geochemical profiles from piston cores and heat flow data will help reconcile the discrepancies observed between the seismic and heat flow observations. Previous DTAGS data is coupled with the heat flow data to interpret the variation observed in the geochemical profiles.

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APPENDIX B

Gas Hydrate Seismic Characterisation and Distribution on New Zealand's Continental Margins

Andrew R. Gorman, Ingo A. Pecher, Miko Fohrmann and Stuart A. Henrys

The continental margins off the east coast of New Zealand's North Island (the Hikurangi Margin) and the southwest coast of the South Island (the Fiordland Margin) contain significant quantities of gas hydrates. Current analyses are focussed on these regions to determine the distribution and concentrations of gas hydrate, their resource potential, and their involvement in seafloor stability. The Hikurangi Margin, off the east coast of the North Island, has the highest economic potential of these gas hydrate deposits for future gas production because of its proximity to larger population centres.

Analysis of gas hydrate deposits is primarily based on the interpretation of bottom simulating reflections (BSRs) from a substantial data set of seismic data acquired for a number of geological reasons over the last 30 years. On both the Fiordland and Hikurangi Margins, BSRs are prevalent (1) beneath structural highs, and (2) at locations where dipping layers crop out at the seafloor. Both of these features are known to focus fluid flow through the sediment to the seafloor. In the methane-rich environment of the Hikurangi Margin, we presume that a substantial amount of methane is supplied to the system in regions of high fluid flow. Because an ongoing methane supply is known to be a key factor controlling gas hydrate concentration, high methane flux regions are likely to be proximal to regions of high gas hydrate concentration. These "sweet spot" locations are a focus of our work and may contain gas hydrate concentrations that are high enough for the commercial production of natural gas in the future. The role of gas hydrates in slope stability is being investigated at locations where BSRs crop out on the seafloor at locations coincident with submarine erosion/landslide features.

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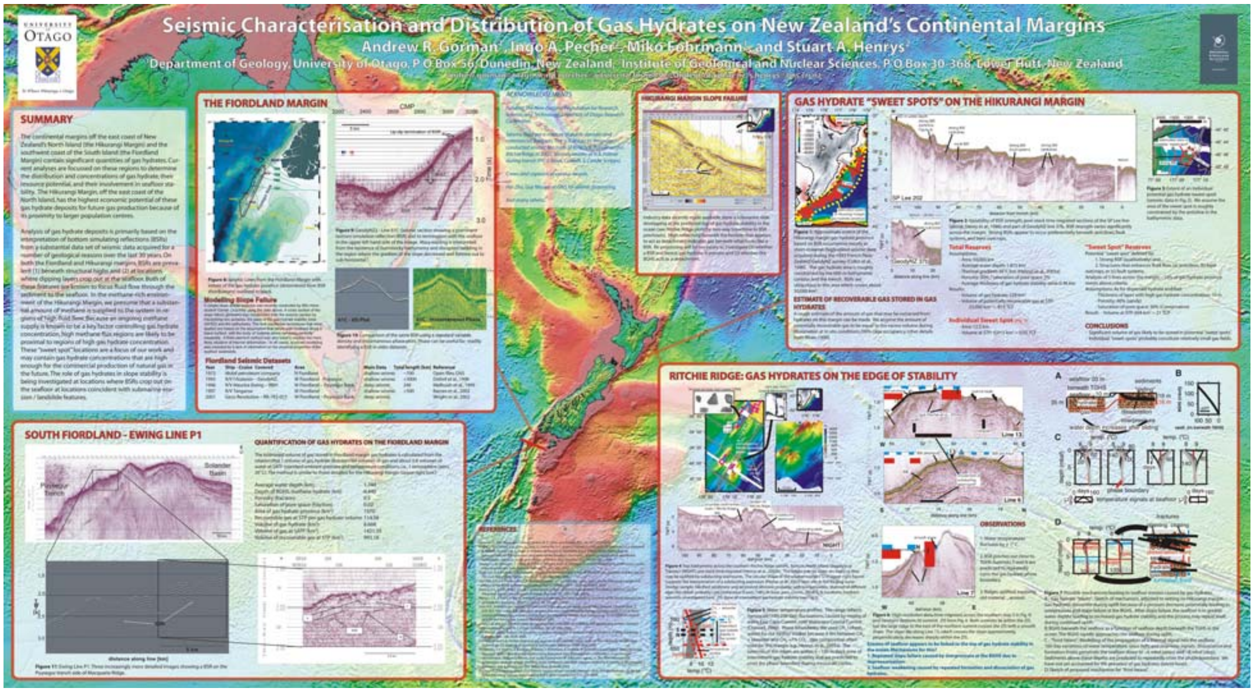
APPENDIX B



UNIVERSITY OF OTAGO

Seismic Characterisation and Distribution of Gas Hydrates on New Zealand's Continental Margins

Andrew R. Gorman[1], Ingo A. Pecher[2], Miko Fohrmann[1] and Stuart A. Henrys[2]

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SUMMARY

THE FIORDLAND MARGIN

ACKNOWLEDGEMENTS

HIKURANGI MARGIN SLOPE FAILURE

GAS HYDRATE "SWEET SPOTS" ON THE HIKURANGI MARGIN

SOUTH FIORDLAND - EWING LINE P1

QUANTIFICATION OF GAS HYDRATES ON THE FIORDLAND MARGIN

REFERENCES

RITCHIE RIDGE: GAS HYDRATES ON THE EDGE OF STABILITY

APPENDIX B

A Multidisciplinary Investigation of a Deep-water Gas Hydrate Mound, Atwater Valley, Northern Gulf of Mexico

P. E. Hart, D.R. Hutchinson, B. Dugan, M. Fowler, W. Wood, F. Snyder, N. Dutta, R. Coffin, J. Gardner, R. Hagen, R. Evans and D. Fornari

Natural marine gas hydrates exist on the seafloor of the continental slope of the northern Gulf of Mexico, but in spite of extensive geological and geophysical data, little is certain regarding their subsurface distribution and concentration and traditional geophysical indicators (e.g., bottom simulating reflections) are rare. This has motivated numerous ongoing hydrate studies, including the Gulf of Mexico Gas Hydrates Joint Industry Project (JIP), a collaboration among industry, academia and government agencies. Two goals of the JIP are to better understand the physical system and the seismic reflection characteristics of gas hydrates and free gas associated with surficial gas hydrate mounds. In the Atwater Valley region of the Mississippi Canyon, 150 km south of Louisiana, at about 1300 m water depth, there are several seafloor mounds that may be active vents with significant accumulations of gas hydrate adjacent to the gas and fluid migration pathways. Several recent research cruises, led by the U.S. Geological Survey, the Naval Research Laboratory and the Woods Hole Oceanographic Institute, have investigated this site and collected high-resolution seismic reflection data, piston cores, heat flow measurements, electromagnetic readings, near-bottom photographs, side-scan sonar and multibeam bathymetric data. Additionally, the JIP has 3-D seismic coverage of the area provided by WesternGeco.

A shallow, convex-upward reflection in seismic profiles over the largest of the seafloor mounds (Mound F) and high heat flow and chloride concentrations indicate that the base of the gas hydrate stability zone is anomalously shallow beneath the mound. High seafloor reflectivity observed over the mounds on the seismic profiles is indicative of hydrate or authigenic carbonates at or near the seafloor. Bottom photographs show evidence of mud flows from the flank of Mound F. A drilling and coring program planned by the JIP for spring 2005 will provide ground truth for present interpretations and theoretical models while providing quantitative estimates of subsurface hydrate deposits near Mound F.

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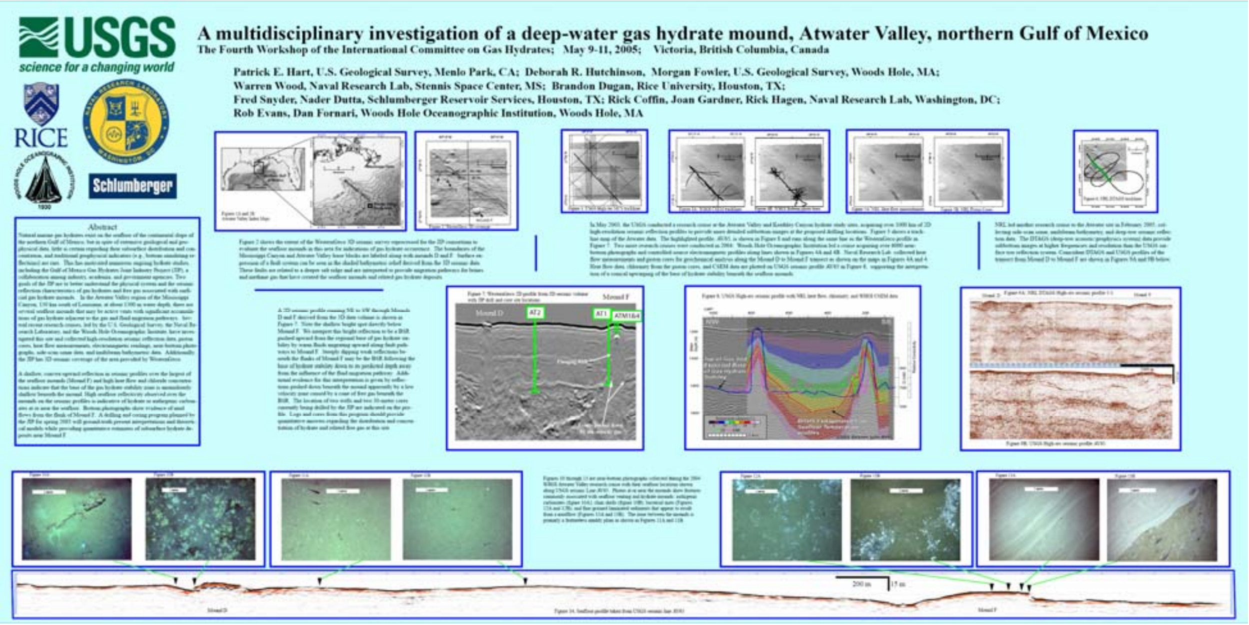
APPENDIX B



A multidisciplinary investigation of a deep-water gas hydrate mound, Atwater Valley, northern Gulf of Mexico

The Fourth Workshop of the International Committee on Gas Hydrates; May 9-11, 2005; Victoria, British Columbia, Canada

Patrick E. Hart, U.S. Geological Survey, Menlo Park, CA; Deborah R. Hutchinson, Morgan Fowler, U.S. Geological Survey, Woods Hole, MA;
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Fred Snyder, Nader Dutta, Schlumberger Reservoir Services, Houston, TX; Rick Coffin, Joan Gardner, Rick Hagen, Naval Research Lab, Washington, DC;
Rob Evans, Dan Fornari, Woods Hole Oceanographic Institution, Woods Hole, MA

Abstract

APPENDIX B

Geophysical and Geochemical Characterization of the Hydrate Stability Zone in a Region of Active Salt Tectonics, Keathley Canyon, Northern Gulf of Mexico

D.R. Hutchinson, C.D. Ruppel, J. Pohlman, P. E. Hart, F. Snyder, N. Dutta B. Dugan and R. Coffin

The northern Gulf of Mexico contains conditions suitable for gas hydrate: appropriate pressures from continental slope water depths, moderate thermal gradients typical of continental margins and abundant methane from a well-known leaky petroleum system. Surficial gas hydrate is present in seafloor mounds, but geophysical evidence for subsurface gas hydrate (bottom simulating reflection [BSR] or blanking) is generally lacking. One exception occurs near lease block Keathley Canyon 195, in about 1300-m water depth, where a weak BSR occurs on the flank of a salt-withdrawal minibasin. A multidisciplinary study involving government agencies, industry and academia has collected 2-D and 3-D multichannel seismic reflection data, made heat flow measurements and analyzed geochemical constituents in piston cores in order to understand the subsurface distribution, behavior and seismo-stratigraphic indicators of gas hydrate.

The base of hydrate stability, interpreted as the BSR, ranges from 200 to more than 450-m below the seafloor in the minibasin. High amplitudes along the BSR are interpreted to represent gas-charged coarser deposits in a well-layered and unconformity-rich stratigraphic sequence. An intensely deformed, salt-cored, structural high lacking a BSR occurs adjacent to the east side of the minibasin. Heat-flow penetrations and piston core analyses show lower thermal gradients, reduced pore-water salinities and greater depths to the base of the sulfate depletion zone in the minibasin than on the structural high. These data indicate that the flux of fluid, methane and heat are lower in the minibasin and increase on the structural high, consistent with an interpretation of warmer, more saline fluids migrating up faults on the structural high and inhibiting gas hydrate formation. Age reversals in the shallowest sediments suggest mass wasting complicates surficial dynamics. The complex interplay between thermal and chemical heterogeneity of the system plays a key role in determining the presence or absence of subsurface gas hydrate.

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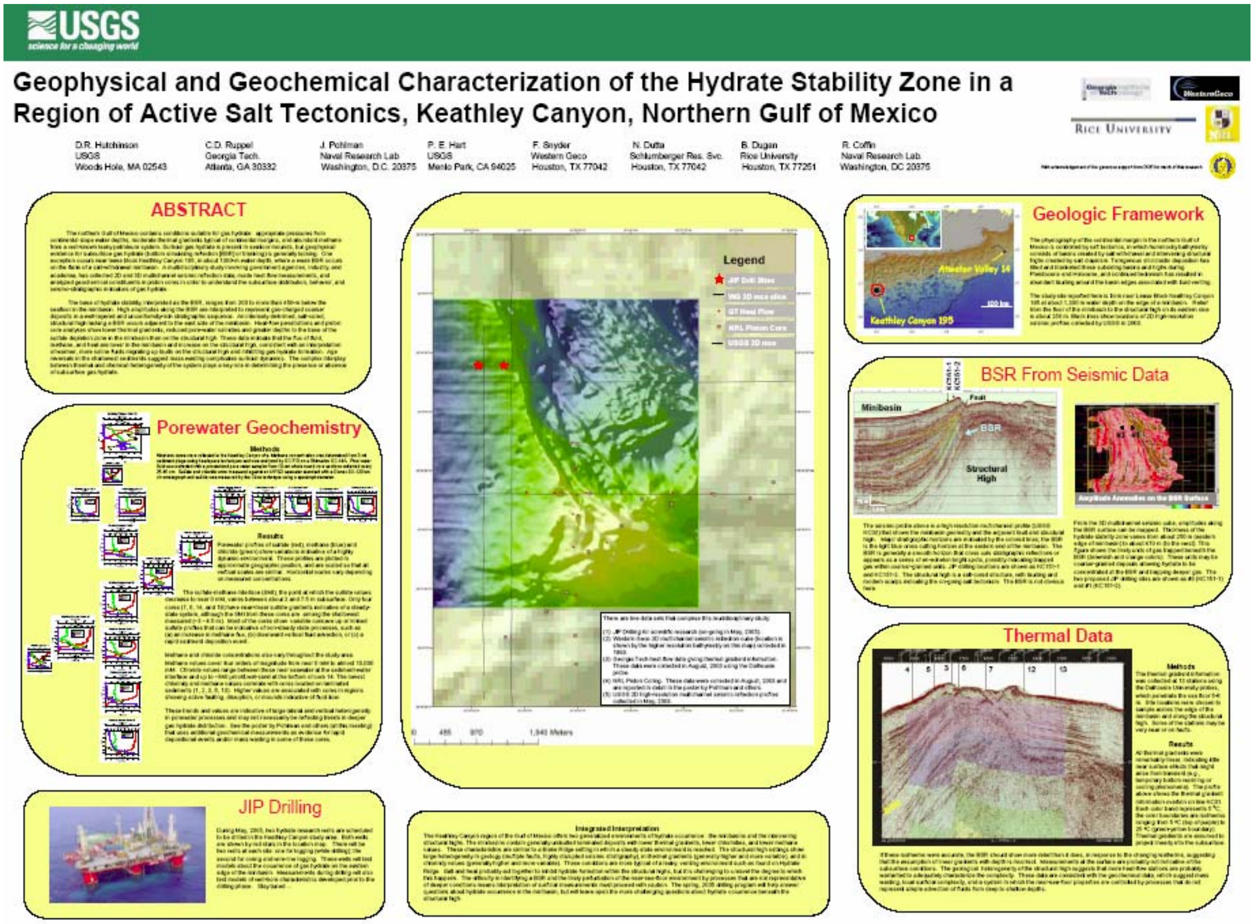

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Geophysical and Geochemical Characterization of the Hydrate Stability Zone in a Region of Active Salt Tectonics, Keathley Canyon, Northern Gulf of Mexico

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ABSTRACT

Porewater Geochemistry

Methods

Results

JIP Drilling

Integrated Interpretation

Geologic Framework

BSR From Seismic Data

Thermal Data

Methods

Results

APPENDIX B

Slope Stability Issues in Hydrate-Bearing Sediments Under Seismic Loading

P. Jackson, D. Gunn, K. Howard, D. Long, M. Lovell, J. Rees, C. Rochelle, P. Hobbs and L. Nelder

While there is debate concerning total gas-hydrate reserves, researchers have suggested boundary surfaces of stable hydrates are far larger than originally anticipated. Recently, a theoretical basis has begun to emerge supporting the hypothesis that pore pressures may increase on hydrate dissociation. Therefore, re-assessment of risk (e.g., earthquake triggers) to seafloor installations is required. Typically, regional seismic assessments exclude site-scale sediment property data. Consequently, the potential for underestimating risk is significant, particularly when shear strengths are reduced by increased pore pressure. This suggests, for example, there is a need for improved geophysical and geotechnical property-models for sediment-hosted methane-hydrates.

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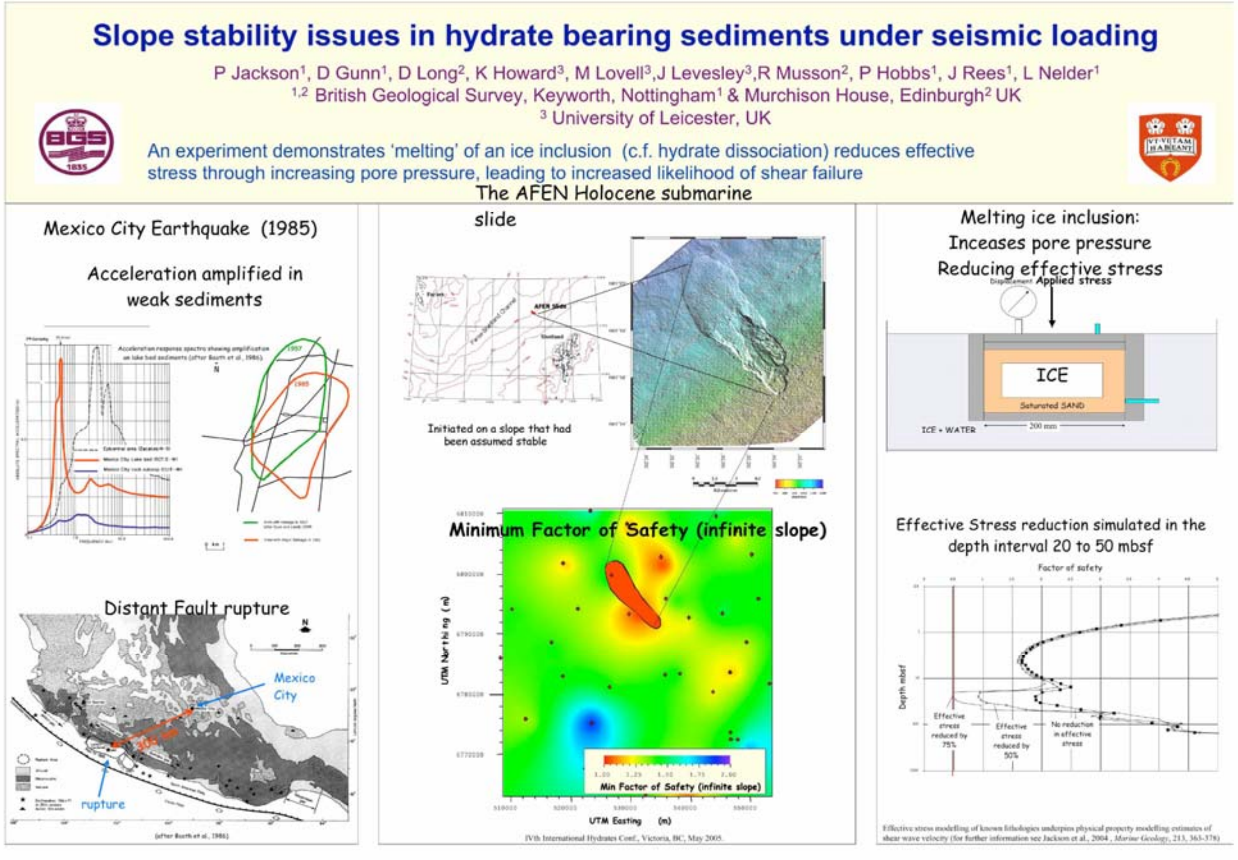

Slope stability issues in hydrate bearing sediments under seismic loading

P Jackson[1], D Gunn[1], D Long[2], K Howard[3], M Lovell[3], J Levesley[3], R Musson[2], P Hobbs[1], J Rees[1], L Nelder[1]
[1,2] British Geological Survey, Keyworth, Nottingham[1] & Murchison House, Edinburgh[2] UK
[3] University of Leicester, UK

An experiment demonstrates 'melting' of an ice inclusion (c.f. hydrate dissociation) reduces effective stress through increasing pore pressure, leading to increased likelihood of shear failure

Mexico City Earthquake (1985)

Acceleration amplified in weak sediments

Distant Fault rupture

(after Booth et al., 1986)

The AFEN Holocene submarine slide

Initiated on a slope that had been assumed stable

Minimum Factor of Safety (infinite slope)

IVth International Hydrates Conf., Victoria, BC, May 2005.

Melting ice inclusion:
Inceases pore pressure
Reducing effective stress

Effective Stress reduction simulated in the depth interval 20 to 50 mbsf

Effective stress modelling of known lithologies underpins physical property modelling estimates of shear wave velocity (for further information see Jackson et al., 2004 , *Marine Geology*, 213, 363-378)

APPENDIX B

Watching Hydrate Crystals Grow: Insights from Computer Simulations

Peter Kusalik

While the molecular behaviour within liquids and solids has been extensively studied, one important aspect of these systems that has remained poorly understood is the first order phase transition between them. One of the reasons for this is that there are very few experiments that are able to probe directly the microscopic environment of a growing crystal. Computer simulations thus afford us an excellent opportunity to investigate liquid/solid interfaces and mechanisms of crystal growth at the molecular level. In this paper I will describe a new approach we have developed for the simulation of heterogeneous crystal growth and will briefly discuss its success with simple atomic systems. I will report specific results for the growth of ice (I) crystals, where I will clearly demonstrate that the process of crystal growth is characterized by a collective phenomenon involving many molecules (rather than the "sticking" of individual molecules). I will present results characterizing the interfacial properties of various ice I crystal faces, including interfacial widths and surface tensions. Finally, I will report very recent results for the growth of methane hydrates, where we have already been able to gain some important insights.

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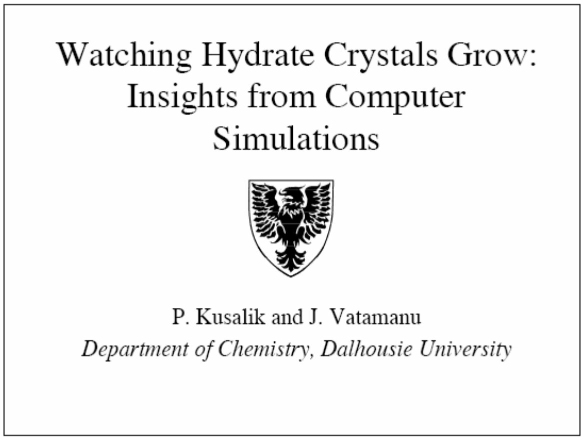

Watching Hydrate Crystals Grow:
Insights from Computer
Simulations

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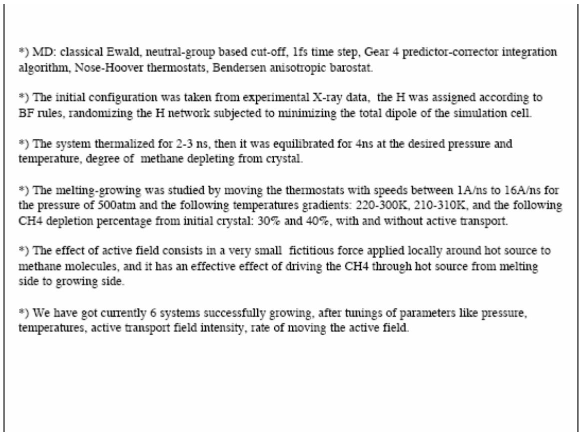

*) MD: classical Ewald, neutral-group based cut-off, 1fs time step, Gear 4 predictor-corrector integration algorithm, Nose-Hoover thermostats, Bendersen anisotropic barostat.

*) The initial configuration was taken from experimental X-ray data, the H was assigned according to BF rules, randomizing the H network subjected to minimizing the total dipole of the simulation cell.

*) The system thermalized for 2-3 ns, then it was equilibrated for 4ns at the desired pressure and temperature, degree of methane depleting from crystal.

*) The melting-growing was studied by moving the thermostats with speeds between 1A/ns to 16A/ns for the pressure of 500atm and the following temperatures gradients: 220-300K, 210-310K, and the following CH4 depletion percentage from initial crystal: 30% and 40%, with and without active transport.

*) The effect of active field consists in a very small fictitious force applied locally around hot source to methane molecules, and it has an effective effect of driving the CH4 through hot source from melting side to growing side.

*) We have got currently 6 systems successfully growing, after tunings of parameters like pressure, temperatures, active transport field intensity, rate of moving the active field.

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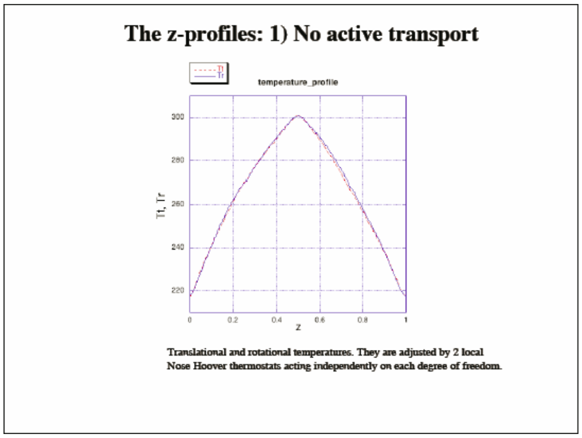
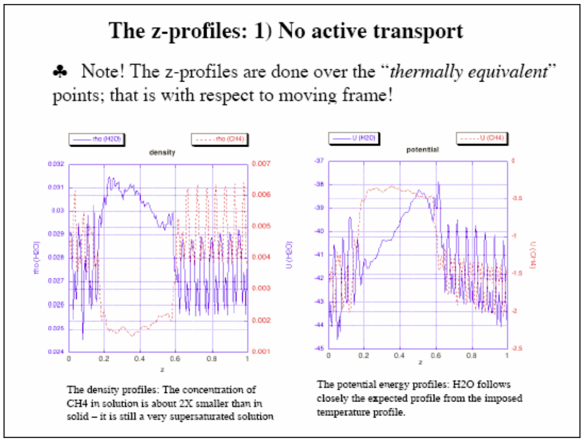


The z-profiles: 1) No active transport

Translational and rotational temperatures. They are adjusted by 2 local Nose Hoover thermostats acting independently on each degree of freedom.

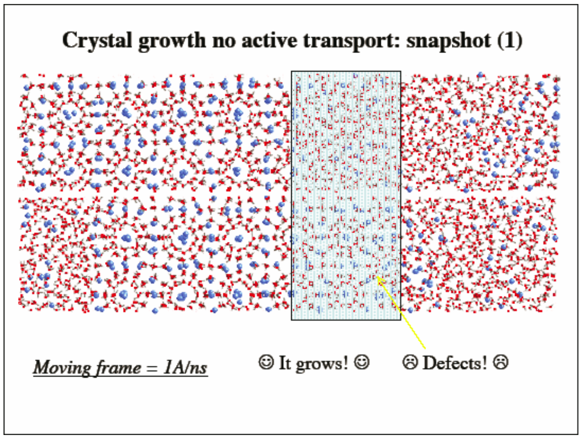


The z-profiles: 1) No active transport

♣ Note! The z-profiles are done over the "*thermally equivalent*" points; that is with respect to moving frame!

The density profiles: The concentration of CH4 in solution is about 2X smaller than in solid – it is still a very supersaturated solution

The potential energy profiles: H2O follows closely the expected profile from the imposed temperature profile.

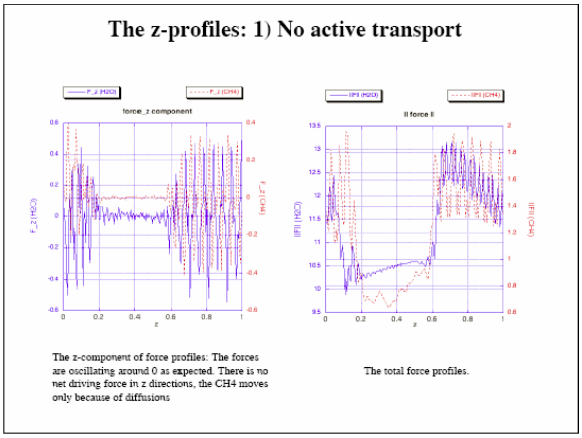


Crystal growth no active transport: snapshot (1)

Moving frame = 1A/ns

☺ It grows! ☺

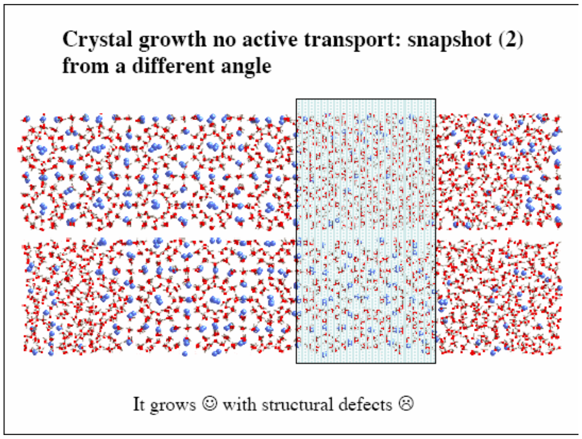
☹ Defects! ☹



The z-profiles: 1) No active transport

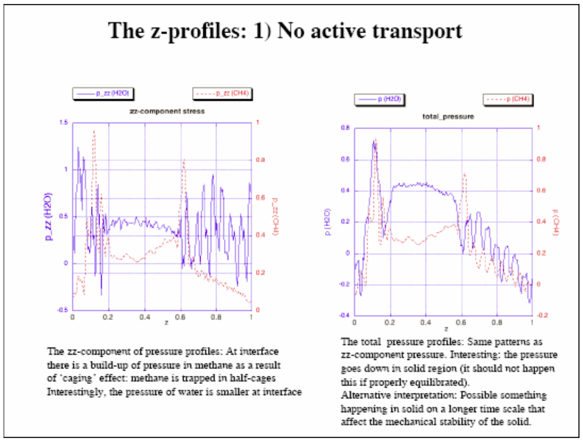
The z-component of force profiles: The forces are oscillating around 0 as expected. There is no net driving force in z directions, the CH4 moves only because of diffusions

The total force profiles.



Crystal growth no active transport: snapshot (2) from a different angle

It grows ☺ with structural defects ☹



The z-profiles: 1) No active transport

The zz-component of pressure profiles: At interface there is a build-up of pressure in methane as a result of 'caging' effect: methane is trapped in half-cages Interestingly, the pressure of water is smaller at interface

The total pressure profiles: Same patterns as zz-component pressure. Interesting: the pressure goes down in solid region (it should not happen this if properly equilibrated).
Alternative interpretation: Possible something happening in solid on a longer time scale that affect the mechanical stability of the solid.

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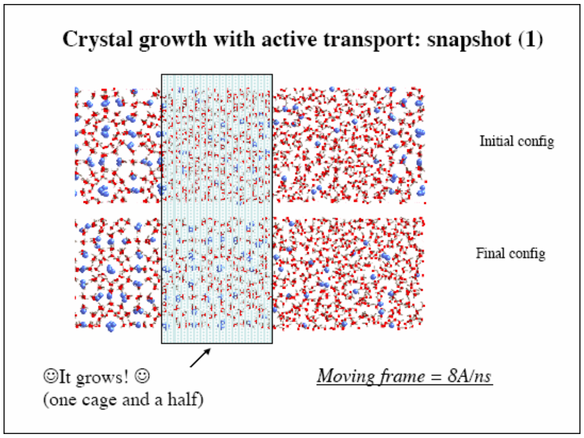


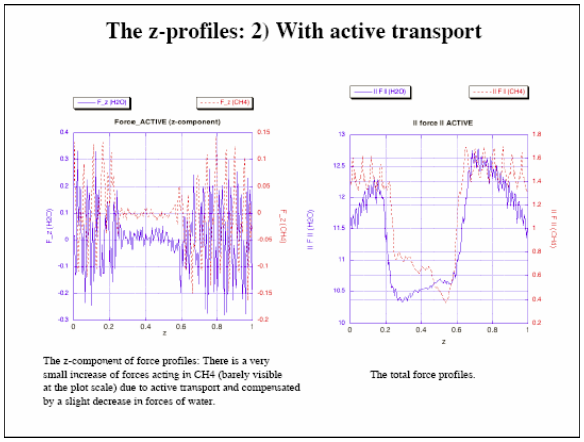
Crystal growth with active transport: snapshot (1)

Initial config

Final config

☺It grows! ☺
(one cage and a half)

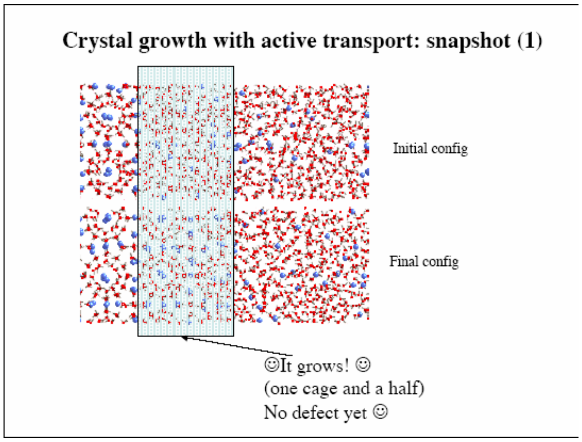
Moving frame = 8A/ns



The z-profiles: 2) With active transport

The z-component of force profiles: There is a very small increase of forces acting in CH4 (barely visible at the plot scale) due to active transport and compensated by a slight decrease in forces of water.

The total force profiles.

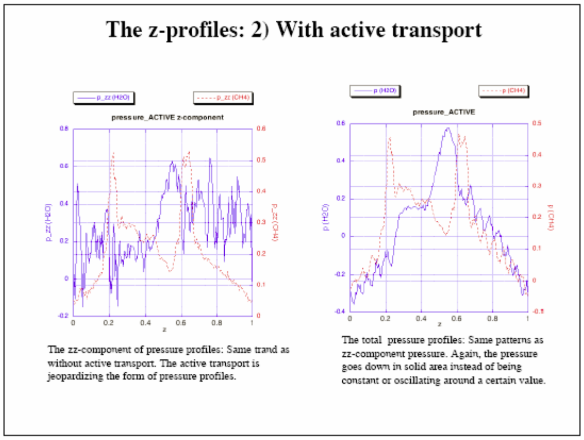


Crystal growth with active transport: snapshot (1)

Initial config

Final config

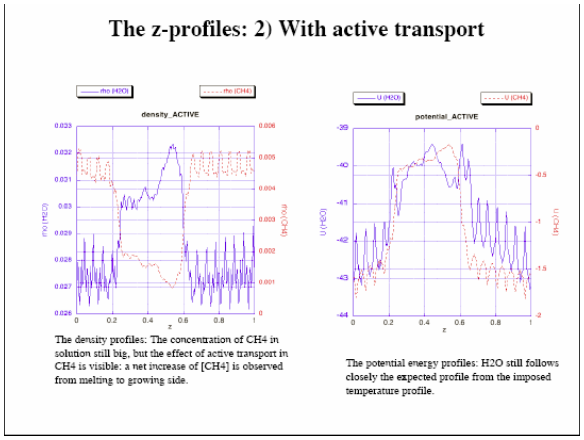
☺It grows! ☺
(one cage and a half)
No defect yet ☺



The z-profiles: 2) With active transport

The zz-component of pressure profiles: Same trand as without active transport. The active transport is jeopardizing the form of pressure profiles.

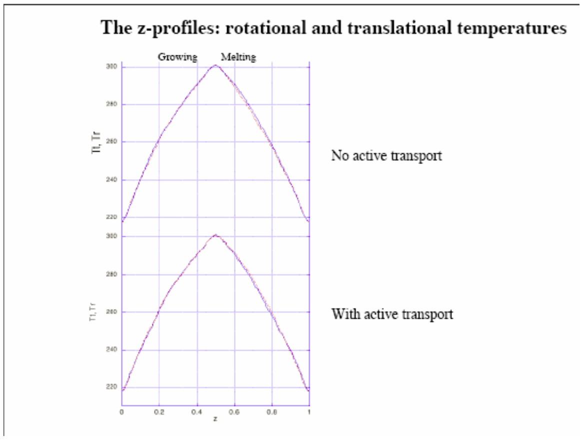
The total pressure profiles: Same patterns as zz-component pressure. Again, the pressure goes down in solid area instead of being constant or oscillating around a certain value.



The z-profiles: 2) With active transport

The density profiles: The concentration of CH4 in solution still big, but the effect of active transport in CH4 is visible: a net increase of [CH4] is observed from melting to growing side.

The potential energy profiles: H2O still follows closely the expected profile from the imposed temperature profile.

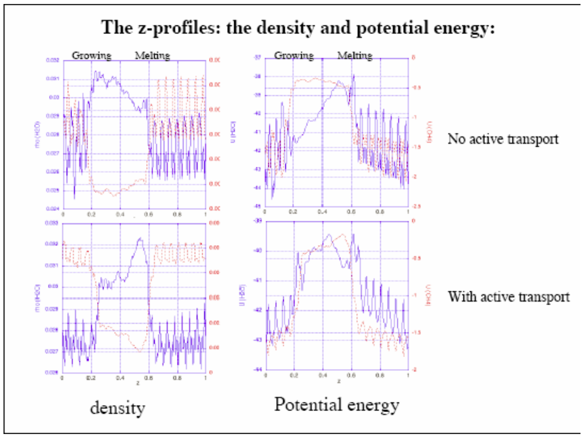


The z-profiles: rotational and translational temperatures

No active transport

With active transport

APPENDIX B



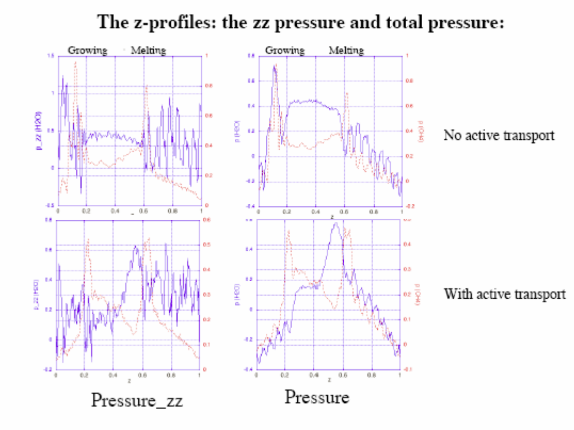
The z-profiles: the density and potential energy:

No active transport

With active transport

density

Potential energy



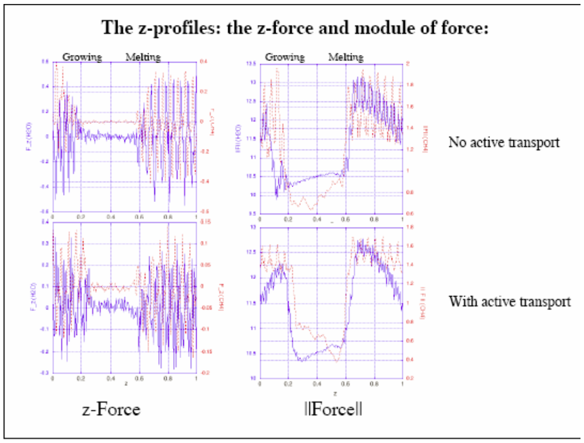
The z-profiles: the zz pressure and total pressure:

No active transport

With active transport

Pressure_zz

Pressure



The z-profiles: the z-force and module of force:

No active transport

With active transport

z-Force

||Force||

APPENDIX B

Microbial Respiration Species Concentration in Pore Fluids Near a Large Gas Hydrate Reservoir, Southern Hydrate Ridge, Offshore Oregon, USA

Thomas D. Lorenson, Frederick S. Colwell, Mark Delwiche, and Jennifer A. Dougherty

Acetate and hydrogen are common products of microbial fermentation and pyrolysis of organic matter. They are also common energy sources for microbial respiration reactions. Thus, these molecules are expected to be key intermediates in subsurface microbial activities and present where living bacteria and archaea reside in marine sediment.

Acetate and hydrogen concentrations in pore fluids were measured in samples taken at seven sites from southern Hydrate Ridge (SHR) offshore Oregon, USA. Acetate concentrations ranged from 3.17 mM to 2515 mM. The maximum acetate concentrations occurred at Site 1251, an area to the east of SHR considered to be a control site relative to SHR sites at just above the bottom simulating reflector (BSR), marking the boundary of gas hydrate above and free gas below. Acetate maxima or locally high concentrations of acetate occur at the BSR at all sites, and frequently correspond with areas of gas hydrate accumulation suggesting an empirical relationship. Acetate concentrations are typically at a minimum near the seafloor where sulfate-reducing bacteria may consume acetate. High acetate concentrations sometimes occurred in sediments with low methanogen cell numbers suggesting that acetate may accumulate where methanogens are not present. Hydrogen concentrations in pressure core samples (PCS) ranged from 16.45 to 1036 parts per million by volume (ppmv). In some cases hydrogen and acetate concentrations were elevated concurrently suggesting a positive correlation. However, sampling of hydrogen was limited in comparison to acetate resulting in unconstrained correlations.

Our working hypothesis gleaned from these observationsis that methanogenic acetate fermentation ($CH_3COOH \rightarrow CH_4 + CO_2$) is inhibited by the buildup of methane in gas hydrate or free gas-rich sediments. Acetate production via reductive acetogenesis ($2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$) is enhanced when hydrogen concentrations are elevated thus providing a likely source for acetate. Taken together, we suggest that high acetate concentration maybe used as a proxy for predicting low counts of live methanogens and that active acetoclastic methanogenesis is inhibited in and near the zone of gas hydrate formation where the methanogens may be constrained by high levels of methane.

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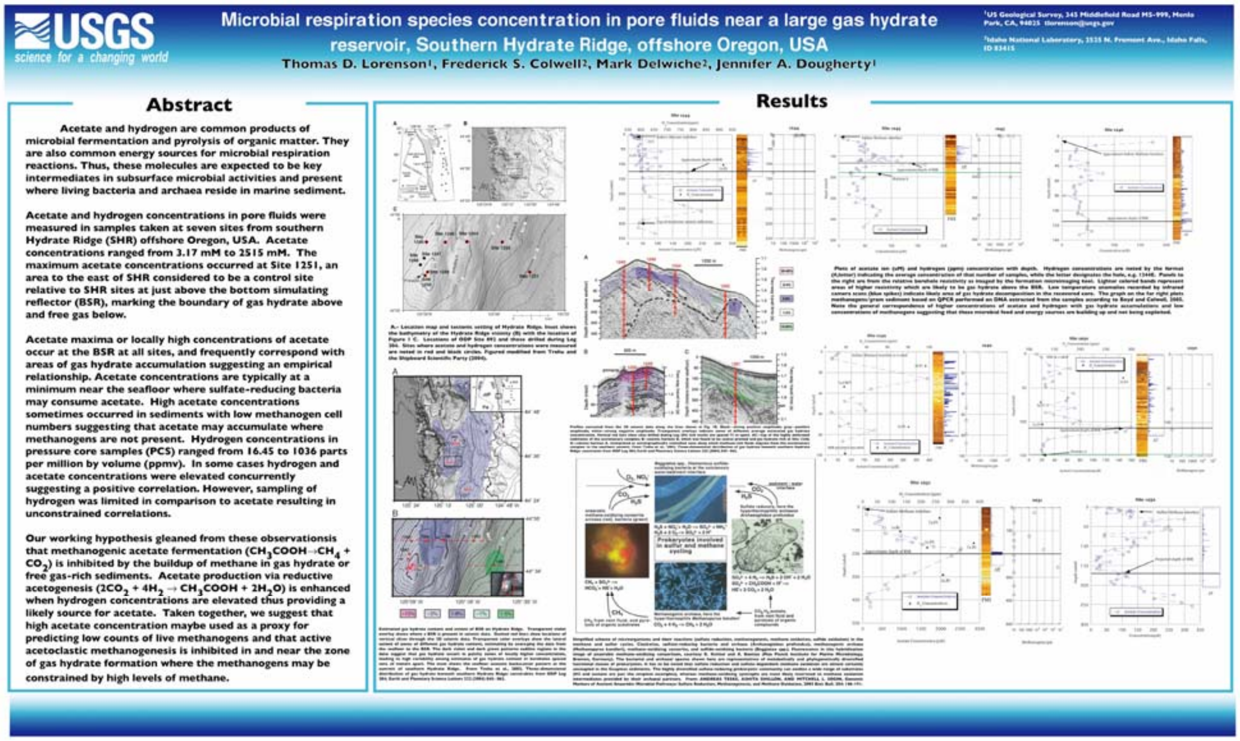
APPENDIX B



Microbial respiration species concentration in pore fluids near a large gas hydrate reservoir, Southern Hydrate Ridge, offshore Oregon, USA

Thomas D. Lorenson[1], Frederick S. Colwell[2], Mark Delwiche[2], Jennifer A. Dougherty[1]

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Abstract

Acetate and hydrogen are common products of microbial fermentation and pyrolysis of organic matter. They are also common energy sources for microbial respiration reactions. Thus, these molecules are expected to be key intermediates in subsurface microbial activities and present where living bacteria and archaea reside in marine sediment.

Acetate and hydrogen concentrations in pore fluids were measured in samples taken at seven sites from southern Hydrate Ridge (SHR) offshore Oregon, USA. Acetate concentrations ranged from 3.17 mM to 2515 mM. The maximum acetate concentrations occurred at Site 1251, an area to the east of SHR considered to be a control site relative to SHR sites at just above the bottom simulating reflector (BSR), marking the boundary of gas hydrate above and free gas below.

Acetate maxima or locally high concentrations of acetate occur at the BSR at all sites, and frequently correspond with areas of gas hydrate accumulation suggesting an empirical relationship. Acetate concentrations are typically at a minimum near the seafloor where sulfate-reducing bacteria may consume acetate. High acetate concentrations sometimes occurred in sediments with low methanogen cell numbers suggesting that acetate may accumulate where methanogens are not present. Hydrogen concentrations in pressure core samples (PCS) ranged from 16.45 to 1036 parts per million by volume (ppmv). In some cases hydrogen and acetate concentrations were elevated concurrently suggesting a positive correlation. However, sampling of hydrogen was limited in comparison to acetate resulting in unconstrained correlations.

Our working hypothesis gleaned from these observationsis that methanogenic acetate fermentation ($CH_3COOH \rightarrow CH_4 + CO_2$) is inhibited by the buildup of methane in gas hydrate or free gas-rich sediments. Acetate production via reductive acetogenesis ($2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$) is enhanced when hydrogen concentrations are elevated thus providing a likely source for acetate. Taken together, we suggest that high acetate concentration maybe used as a proxy for predicting low counts of live methanogens and that active acetoclastic methanogenesis is inhibited in and near the zone of gas hydrate formation where the methanogens may be constrained by high levels of methane.

Results

APPENDIX B

Magnetic Characterization of Gas Hydrate-bearing Sediments: Do Magnetic Methods Have Potential to Locate and Assess Gas Hydrate Deposits?

POSTER NOT AVAILABLE

C. Lowe, R.J. Enkin, J. Baker and S.R. Dallimore

The utility of magnetic methods in the exploration for natural gas hydrate remains largely untested. Systematic magnetic susceptibility (m.s.) measurements were conducted on recovered core from the JAPEX/JNOC/GSC Mallik 5L-38 gas hydrate production research well located in the northern part of the Mallik gas hydrate field. The mean m.s. of sand recovered in the drill core is thee times smaller than that of silt. Further differences between sands and silts were revealed by detailed magnetic characterization studies that show sands have lost their original magnetic remanence whereas silts retain it, and that the sands contain a higher proportion of hard magnetic carriers, such as pyrrhotite. These findings are attributed to diagenetic reactions in sand units which reduce magnetite to iron sulphides. These reactions have been inhibited in silts because of their lower porosity and permeability. This interpretation is supported by a comparison of m.s. with the CMR-derived log of hydrate saturation which reveals that the m.s. of sand decreases by a factor of two with increasing hydrate saturation. This observation is consistent with sulphate reduction and changes in the geochemical regime associated with gas hydrate formation and dissociation.

We use these findings to analyze magnetic field observations in the Mallik region. Forward magnetic models demonstrate that the measured m.s. contrasts between hydrate and non-hydrate-bearing sediments generate anomalies with amplitudes significantly smaller than those observed in the region. This implies that magnetic methods may not be a useful exploration tool in this particular environment. However, independent studies conducted in the marine hydrate setting in Cascadia document magnetic susceptibility contrasts between hydrate and non-hydrate-bearing sediments that are an order of magnitude larger than those observed at Mallik. In this case, forward models demonstrate that the resulting magnetic anomalies should be detectable at the seafloor. More studies are underway to determine the triggers for the observed magnetic reduction in gas hydrate-bearing sediments, the reaction pathways and the circumstances under which magnetic methods may be a viable exploration aid for gas hydrate deposits.

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APPENDIX B

Can Fractures in Soft Sediments Host Significant Quantities of Gas Hydrates?

POSTER NOT AVAILABLE

Tom McGee, Carol Lutken, Bob Woolsey, Rudy Rogers, Jennifer Dearman, F.L. Lynch, Charlotte Brunner, and Jenny Kuykendall

Current interest concerning what types of geologic features contain significant accumulations of gas hydrate arises from the expectation that some day commercial quantities of natural gas will be produced from hydrates. Various geologic structures within the hydrate stability zone have been imaged seismically but there is little consensus concerning serious candidates for exploratory drilling. Some investigators favor targeting sandy sediments where porosity and permeability are greater than in silts and clays. Others expect fractures within fine-grained sediments may host greater volumes of hydrates. The latter scenario seems to fit better with conditions in the hydrate stability zone in the northern Gulf of Mexico and with laboratory results.

Hydrates have been created in the laboratory by adding natural gas, sea water and naturally occurring microbial surfactants to artificial sediments comprised of smectite, kaolinite and sand under appropriate conditions of pressure and temperature. Findings show that biosurfactants greatly enhance hydrate formation and that hydrates form preferentially on smectite (a known component of soft sediments in the Gulf) rather than kaolinite or sand. Given sufficient natural gas, all that remains to complete the formation of hydrates is a mechanism of producing a dense population of fractures open to gas and water circulation. This presentation postulates that the mechanism is polygonal faulting and provides supporting evidence.

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APPENDIX B

Detecting Methane Hydrates Using Controlled Source Electromagnetic Imaging

Simone Medonos

Methane hydrates are electrically insulating with a high resistivity signature relative to surrounding porous sediments. Seismic reflection profiling has been predominantly used to infer their presence. The bottom simulating reflector (BSR) indicates the lower boundary of the hydrate. In some cases, seismic profiling falls short of detecting hydrates. For example, when the BSR is present, the upper limit of the hydrate can be difficult to delineate, and occasionally is not present at all. There is also general difficulty in inferring the extent and mass of hydrate prior to drilling. CSEMI may provide a solution to such problems.

Modelling has determined that CSEMI can detect hydrates in various scenarios. Controlled source electromagnetic imaging is a method of mapping subsurface electrical resistivity variations in the seafloor and has potential to detect resistivity contrasts between resistive hydrates and the surrounding more conductive sediments.

Controlled source EM imaging uses a towed horizontal electric dipole (HED) source to transmit a low frequency EM field to an array of static seafloor receivers. By studying the variation of the received signal as the source is towed through the array, the electric resistivity structure of the underlying earth can be determined at depth scales of a few tens of metres to several km. The resulting fields are particularly sensitive to resistive layers which are thin relative to their depth of burial. In favourable circumstances these layers can be linked to the presence of methane hydrate.

This poster will briefly outline the principles of the CSEMI method, and focus on presenting results from modelled hydrate case studies.

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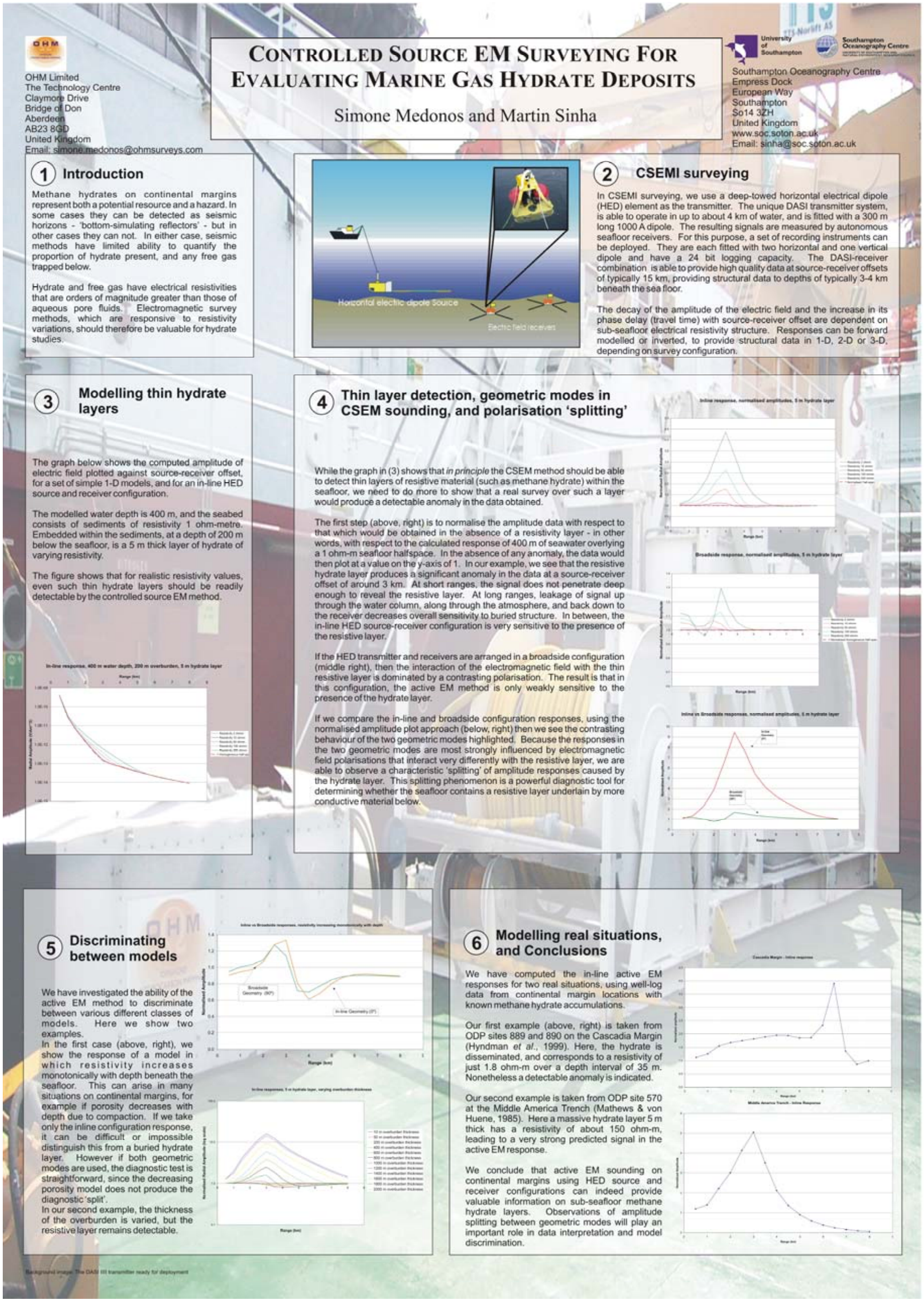

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CONTROLLED SOURCE EM SURVEYING FOR EVALUATING MARINE GAS HYDRATE DEPOSITS

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1 Introduction

Methane hydrates on continental margins represent both a potential resource and a hazard. In some cases they can be detected as seismic horizons - 'bottom-simulating reflectors' - but in other cases they can not. In either case, seismic methods have limited ability to quantify the proportion of hydrate present, and any free gas trapped below.

Hydrate and free gas have electrical resistivities that are orders of magnitude greater than those of aqueous pore fluids. Electromagnetic survey methods, which are responsive to resistivity variations, should therefore be valuable for hydrate studies.

2 CSEMI surveying

In CSEMI surveying, we use a deep-towed horizontal electrical dipole (HED) element as the transmitter. The unique DASI transmitter system, is able to operate in up to about 4 km of water, and is fitted with a 300 m long 1000 A dipole. The resulting signals are measured by autonomous seafloor receivers. For this purpose, a set of recording instruments can be deployed. They are each fitted with two horizontal and one vertical dipole and have a 24 bit logging capacity. The DASI-receiver combination is able to provide high quality data at source-receiver offsets of typically 15 km, providing structural data to depths of typically 3-4 km beneath the sea floor.

The decay of the amplitude of the electric field and the increase in its phase delay (travel time) with source-receiver offset are dependent on sub-seafloor electrical resistivity structure. Responses can be forward modelled or inverted, to provide structural data in 1-D, 2-D or 3-D, depending on survey configuration.

3 Modelling thin hydrate layers

The graph below shows the computed amplitude of electric field plotted against source-receiver offset, for a set of simple 1-D models, and for an in-line HED source and receiver configuration.

The modelled water depth is 400 m, and the seabed consists of sediments of resistivity 1 ohm-metre. Embedded within the sediments, at a depth of 200 m below the seafloor, is a 5 m thick layer of hydrate of varying resistivity.

The figure shows that for realistic resistivity values, even such thin hydrate layers should be readily detectable by the controlled source EM method.

4 Thin layer detection, geometric modes in CSEM sounding, and polarisation 'splitting'

While the graph in (3) shows that *in principle* the CSEM method should be able to detect thin layers of resistive material (such as methane hydrate) within the seafloor, we need to do more to show that a real survey over such a layer would produce a detectable anomaly in the data obtained.

The first step (above, right) is to normalise the amplitude data with respect to that which would be obtained in the absence of a resistivity layer - in other words, with respect to the calculated response of 400 m of seawater overlying a 1 ohm-m seafloor halfspace. In the absence of any anomaly, the data would then plot at a value on the y-axis of 1. In our example, we see that the resistive hydrate layer produces a significant anomaly in the data at a source-receiver offset of around 3 km. At short ranges, the signal does not penetrate deep enough to reveal the resistive layer. At long ranges, leakage of signal up through the water column, along through the atmosphere, and back down to the receiver decreases overall sensitivity to buried structure. In between, the in-line HED source-receiver configuration is very sensitive to the presence of the resistive layer.

If the HED transmitter and receivers are arranged in a broadside configuration (middle right), then the interaction of the electromagnetic field with the thin resistive layer is dominated by a contrasting polarisation. The result is that in this configuration, the active EM method is only weakly sensitive to the presence of the hydrate layer.

If we compare the in-line and broadside configuration responses, using the normalised amplitude plot approach (below, right) then we see the contrasting behaviour of the two geometric modes highlighted. Because the responses in the two geometric modes are most strongly influenced by electromagnetic field polarisations that interact very differently with the resistive layer, we are able to observe a characteristic 'splitting' of amplitude responses caused by the hydrate layer. This splitting phenomenon is a powerful diagnostic tool for determining whether the seafloor contains a resistive layer underlain by more conductive material below.

5 Discriminating between models

We have investigated the ability of the active EM method to discriminate between various different classes of models. Here we show two examples.

In the first case (above, right), we show the response of a model in which resistivity increases monotonically with depth beneath the seafloor. This can arise in many situations on continental margins, for example if porosity decreases with depth due to compaction. If we take only the inline configuration response, it can be difficult or impossible distinguish this from a buried hydrate layer. However if both geometric modes are used, the diagnostic test is straightforward, since the decreasing porosity model does not produce the diagnostic 'split'.

In our second example, the thickness of the overburden is varied, but the resistive layer remains detectable.

6 Modelling real situations, and Conclusions

We have computed the in-line active EM responses for two real situations, using well-log data from continental margin locations with known methane hydrate accumulations.

Our first example (above, right) is taken from ODP sites 889 and 890 on the Cascadia Margin (Hyndman *et al.*, 1999). Here, the hydrate is disseminated, and corresponds to a resistivity of just 1.8 ohm-m over a depth interval of 35 m. Nonetheless a detectable anomaly is indicated.

Our second example is taken from ODP site 570 at the Middle America Trench (Mathews & von Huene, 1985). Here a massive hydrate layer 5 m thick has a resistivity of about 150 ohm-m, leading to a very strong predicted signal in the active EM response.

We conclude that active EM sounding on continental margins using HED source and receiver configurations can indeed provide valuable information on sub-seafloor methane hydrate layers. Observations of amplitude splitting between geometric modes will play an important role in data interpretation and model discrimination.

Background image: The DASI III transmitter ready for deployment

APPENDIX B

Subsurface and Morphologic Setting of 2778 Methane Seeps in the Dnepr Paleo-delta, Northwestern Black Sea

Lieven Naudts, Jens Greinert, Yuriy Artemov and Marc De Batist

The Dnepr paleo-delta area in the NW Black Sea is characterized by an abundant presence of methane seeps, which were observed for the first time by Polikarpov et al. in 1989. During the CRIMEA expedition of May–June 2003 and 2004 detailed multibeam, seismic and hydroacoustic water-column investigations were carried out in the area to study the relation between the spatial distribution of the methane seeps, seafloor morphology and subsurface structures.

During the two expeditions, 2778 new methane seeps were detected on echosounding records in an area of 1540 km2. All seeps are located in the transition zone between the continental shelf and slope, in water depths of 66 to 825 m. The integration of the hydroacoustic and geophysical datasets clearly indicates that methane seeps are not randomly distributed in this area, but are concentrated in specific locations.

The depth limit for the majority of the detected seeps (725 m water depth) coincides more or less with the stability boundary of pure methane hydrates. This suggests that, where gas hydrates are stable, they play the role of buffer for the upward migration of methane gas and thus prevent seepage of methane bubbles into the water column.

Higher up on the margin, gas seeps are widespread, but careful mapping and integration of the datasets illustrates that seeps occur preferentially in association with particular morphologic and subsurface features. On the shelf the highest concentration of seeps can be found in combination with elongated depressions. On the continental slope seeps are concentrated on crests of sedimentary ridges, in the vicinity of canyons (bottom, flanks and margins) or in relation with submarine landslides. The seismic data show the presence of a distinct “gas front” within the seafloor sediments, which is characterised by acoustic blanking and enhanced reflections. The depth of this gas front is variable and locally it domes up to the seafloor. These areas of gas front updoming coincide with areas where seeps were detected in the water column. A regional map of the subsurface depth of the gas front emphasises this “gas front–seep” relationship.

The integration of all data sets allows us to suggest that the spatial distribution of methane seeps in our study area is controlled by several factors (stratigraphic/sedimentary/structural). The presence of seeps at the crest lines of the sediment ridges can be a result of relief inversion. Coarse-grained sediments deposited on canyon floors can act as a focused conduit for seepage. As a result of the seepage, sediments are carbonate-cemented and stand out as ridges after a period of erosion. Seeps associated with submarine landslides can be due to upward migration of fluids along faults, resulting in a reduction of slope stability or can be the result of steepened pore-pressure gradients adjacent to scarps due to the sudden erosion associated with slumping.

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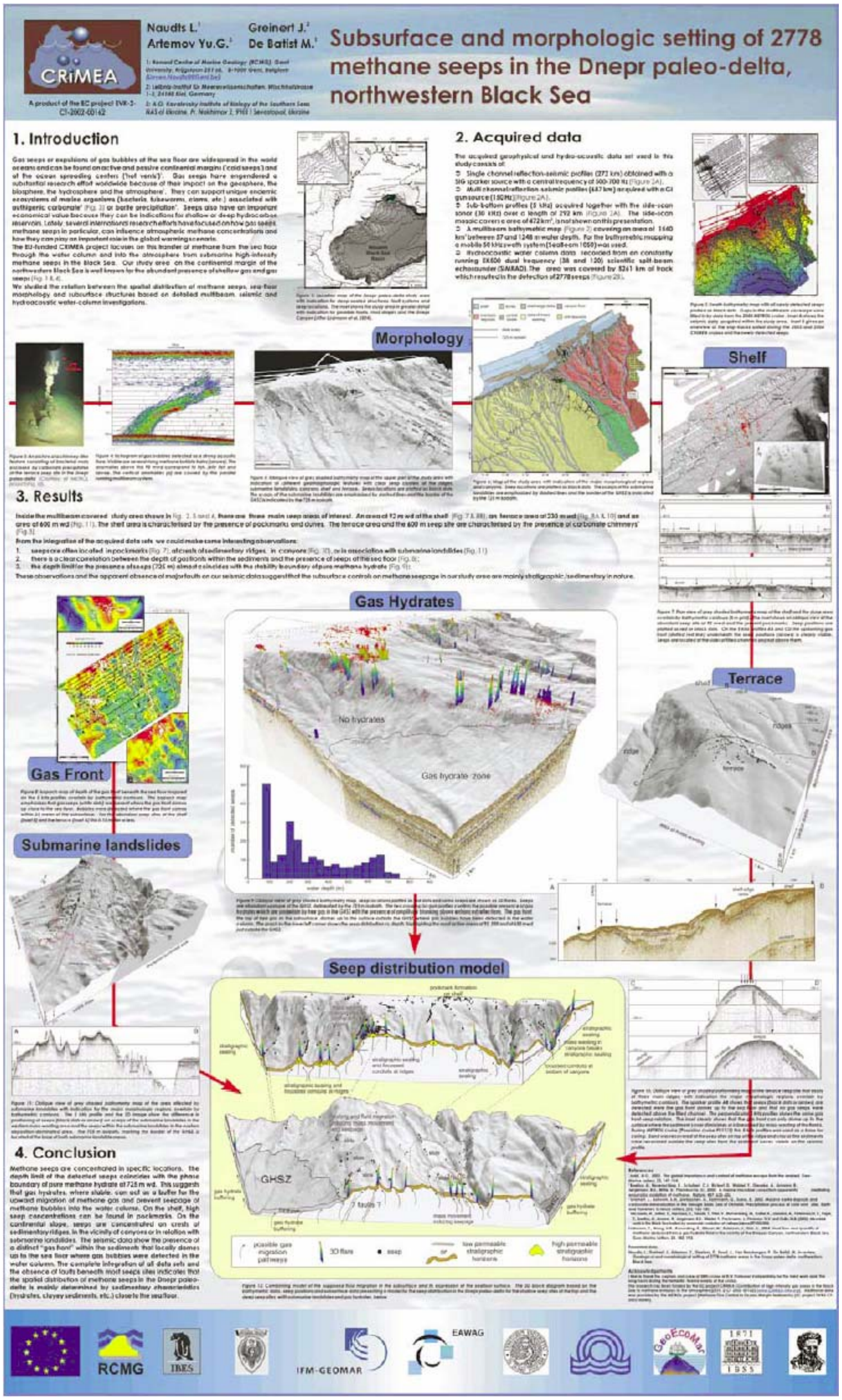

Subsurface and morphologic setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea

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1. Introduction

Gas seeps or expulsions of gas bubbles at the sea floor are widespread in the world oceans and can be found on active and passive continental margins ('cold seeps') and at the ocean spreading centers ('hot vents'). Gas seeps have engendered a substantial research effort worldwide because of their impact on the geosphere, the biosphere, the hydrosphere and the atmosphere. They can support unique endemic ecosystems of marine organisms (bacteria, tubeworms, clams, etc.) associated with authigenic carbonate (Fig. 3) or barite precipitation. Seeps also have an important economical value because they can be indications for shallow or deep hydrocarbon reservoirs. Lately, several international research efforts have focused on how gas seeps, methane seeps in particular, can influence atmospheric methane concentrations and how they can play an important role in the global warming scenario.
The EU-funded CRIMEA project focuses on the transfer of methane from the sea floor through the water column and into the atmosphere from submarine high-intensity methane seeps in the Black Sea. Our study area on the continental margin of the northwestern Black Sea is well known for the abundant presence of shallow gas and gas seeps (Fig. 1 & 4).
We studied the relation between the spatial distribution of methane seeps, sea-floor morphology and subsurface structures based on detailed multibeam, seismic and hydroacoustic water-column investigations.

2. Acquired data

The acquired geophysical and hydro-acoustic data set used in this study consists of:
- Single channel reflection-seismic profiles (272 km) obtained with a SIG sparker source with a central frequency of 500-700 Hz (Figure 2A).
- Multi channel reflection seismic profiles (687 km) acquired with a GI gun source (150 Hz) (Figure 2A).
- Sub-bottom profiles (5 kHz) acquired together with the side-scan sonar (30 kHz) over a length of 292 km (Figure 2A). The side-scan mosaic covers a area of 472 km², is not shown on this presentation.
- A multibeam bathymetric map (Figure 2) covering an area of 1540 km² between 37 and 1248 m water depth. For the bathymetric mapping a mobile 50 kHz swath system (SeaBeam 1050) was used.
- Hydroacoustic water column data recorded from an constantly running EK500 dual frequency (38 and 120) scientific split-beam echosounder (SIMRAD). The area was covered by 8261 km of track which resulted in the detection of 2778 seeps (Figure 2B).

Morphology

Shelf

3. Results

Inside the multibeam covered study area shown in Fig. 2, 5 and 6, there are three main seep areas of interest: An area at 92 m wd at the shelf (Fig. 7 & 8B), an terrace area at 230 m wd (Fig. 8A & 10) and an area at 600 m wd (Fig. 11). The shelf area is characterised by the presence of pockmarks and dunes. The terrace area and the 600 m seep site are characterised by the presence of carbonate chimneys (Fig. 3).

From the integration of the acquired data sets we could make some interesting observations:
1. seeps are often located in pockmarks (Fig. 7), at crests of sedimentary ridges, in canyons (Fig. 10), or in association with submarine landslides (Fig. 11);
2. there is a clear correlation between the depth of gas fronts within the sediments and the presence of seeps at the sea floor (Fig. 8);
3. the depth limit for the presence of seeps (725 m) almost coincides with the stability boundary of pure methane hydrate (Fig. 9).

These observations and the apparent absence of major faults on our seismic data suggest that the subsurface controls on methane seepage in our study area are mainly stratigraphic/sedimentary in nature.

Gas Hydrates

Terrace

Gas Front

Submarine landslides

Seep distribution model

4. Conclusion

Methane seeps are concentrated in specific locations. The depth limit of the detected seeps coincides with the phase boundary of pure methane hydrate at 725 m wd. This suggests that gas hydrates, where stable, can act as a buffer for the upward migration of methane gas and prevent seepage of methane bubbles into the water column. On the shelf, high seep concentrations can be found in pockmarks. On the continental slope, seeps are concentrated on crests of sedimentary ridges, in the vicinity of canyons or in relation with submarine landslides. The seismic data show the presence of a distinct "gas front" within the sediments that locally domes up to the sea floor where gas bubbles were detected in the water column. The complete integration of all data sets and the absence of faults beneath most seeps sites indicates that the spatial distribution of methane seeps in the Dnepr paleo-delta is mainly determined by sedimentary characteristics (hydrates, clayey sediments, etc.) close to the sea floor.

APPENDIX B

A Re-examination of Beaufort Sea—MacKenzie Delta Basin Gas Hydrate Resource Potential Using a Petroleum Play Approach

Kirk G. Osadetz and Zhuoheng Chen

An environment favoring gas hydrate stability and a timely petroleum flux of appropriate composition into suitable reservoirs are necessary conditions for gas hydrate accumulation. A re-examination of regional Beaufort Sea–Mackenzie Delta Basin gas hydrate resources derived using both deterministic spatial and reservoir parameter probabilistic models permit regional resource characterization as a function of reservoir parameters that are potential proxies for technological and economic supply definitions. The deterministic total estimate = 8.82×10^{12} m^3 GIP portrays resource geographic distribution, illustrated by gas hydrate saturation (6.40×10^{12} m^3 and 4.59×10^{12} m^3 GIP if average gas saturation is >30% and >50%, respectively). A comparable expected total = 10.23×10^{12} m^3 GIP, similarly constrained (expected 6.93×10^{12} m^3 and 4.20×10^{12} m3 GIP if gas saturation is >30% and >50%, respectively) is obtained using a probabilistic method that describes resource potential with an associated uncertainty. Estimates of regionally sequestered methane in gas hydrates constrain long-term regional methane flux rates from tectonically active petroliferous provinces, here <0.09-4.20 $mg/m^2/d$, which is lower than the tens to hundreds of $mg/m^2/d$ suggested recently.

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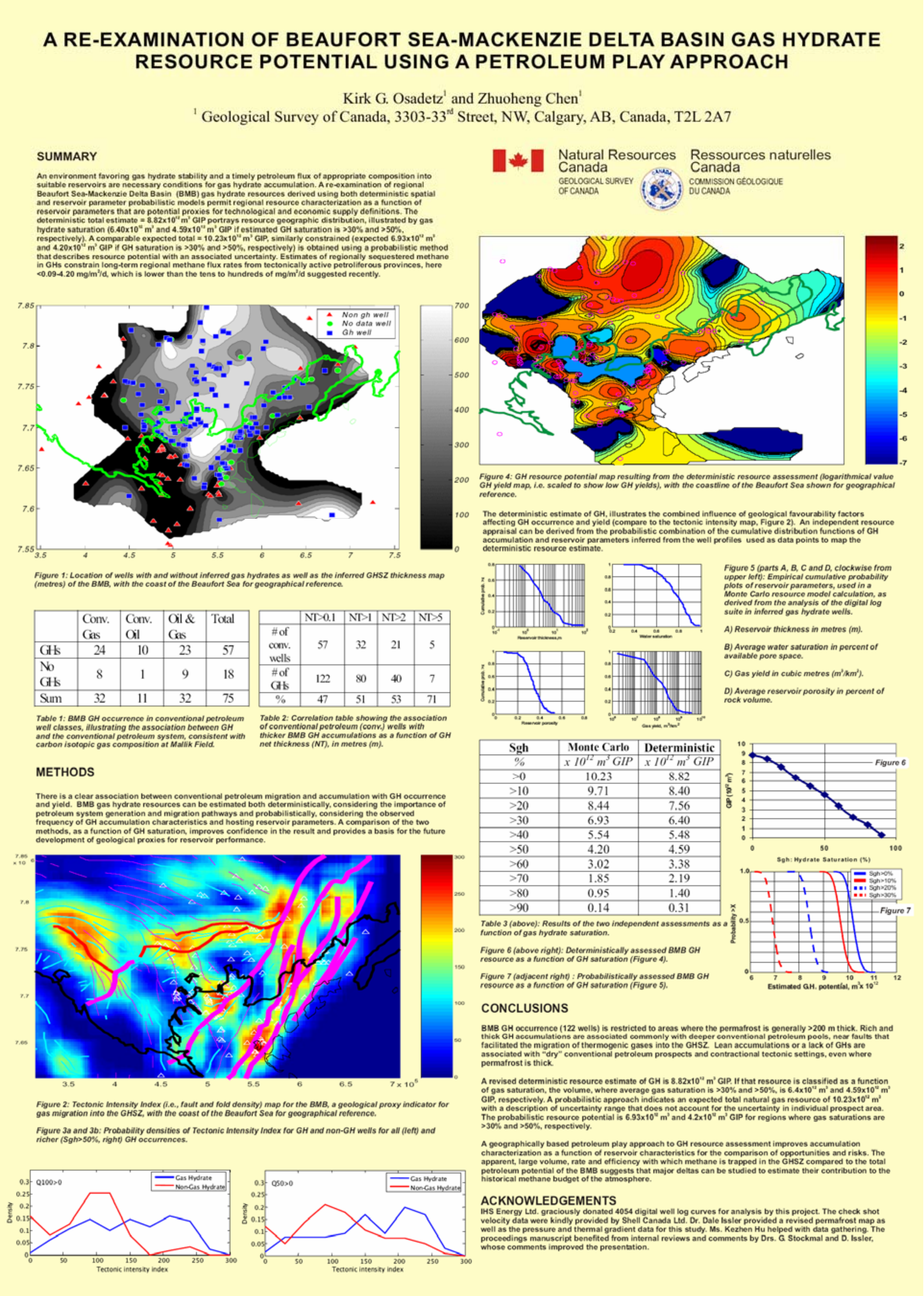

A RE-EXAMINATION OF BEAUFORT SEA-MACKENZIE DELTA BASIN GAS HYDRATE RESOURCE POTENTIAL USING A PETROLEUM PLAY APPROACH

Kirk G. Osadetz[1] and Zhuoheng Chen[1]
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Natural Resources Canada
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SUMMARY

An environment favoring gas hydrate stability and a timely petroleum flux of appropriate composition into suitable reservoirs are necessary conditions for gas hydrate accumulation. A re-examination of regional Beaufort Sea-Mackenzie Delta Basin (BMB) gas hydrate resources derived using both deterministic spatial and reservoir parameter probabilistic models permit regional resource characterization as a function of reservoir parameters that are potential proxies for technological and economic supply definitions. The deterministic total estimate = 8.82×10^{12} m^3 GIP portrays resource geographic distribution, illustrated by gas hydrate saturation (6.40×10^{12} m^3 and 4.59×10^{12} m^3 GIP if estimated GH saturation is >30% and >50%, respectively). A comparable expected total = 10.23×10^{12} m^3 GIP, similarly constrained (expected 6.93×10^{12} m^3 and 4.20×10^{12} m^3 GIP if GH saturation is >30% and >50%, respectively) is obtained using a probabilistic method that describes resource potential with an associated uncertainty. Estimates of regionally sequestered methane in GHs constrain long-term regional methane flux rates from tectonically active petroliferous provinces, here <0.09-4.20 mg/m^2/d, which is lower than the tens to hundreds of mg/m^2/d suggested recently.

Figure 1: Location of wells with and without inferred gas hydrates as well as the inferred GHSZ thickness map (metres) of the BMB, with the coast of the Beaufort Sea for geographical reference.

	Conv. Gas	Conv. Oil	Oil & Gas	Total
GHs	24	10	23	57
No GHs	8	1	9	18
Sum	32	11	32	75

Table 1: BMB GH occurrence in conventional petroleum well classes, illustrating the association between GH and the conventional petroleum system, consistent with carbon isotopic gas composition at Mallik Field.

	NT>0.1	NT>1	NT>2	NT>5
# of conv. wells	57	32	21	5
# of GHs	122	80	40	7
%	47	51	53	71

Table 2: Correlation table showing the association of conventional petroleum (conv.) wells with thicker BMB GH accumulations as a function of GH net thickness (NT), in metres (m).

METHODS

There is a clear association between conventional petroleum migration and accumulation with GH occurrence and yield. BMB gas hydrate resources can be estimated both deterministically, considering the importance of petroleum system generation and migration pathways and probabilistically, considering the observed frequency of GH accumulation characteristics and hosting reservoir parameters. A comparison of the two methods, as a function of GH saturation, improves confidence in the result and provides a basis for the future development of geological proxies for reservoir performance.

Figure 2: Tectonic Intensity Index (i.e., fault and fold density) map for the BMB, a geological proxy indicator for gas migration into the GHSZ, with the coast of the Beaufort Sea for geographical reference.

Figure 3a and 3b: Probability densities of Tectonic Intensity Index for GH and non-GH wells for all (left) and richer (Sgh>50%, right) GH occurrences.

Figure 4: GH resource potential map resulting from the deterministic resource assessment (logarithmical value GH yield map, i.e. scaled to show low GH yields), with the coastline of the Beaufort Sea shown for geographical reference.

The deterministic estimate of GH, illustrates the combined influence of geological favourability factors affecting GH occurrence and yield (compare to the tectonic intensity map, Figure 2). An independent resource appraisal can be derived from the probabilistic combination of the cumulative distribution functions of GH accumulation and reservoir parameters inferred from the well profiles used as data points to map the deterministic resource estimate.

Figure 5 (parts A, B, C and D, clockwise from upper left): Empirical cumulative probability plots of reservoir parameters, used in a Monte Carlo resource model calculation, as derived from the analysis of the digital log suite in inferred gas hydrate wells.

A) Reservoir thickness in metres (m).

B) Average water saturation in percent of available pore space.

C) Gas yield in cubic metres (m^3/km^2).

D) Average reservoir porosity in percent of rock volume.

Sgh	Monte Carlo	Deterministic
%	x 10^{12} m^3 GIP	x 10^{12} m^3 GIP
>0	10.23	8.82
>10	9.71	8.40
>20	8.44	7.56
>30	6.93	6.40
>40	5.54	5.48
>50	4.20	4.59
>60	3.02	3.38
>70	1.85	2.19
>80	0.95	1.40
>90	0.14	0.31

Table 3 (above): Results of the two independent assessments as a function of gas hydrate saturation.

Figure 6 (above right): Deterministically assessed BMB GH resource as a function of GH saturation (Figure 4).

Figure 7 (adjacent right) : Probabilistically assessed BMB GH resource as a function of GH saturation (Figure 5).

CONCLUSIONS

BMB GH occurrence (122 wells) is restricted to areas where the permafrost is generally >200 m thick. Rich and thick GH accumulations are associated commonly with deeper conventional petroleum pools, near faults that facilitated the migration of thermogenic gases into the GHSZ. Lean accumulations or a lack of GHs are associated with "dry" conventional petroleum prospects and contractional tectonic settings, even where permafrost is thick.

A revised deterministic resource estimate of GH is 8.82×10^{12} m^3 GIP. If that resource is classified as a function of gas saturation, the volume, where average gas saturation is >30% and >50%, is 6.4×10^{12} m^3 and 4.59×10^{12} m^3 GIP, respectively. A probabilistic approach indicates an expected total natural gas resource of 10.23×10^{12} m^3 with a description of uncertainty range that does not account for the uncertainty in individual prospect area. The probabilistic resource potential is 6.93×10^{12} m^3 and 4.2×10^{12} m^3 GIP for regions where gas saturations are >30% and >50%, respectively.

A geographically based petroleum play approach to GH resource assessment improves accumulation characterization as a function of reservoir characteristics for the comparison of opportunities and risks. The apparent, large volume, rate and efficiency with which methane is trapped in the GHSZ compared to the total petroleum potential of the BMB suggests that major deltas can be studied to estimate their contribution to the historical methane budget of the atmosphere.

ACKNOWLEDGEMENTS

IHS Energy Ltd. graciously donated 4054 digital well log curves for analysis by this project. The check shot velocity data were kindly provided by Shell Canada Ltd. Dr. Dale Issler provided a revised permafrost map as well as the pressure and thermal gradient data for this study. Ms. Kezhen Hu helped with data gathering. The proceedings manuscript benefited from internal reviews and comments by Drs. G. Stockmal and D. Issler, whose comments improved the presentation.

APPENDIX B

The Biogeochemical Cycling of Methane in Sediments Overlying Gas Hydrates in Barkley Canyon: Fatty Acid and Pore Water Geochemical Evidence

John Pohlman, Elizabeth Canuel, Laura Lapham, Jeffery Chanton,
Ross Chapman and Richard Coffin

Massive seafloor-exposed thermogenic gas hydrates were recently reported from Barkley Canyon (Northern Cascadia Margin, offshore Vancouver Island). Profiles of dissolved constituents from sediment push cores collected with the ROV ROPOS around these hydrate mounds were obtained from samples collected in June 2003 to investigate the biogeochemical cycling of dissolved methane in sediments overlying and adjacent to gas hydrate mounds. The cores were collected from within four distinct ecological regions near the hydrates: 1) bare sediment; 2) vesicomyid clam communities; 3) bacterial mats; and 4) carbonate encrusted sediments. Of nine cores analyzed, four had high concentrations of methane (0.4–12 mM) and offered evidence for extensive anaerobic oxidation of methane (AOM). For example, within the sulfate–methane interface (SMI), we observed depletion of methane and sulfate (AOM substrate) and enrichment of dissolved inorganic carbon (DIC) (14–26 mM) (AOM products). Below the SMI, near-surface methanogenesis contributed to the high methane concentrations. AOM in sediments covering gas hydrates was an efficient mechanism for blocking the transfer of methane from hydrates into the water column. On average, the near-surface dissolved methane pore water concentrations were 93% lower than the highest concentration within each push core. These observations will help us understand the factors that control the fate of methane in seafloor hydrate fields and have implications for delineating the contribution of gas hydrates in global carbon and methane budgets. Compound specific carbon stable isotope analysis was performed on fatty acids from a gas-charged core exhibiting evidence of AOM. Depletion of ^{13}C in fatty acids known to occur in sulfate reducing bacteria (SRB) supports the hypothesis that these bacteria were associated with AOM. Recent studies from cores collected near hydrate accumulations at Hydrate Ridge and Bush Hill (Gulf of Mexico) also reported ^{13}C depletion in fatty acids. The fatty acids exhibiting the ^{13}C depletion, however, were different. The difference was attributed to the presence of different SRB or other bacterial species. We observed ^{13}C depletion in the fatty acids reported from both sites, which may suggest a more diverse SRB community in Barkley Canyon. Future studies will investigate the chemotaxonomic diversity of additional cores collected within the distinct ecological regions observed in Barkley Canyon.

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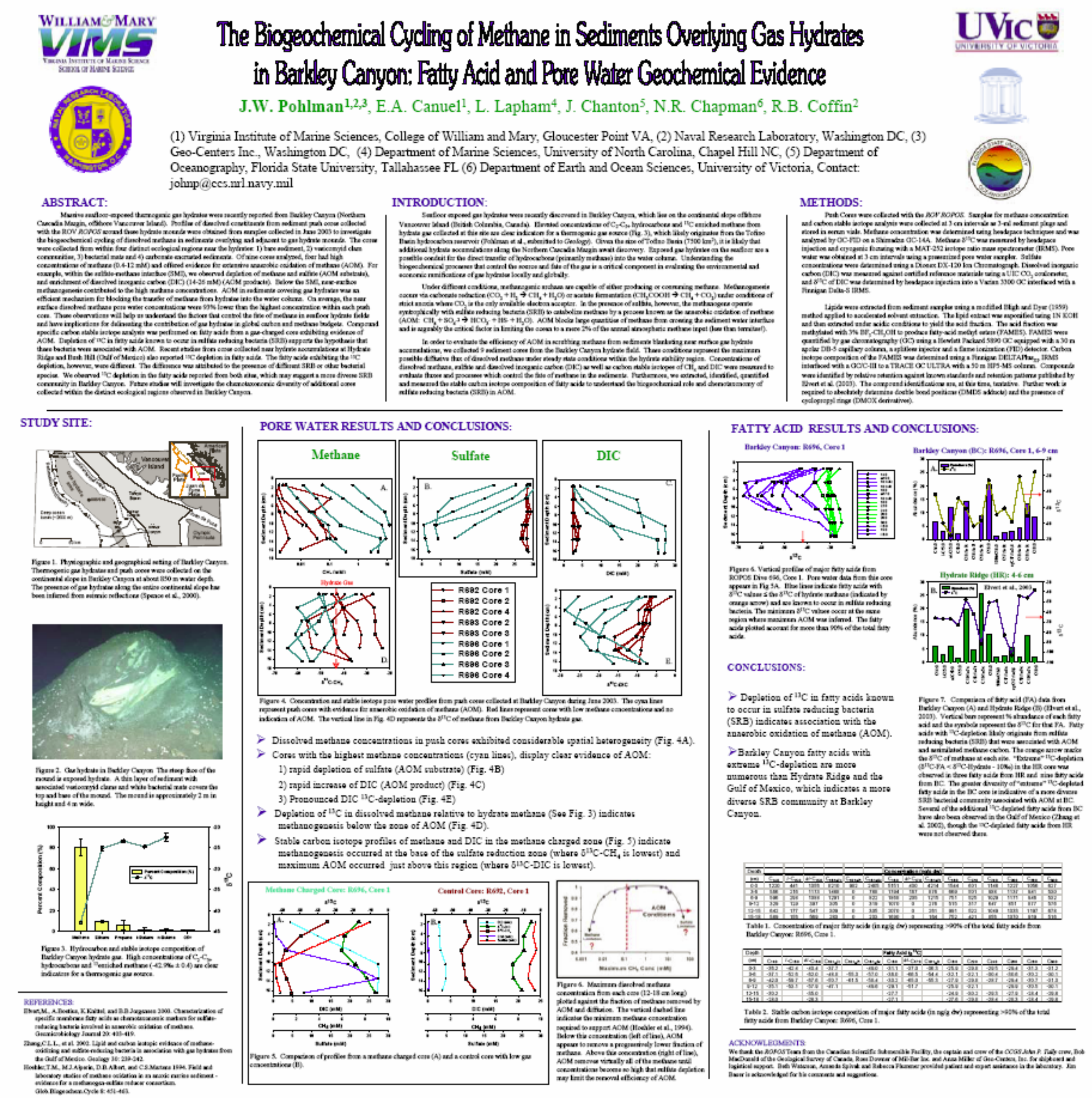

The Biogeochemical Cycling of Methane in Sediments Overlying Gas Hydrates in Barkley Canyon: Fatty Acid and Pore Water Geochemical Evidence

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ABSTRACT:

Massive seafloor-exposed thermogenic gas hydrates were recently reported from Barkley Canyon (Northern Cascadia Margin, offshore Vancouver Island). Profiles of dissolved constituents from sediment push cores collected with the ROV *ROPOS* around these hydrate mounds were obtained from samples collected in June 2003 to investigate the biogeochemical cycling of dissolved methane in sediments overlying and adjacent to gas hydrate mounds. The cores were collected from within four distinct ecological regions near the hydrates: 1) bare sediment, 2) vesicomyid clam communities, 3) bacterial mats and 4) carbonate encrusted sediments. Of nine cores analyzed, four had high concentrations of methane (0.4-12 mM) and offered evidence for extensive anaerobic oxidation of methane (AOM). For example, within the sulfate-methane interface (SMI), we observed depletion of methane and sulfate (AOM substrate), and enrichment of dissolved inorganic carbon (DIC) (14-26 mM) (AOM products). Below the SMI, near-surface methanogenesis contributed to the high methane concentrations. AOM in sediments covering gas hydrates was an efficient mechanism for blocking the transfer of methane from hydrates into the water column. On average, the near surface dissolved methane pore water concentrations were 93% lower than the highest concentration within each push core. These observations will help us understand the factors that control the fate of methane in seafloor hydrate fields and have implications for delineating the contribution of gas hydrates in global carbon and methane budgets. Compound specific carbon stable isotope analysis was performed on fatty acids from a gas-charged core exhibiting evidence of AOM. Depletion of ^{13}C in fatty acids known to occur in sulfate reducing bacteria (SRB) supports the hypothesis that these bacteria were associated with AOM. Recent studies from cores collected near hydrate accumulations at Hydrate Ridge and Bush Hill (Gulf of Mexico) also reported ^{13}C depletion in fatty acids. The fatty acids exhibiting the ^{13}C depletion, however, were different. The difference was attributed to the presence of different SRB or other bacterial species. We observed ^{13}C depletion in the fatty acids reported from both sites, which may suggest a more diverse SRB community in Barkley Canyon. Future studies will investigate the chemotaxonomic diversity of additional cores collected within the distinct ecological regions observed in Barkley Canyon.

INTRODUCTION:

Seafloor exposed gas hydrates were recently discovered in Barkley Canyon, which lies on the continental slope offshore Vancouver Island (British Columbia, Canada). Elevated concentrations of C_2-C_{5+} hydrocarbons and ^{13}C enriched methane from hydrate gas collected at this site are clear indicators for a thermogenic gas source (Fig. 3), which likely originates from the Tofino Basin hydrocarbon reservoir (Pohlman et al., submitted to *Geology*). Given the size of Tofino Basin (7500 km^2), it is likely that additional hydrate accumulations along the Northern Cascadia Margin await discovery. Exposed gas hydrates on the seafloor are a possible conduit for the direct transfer of hydrocarbons (primarily methane) into the water column. Understanding the biogeochemical processes that control the source and fate of the gas is a critical component in evaluating the environmental and economic ramifications of gas hydrates locally and globally.

Under different conditions, methanogenic archaea are capable of either producing or consuming methane. Methanogenesis occurs via carbonate reduction ($CO_2 + H_2 \rightarrow CH_4 + H_2O$) or acetate fermentation ($CH_3COOH \rightarrow CH_4 + CO_2$) under conditions of strict anoxia where CO_2 is the only available electron acceptor. In the presence of sulfate, however, the methanogens operate syntrophically with sulfate reducing bacteria (SRB) to catabolize methane by a process known as the anaerobic oxidation of methane (AOM: $CH_4 + SO_4^{-2} \rightarrow HCO_3^- + HS^- + H_2O$). AOM blocks large quantities of methane from crossing the sediment water interface and is arguably the critical factor in limiting the ocean to a mere 2% of the annual atmospheric methane input (less than termites!).

In order to evaluate the efficiency of AOM in scrubbing methane from sediments blanketing near surface gas hydrate accumulations, we collected 9 sediment cores from the Barkley Canyon hydrate field. These conditions represent the maximum possible diffusive flux of dissolved methane under steady state conditions within the hydrate stability region. Concentrations of dissolved methane, sulfate and dissolved inorganic carbon (DIC) as well as carbon stable isotopes of CH_4 and DIC were measured to evaluate fluxes and processes which control the fate of methane in the sediments. Furthermore, we extracted, identified, quantified and measured the stable carbon isotope composition of fatty acids to understand the biogeochemical role and chemotaxonomy of sulfate reducing bacteria (SRB) in AOM.

METHODS:

Push Cores were collected with the *ROV ROPOS*. Samples for methane concentration and carbon stable isotope analysis were collected at 3 cm intervals as 3-ml sediment plugs and stored in serum vials. Methane concentration was determined using headspace techniques and was analyzed by GC-FID on a Shimadzu GC-14A. Methane $\delta^{13}C$ was measured by headspace injection and cryogenic focusing with a MAT-252 isotope ratio mass spectrometer (IRMS). Pore water was obtained at 3 cm intervals using a pressurized pore water sampler. Sulfate concentrations were determined using a Dionex DX-120 Ion Chromatograph. Dissolved inorganic carbon (DIC) was measured against certified reference materials using a UIC CO_2 coulometer, and $\delta^{13}C$ of DIC was determined by headspace injection into a Varian 3300 GC interfaced with a Finnigan Delta-S IRMS.

Lipids were extracted from sediment samples using a modified Bligh and Dyer (1959) method applied to accelerated solvent extraction. The lipid extract was saponified using 1N KOH and then extracted under acidic conditions to yield the acid fraction. The acid fraction was methylated with 3% BF_3-CH_3OH to produce fatty-acid methyl esters (FAMES). FAMES were quantified by gas chromatography (GC) using a Hewlett Packard 5890 GC equipped with a 30 m apolar DB-5 capillary column, a splitless injector and a flame ionization (FID) detector. Carbon isotope composition of the FAMES was determined using a Finnigan DELTAPlus$_{XP}$ IRMS interfaced with a GC/C-III to a TRACE GC ULTRA with a 50 m HP5-MS column. Compounds were identified by relative retention against known standards and retention patterns published by Elvert et al. (2003). The compound identifications are, at this time, tentative. Further work is required to absolutely determine double bond positions (DMDS adducts) and the presence of cyclopropyl rings (DMOX derivatives).

STUDY SITE:

Figure 1. Physiographic and geographical setting of Barkley Canyon. Thermogenic gas hydrates and push cores were collected on the continental slope in Barkley Canyon at about 850 m water depth. The presence of gas hydrates along the entire continental slope has been inferred from seismic reflections (Spence et al., 2000).

Figure 2. Gas hydrate in Barkley Canyon. The steep face of the mound is exposed hydrate. A thin layer of sediment with associated vesicomyid clams and white bacterial mats covers the top and base of the mound. The mound is approximately 2 m in height and 4 m wide.

Figure 3. Hydrocarbon and stable isotope composition of Barkley Canyon hydrate gas. High concentrations of C_2-C_{5+} hydrocarbons and ^{13}C enriched methane (-42.9‰ ± 0.4) are clear indicators for a thermogenic gas source.

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PORE WATER RESULTS AND CONCLUSIONS:

Figure 4. Concentration and stable isotope pore water profiles from push cores collected at Barkley Canyon during June 2003. The cyan lines represent push cores with evidence for anaerobic oxidation of methane (AOM). Red lines represent cores with low methane concentrations and no indication of AOM. The vertical line in Fig. 4D represents the $\delta^{13}C$ of methane from Barkley Canyon hydrate gas.

- ➢ Dissolved methane concentrations in push cores exhibited considerable spatial heterogeneity (Fig. 4A).
- ➢ Cores with the highest methane concentrations (cyan lines), display clear evidence of AOM:
  1) rapid depletion of sulfate (AOM substrate) (Fig. 4B)
  2) rapid increase of DIC (AOM product) (Fig. 4C)
  3) Pronounced DIC ^{13}C-depletion (Fig. 4E)
- ➢ Depletion of ^{13}C in dissolved methane relative to hydrate methane (See Fig. 3) indicates methanogenesis below the zone of AOM (Fig. 4D).
- ➢ Stable carbon isotope profiles of methane and DIC in the methane charged zone (Fig. 5) indicate methanogenesis occurred at the base of the sulfate reduction zone (where $\delta^{13}C$-CH_4 is lowest) and maximum AOM occurred just above this region (where $\delta^{13}C$-DIC is lowest).

Figure 5. Comparison of profiles from a methane charged core (A) and a control core with low gas concentrations (B).

Figure 6. Maximum dissolved methane concentration from each core (12-18 cm long) plotted against the fraction of methane removed by AOM and diffusion. The vertical dashed line indicates the minimum methane concentration required to support AOM (Hoehler et al., 1994). Below this concentration (left of line), AOM appears to remove a progressively lower fraction of methane. Above this concentration (right of line), AOM removes virtually all of the methane until concentrations become so high that sulfate depletion may limit the removal efficiency of AOM.

FATTY ACID RESULTS AND CONCLUSIONS:

Figure 6. Vertical profile of major fatty acids from ROPOS Dive 696, Core 1. Pore water data from this core appears in Fig 5A. Blue lines indicate fatty acids with $\delta^{13}C$ values ≤ the $\delta^{13}C$ of hydrate methane (indicated by orange arrow) and are known to occur in sulfate reducing bacteria. The minimum $\delta^{13}C$ values occur at the same region where maximum AOM was inferred. The fatty acids plotted account for more than 90% of the total fatty acids.

Figure 7. Comparison of fatty acid (FA) data from Barkley Canyon (A) and Hydrate Ridge (B) (Elvert et al., 2003). Vertical bars represent % abundance of each fatty acid and the symbols represent the $\delta^{13}C$ for that FA. Fatty acids with ^{13}C-depletion likely originate from sulfate reducing bacteria (SRB) that were associated with AOM and assimilated methane carbon. The orange arrow marks the $\delta^{13}C$ of methane at each site. "Extreme" ^{13}C-depletion ($\delta^{13}C$-FA < $\delta^{13}C$-Hydrate - 10‰) in the HR core was observed in three fatty acids from HR and nine fatty acids from BC. The greater diversity of "extreme" ^{13}C-depleted fatty acids in the BC core is indicative of a more diverse SRB bacterial community associated with AOM at BC. Several of the additional ^{13}C-depleted fatty acids from BC have also been observed in the Gulf of Mexico (Zhang et al. 2002), though the ^{13}C-depleted fatty acids from HR were not observed there.

CONCLUSIONS:

- ➢ Depletion of ^{13}C in fatty acids known to occur in sulfate reducing bacteria (SRB) indicates association with the anaerobic oxidation of methane (AOM).
- ➢ Barkley Canyon fatty acids with extreme ^{13}C-depletion are more numerous than Hydrate Ridge and the Gulf of Mexico, which indicates a more diverse SRB community at Barkley Canyon.

Table 1. Concentration of major fatty acids (in ng/g dw) representing >90% of the total fatty acids from Barkley Canyon: R696, Core 1.

Table 2. Stable carbon isotope composition of major fatty acids (in ng/g dw) representing >90% of the total fatty acids from Barkley Canyon: R696, Core 1.

ACKNOWLEGMENTS:

We thank the *ROPOS* Team from the Canadian Scientific Submersible Facility, the captain and crew of the *CCGS John P. Tully* crew, Bob MacDonald of the Geological Survey of Canada, Ross Downer of Mil-Bar Inc. and Anna Miller of Geo-Centers, Inc. for shipboard and logistical support. Beth Waterson, Amanda Spivak and Rebecca Plummer provided patient and expert assistance in the laboratory. Jim Bauer is acknowledged for his comments and suggestions.

APPENDIX B

Characterizing Methane Hydrate Through Scientific Ocean Drilling

POSTER NOT AVAILABLE

Frank R. Rack

Scientists will focus on characterizing methane hydrate across the Cascadia continental margin, offshore British Columbia, Canada, during Integrated Ocean Drilling Program (IODP) Expedition 311 (http://www.iodp.org) from August 24 to October 7, 2005 using the JOIDES Resolution, a 471-foot-long, riserless, scientific ocean drilling vessel (SODV) operated by the JOI Alliance, or U.S. implementing Organization (http://www.oceandrilling.org). The operations offshore Cascadia are the latest in a long history of scientific ocean drilling investigations of methane hydrate and bottom simulating reflectors (BSR), which began with the Deep Sea Drilling Project (DSDP) in 1968 and continued through the Ocean Drilling Program (ODP), which ended in 2003. The technologies developed and lessons learned from these past activities, which included dedicated hydrate investigations on ODP Legs 164 (Blake Ridge and Carolina Rise) and 204 (Hydrate Ridge, offshore Oregon), will be used to advance the current state of the art on this upcoming IODP expedition. The current operational plans include the potential use of various pressure coring systems (e.g., PCS and HYACINTH tools), wireline downhole temperature and pressure measurements, logging-while-drilling/measurement-while-drilling (LWD/MWD) systems, and other measurement, sampling and laboratory techniques to advance our understanding of these deposits. Collaborative projects are being explored in an attempt to provide the optimum technical, scientific and engineering capabilities to the science party on this expedition.

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APPENDIX B

New Dissociation Model of Methane Hydrate Developed by CFD and Experiment

Wo-Yang Sean, Toru Sato, Akihiro Yamasaki and Fumio Kiyono

The decomposition rate of methane hydrate in aqueous solute is newly modeled. The model consists of two parts: one is mass transfer from the surface to an imaginary buffer layer, and the other is that from the buffer layer to solute. In the buffer layer, chemical potential is the driving force of the decomposition, the flux of which must be equal to that from the buffer layer to the solute, where advection-diffusion takes place. To determine the dissociation rate constant, a single spherical pellet of the hydrate is considered. In order to make calibration curves between the decomposition rate and the methane flux under several conditions of pressure and temperature in the L-H phase regime, we conducted numerical simulations of flow and mass and heat transfer about the pellet with 3-dimensional unstructured grids. The flux from the pellet measured in laboratory experiments were applied to the curves to obtain the intrinsic decomposition rate constant. This rate constant was verified by the measurement of the amount of methane babbles dissociated form the pellet in the V-H phase regime. Eventually, it was shown that the mass flux at the pellet surface calculated by our new dissociation model is in good agreement with that of measurement.

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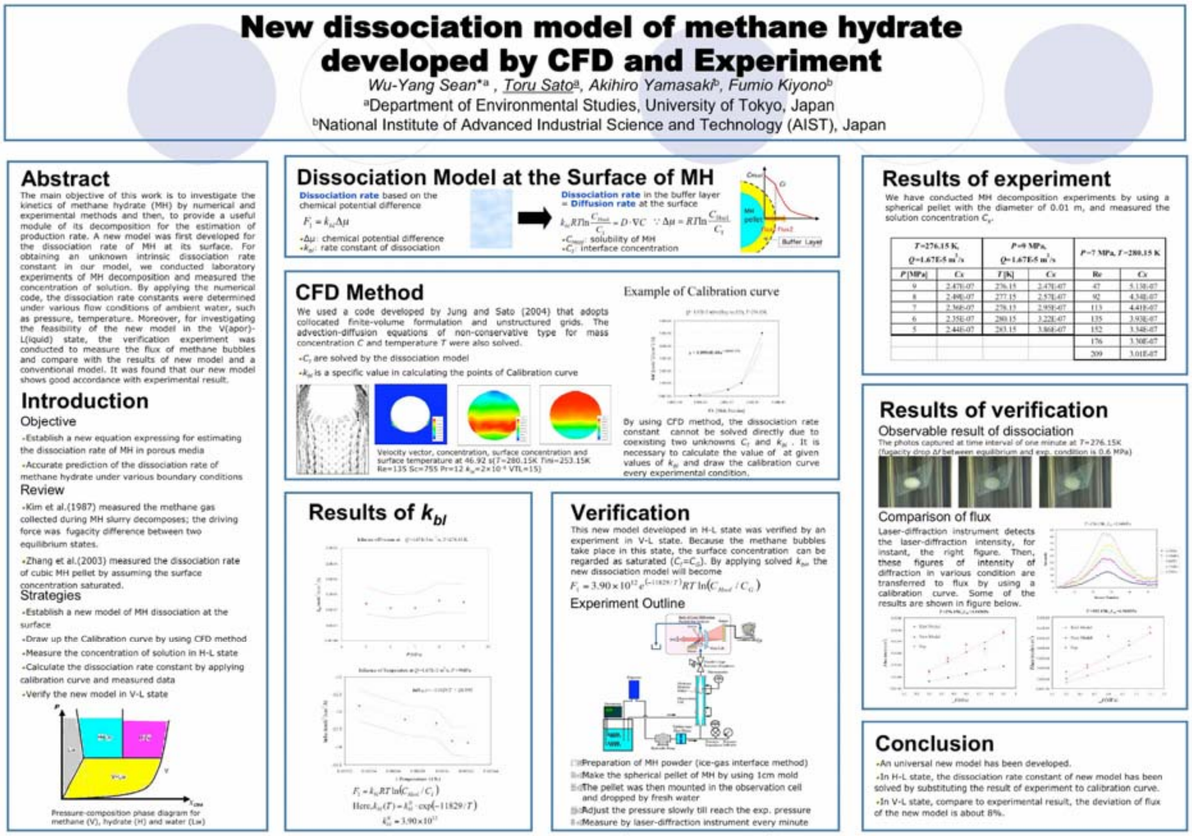

New dissociation model of methane hydrate developed by CFD and Experiment

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Abstract

The main objective of this work is to investigate the kinetics of methane hydrate (MH) by numerical and experimental methods and then, to provide a useful module of its decomposition for the estimation of production rate. A new model was first developed for the dissociation rate of MH at its surface. For obtaining an unknown intrinsic dissociation rate constant in our model, we conducted laboratory experiments of MH decomposition and measured the concentration of solution. By applying the numerical code, the dissociation rate constants were determined under various flow conditions of ambient water, such as pressure, temperature. Moreover, for investigating the feasibility of the new model in the V(apor)-L(iquid) state, the verification experiment was conducted to measure the flux of methane bubbles and compare with the results of new model and a conventional model. It was found that our new model shows good accordance with experimental result.

Introduction

Objective

- Establish a new equation expressing for estimating the dissociation rate of MH in porous media
- Accurate prediction of the dissociation rate of methane hydrate under various boundary conditions

Review

- Kim et al.(1987) measured the methane gas collected during MH slurry decomposes; the driving force was fugacity difference between two equilibrium states.
- Zhang et al.(2003) measured the dissociation rate of cubic MH pellet by assuming the surface concentration saturated.

Strategies

- Establish a new model of MH dissociation at the surface
- Draw up the Calibration curve by using CFD method
- Measure the concentration of solution in H-L state
- Calculate the dissociation rate constant by applying calibration curve and measured data
- Verify the new model in V-L state

Pressure-composition phase diagram for methane (V), hydrate (H) and water (Lw)

Dissociation Model at the Surface of MH

Dissociation rate based on the chemical potential difference

$$F_1 = k_{bl}\Delta\mu$$

- $\Delta\mu$: chemical potential difference
- k_{bl}: rate constant of dissociation

Dissociation rate in the buffer layer = **Diffusion rate** at the surface

$$k_{bl}RT\ln\frac{C_{Hsol}}{C_I} = D\cdot\nabla C \quad \because \Delta\mu = RT\ln\frac{C_{Hsol}}{C_I}$$

- C_{Hsol}: solubility of MH
- C_I: interface concentration

CFD Method

We used a code developed by Jung and Sato (2004) that adopts collocated finite-volume formulation and unstructured grids. The advection-diffusion equations of non-conservative type for mass concentration *C* and temperature *T* were also solved.

- C_I are solved by the dissociation model
- k_{bl} is a specific value in calculating the points of Calibration curve

Velocity vector, concentration, surface concentration and surface temperature at 46.92 s(T=280.15K T_{ini}=253.15K Re=135 Sc=755 Pr=12 k_{bl}=2×10⁻⁴ VTL=15)

Example of Calibration curve

By using CFD method, the dissociation rate constant cannot be solved directly due to coexisting two unknowns C_I and k_{bl} . It is necessary to calculate the value of at given values of k_{bl} and draw the calibration curve every experimental condition.

Results of k_{bl}

$$F_1 = k_{bl}RT\ln(C_{Hsol}/C_I)$$

$$\text{Here}, k_{bl}(T) = k_{bl}^0\cdot\exp(-11829/T)$$

$$k_{bl}^0 = 3.90\times10^{12}$$

Verification

This new model developed in H-L state was verified by an experiment in V-L state. Because the methane bubbles take place in this state, the surface concentration can be regarded as saturated (C_I=C_G). By applying solved k_{bl}, the new dissociation model will become

$$F_1 = 3.90\times10^{12}e^{(-11829/T)}RT\ln(C_{Hsol}/C_G)$$

Experiment Outline

- Preparation of MH powder (ice-gas interface method)
- Make the spherical pellet of MH by using 1cm mold
- The pellet was then mounted in the observation cell and dropped by fresh water
- Adjust the pressure slowly till reach the exp. pressure
- Measure by laser-diffraction instrument every minute

Results of experiment

We have conducted MH decomposition experiments by using a spherical pellet with the diameter of 0.01 m, and measured the solution concentration C_s.

T=276.15 K, Q=1.67E-5 m³/s		P=9 MPa, Q=1.67E-5 m³/s		P=7 MPa, T=280.15 K	
P[MPa]	Cs	T[K]	Cs	Re	Cs
9	2.47E-07	276.15	2.47E-07	47	5.13E-07
8	2.49E-07	277.15	2.57E-07	92	4.34E-07
7	2.36E-07	278.15	2.95E-07	113	4.41E-07
6	2.35E-07	280.15	3.22E-07	135	3.93E-07
5	2.44E-07	283.15	3.86E-07	152	3.34E-07
				176	3.30E-07
				209	3.01E-07

Results of verification

Observable result of dissociation

The photos captured at time interval of one minute at T=276.15K (fugacity drop Δ*f* between equilibrium and exp. condition is 0.6 MPa)

Comparison of flux

Laser-diffraction instrument detects the laser-diffraction intensity, for instant, the right figure. Then, these figures of intensity of diffraction in various condition are transferred to flux by using a calibration curve. Some of the results are shown in figure below.

Conclusion

- An universal new model has been developed.
- In H-L state, the dissociation rate constant of new model has been solved by substituting the result of experiment to calibration curve.
- In V-L state, compare to experimental result, the deviation of flux of the new model is about 8%.

APPENDIX B

Methane Hydrate Research at Heriot-Watt University

Bahman Tohidi

The Centre for Gas Hydrate Research, Heriot-Watt University, has been active in various areas of methane hydrate research since 1986. Among some 20 operational hydrate experimental set-ups, the Centre currently has five designed specifically for investigating hydrates in natural and synthetic sediments samples. These include:

- A Porous Media Rig (Max 400 bar) for investigating hydrate equilibria and kinetics in porous media, including the effects of sediment mineralogy, pore size distribution, wettability, gas/liquid saturation and pore water salinity.

- Two Glass Micromodel Rigs (Max 80 and 400 bar) for visual studies of gas hydrate systems at the pore scale in synthetic 2-D (one pore thickness) models. Micromodels provide novel visual information on the mechanisms of gas hydrate formation (e.g., from free gas and/or dissolved gas) and dissociation, hydrate morphology and distribution of phases within pore space as a function of various parameters (e.g., subcooling, gas composition, salinity, wettability).

- Two Ultrasonic Rigs (Max 400 bar) for investigating physical and mechanical properties of hydrate-bearing sediments. Ultrasonic set-ups can be used to study sonic velocity, resistivity, porosity, apparent relative permeability, hydrate cementing characteristics and sediment mechanical strength as a function of various parameters (e.g., hydrate saturation, pore and overburden pressures, mineralogy, gas and liquid compositions). Additionally, they provide a means to simulate various scenarios such as gas production from hydrates and CO_2 sequestration in the hydrate stability zone.

The aim of this presentation is to provide an overview of experimental set-ups and important results to date, setting the scene for discussion on further studies and the potential for future international collaboration.

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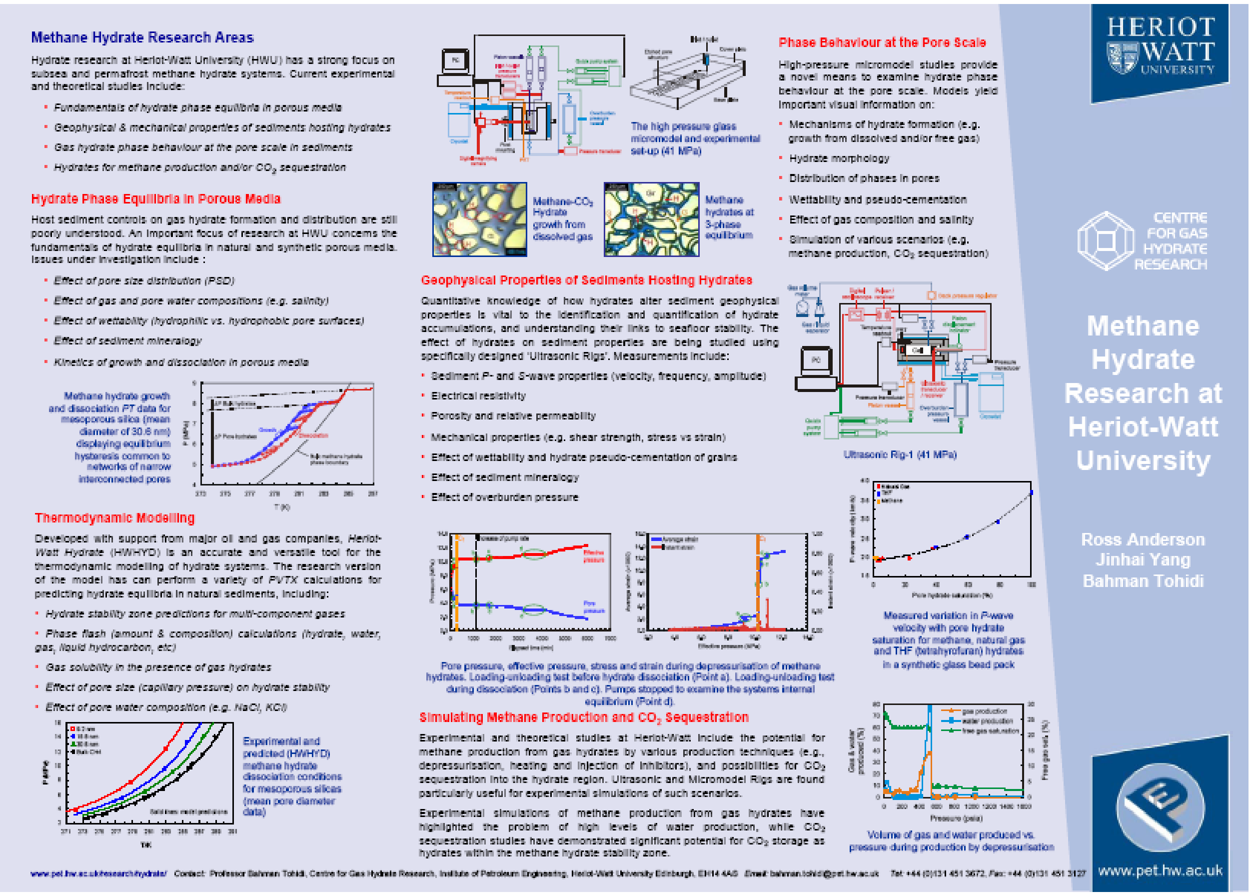

Methane Hydrate Research Areas

Hydrate research at Heriot-Watt University (HWU) has a strong focus on subsea and permafrost methane hydrate systems. Current experimental and theoretical studies include:

- *Fundamentals of hydrate phase equilibria in porous media*
- *Geophysical & mechanical properties of sediments hosting hydrates*
- *Gas hydrate phase behaviour at the pore scale in sediments*
- *Hydrates for methane production and/or CO_2 sequestration*

Hydrate Phase Equilibria in Porous Media

Host sediment controls on gas hydrate formation and distribution are still poorly understood. An important focus of research at HWU concerns the fundamentals of hydrate equilibria in natural and synthetic porous media. Issues under investigation include :

- *Effect of pore size distribution (PSD)*
- *Effect of gas and pore water compositions (e.g. salinity)*
- *Effect of wettability (hydrophilic vs. hydrophobic pore surfaces)*
- *Effect of sediment mineralogy*
- *Kinetics of growth and dissociation in porous media*

Methane hydrate growth and dissociation *PT* data for mesoporous silica (mean diameter of 30.6 nm) displaying equilibrium hysteresis common to networks of narrow interconnected pores

Thermodynamic Modelling

Developed with support from major oil and gas companies, *Heriot-Watt Hydrate* (HWHYD) is an accurate and versatile tool for the thermodynamic modelling of hydrate systems. The research version of the model has can perform a variety of *PVTX* calculations for predicting hydrate equilibria in natural sediments, including:

- *Hydrate stability zone predictions for multi-component gases*
- *Phase flash (amount & composition) calculations (hydrate, water, gas, liquid hydrocarbon, etc)*
- *Gas solubility in the presence of gas hydrates*
- *Effect of pore size (capillary pressure) on hydrate stability*
- *Effect of pore water composition (e.g. NaCl, KCl)*

Experimental and predicted (HWHYD) methane hydrate dissociation conditions for mesoporous silicas (mean pore diameter data)

The high pressure glass micromodel and experimental set-up (41 MPa)

Methane-CO_2 Hydrate growth from dissolved gas

Methane hydrates at 3-phase equilibrium

Geophysical Properties of Sediments Hosting Hydrates

Quantitative knowledge of how hydrates alter sediment geophysical properties is vital to the identification and quantification of hydrate accumulations, and understanding their links to seafloor stability. The effect of hydrates on sediment properties are being studied using specifically designed 'Ultrasonic Rigs'. Measurements include:

- Sediment *P*- and *S*-wave properties (velocity, frequency, amplitude)
- Electrical resistivity
- Porosity and relative permeability
- Mechanical properties (e.g. shear strength, stress vs strain)
- Effect of wettability and hydrate pseudo-cementation of grains
- Effect of sediment mineralogy
- Effect of overburden pressure

Pore pressure, effective pressure, stress and strain during depressurisation of methane hydrates. Loading-unloading test before hydrate dissociation (Point a). Loading-unloading test during dissociation (Points b and c). Pumps stopped to examine the systems internal equilibrium (Point d).

Simulating Methane Production and CO_2 Sequestration

Experimental and theoretical studies at Heriot-Watt include the potential for methane production from gas hydrates by various production techniques (e.g., depressurisation, heating and injection of inhibitors), and possibilities for CO_2 sequestration into the hydrate region. Ultrasonic and Micromodel Rigs are found particularly useful for experimental simulations of such scenarios.

Experimental simulations of methane production from gas hydrates have highlighted the problem of high levels of water production, while CO_2 sequestration studies have demonstrated significant potential for CO_2 storage as hydrates within the methane hydrate stability zone.

Phase Behaviour at the Pore Scale

High-pressure micromodel studies provide a novel means to examine hydrate phase behaviour at the pore scale. Models yield important visual information on:

- Mechanisms of hydrate formation (e.g. growth from dissolved and/or free gas)
- Hydrate morphology
- Distribution of phases in pores
- Wettability and pseudo-cementation
- Effect of gas composition and salinity
- Simulation of various scenarios (e.g. methane production, CO_2 sequestration)

Ultrasonic Rig-1 (41 MPa)

Measured variation in *P*-wave velocity with pore hydrate saturation for methane, natural gas and THF (tetrahyrofuran) hydrates in a synthetic glass bead pack

Volume of gas and water produced vs. pressure during production by depressurisation

HERIOT WATT UNIVERSITY

CENTRE FOR GAS HYDRATE RESEARCH

Methane Hydrate Research at Heriot-Watt University

Ross Anderson
Jinhai Yang
Bahman Tohidi

www.pet.hw.ac.uk/research/hydrate/ Contact: Professor Bahman Tohidi, Centre for Gas Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University Edinburgh, EH14 4AS *Email:* bahman.tohidi@pet.hw.ac.uk *Tel:* +44 (0)131 451 3672, *Fax:* +44 (0)131 451 3127

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APPENDIX B

Seismic Investigations With S-waves of Gas Hydrate Systems in the Continental Margins of NW Svalbard and Western Norway, off Storegga

Graham Westbrook and members of the HYDRATECH Consortium

High-resolution seismic data from arrays of closely spaced four-component ocean-bottom seismic recorders, acquired from two sites off western Svalbard, and from one site on the northern margin of the Storegga slide, off Norway, show S waves, generated by P–S conversion on reflection, in addition to P waves. The P and P–S waves were inverted jointly to provide P and S velocity models, using 3-D travel-time tomography, 2-D ray tracing and 1-D waveform inversion. At the NW Svalbard Site, positive Vp anomalies above a BSR indicate the presence of gas hydrate. A layer up to 150-m thick, containing free gas, beneath the BSR is indicated by a large reduction in Vp without a significant reduction in Vs. At the Storegga slide site, the lateral and vertical variation in Vp and Vs and the variation in amplitude and polarity of reflectors indicate a heterogeneous distribution of hydrate that is controlled by stratigraphically mediated migration of gas. S-wave velocity provides an important constraint in predicting hydrate concentration and yields lower concentrations than predictions based on Vp alone. Hydrate concentrations of up to 5% and 11% of pore space, at the NW Svalbard site, and of up to 10% or 20% at the Storegga site, depending on the model for hydrate cementation, were derived using Biot-theory-based and differential effective medium approaches.

The S waves show clear evidence of azimuthal seismic anisotropy. Analysis of the azimuthal variation in response of the transverse horizontal component, particle-motion hodograms and full-waveform anisotropic modelling indicate an azimuthal variation in velocity of up to 10% in the free-gas zone beneath the BSR, and weaker anisotropy in the hydrate zone above it. The polarisation direction of the fastest shear wave is broadly NW–SE, varying between 115° and 135° as a function of location and, in places, depth. The most probable explanation for this anisotropy is the presence of near vertical, aligned micro-cracks parallel to the fast direction, containing gas below the BSR and a combination of hydrate and pore water above. These cracks may act as migration pathways for methane in solution and free gas.

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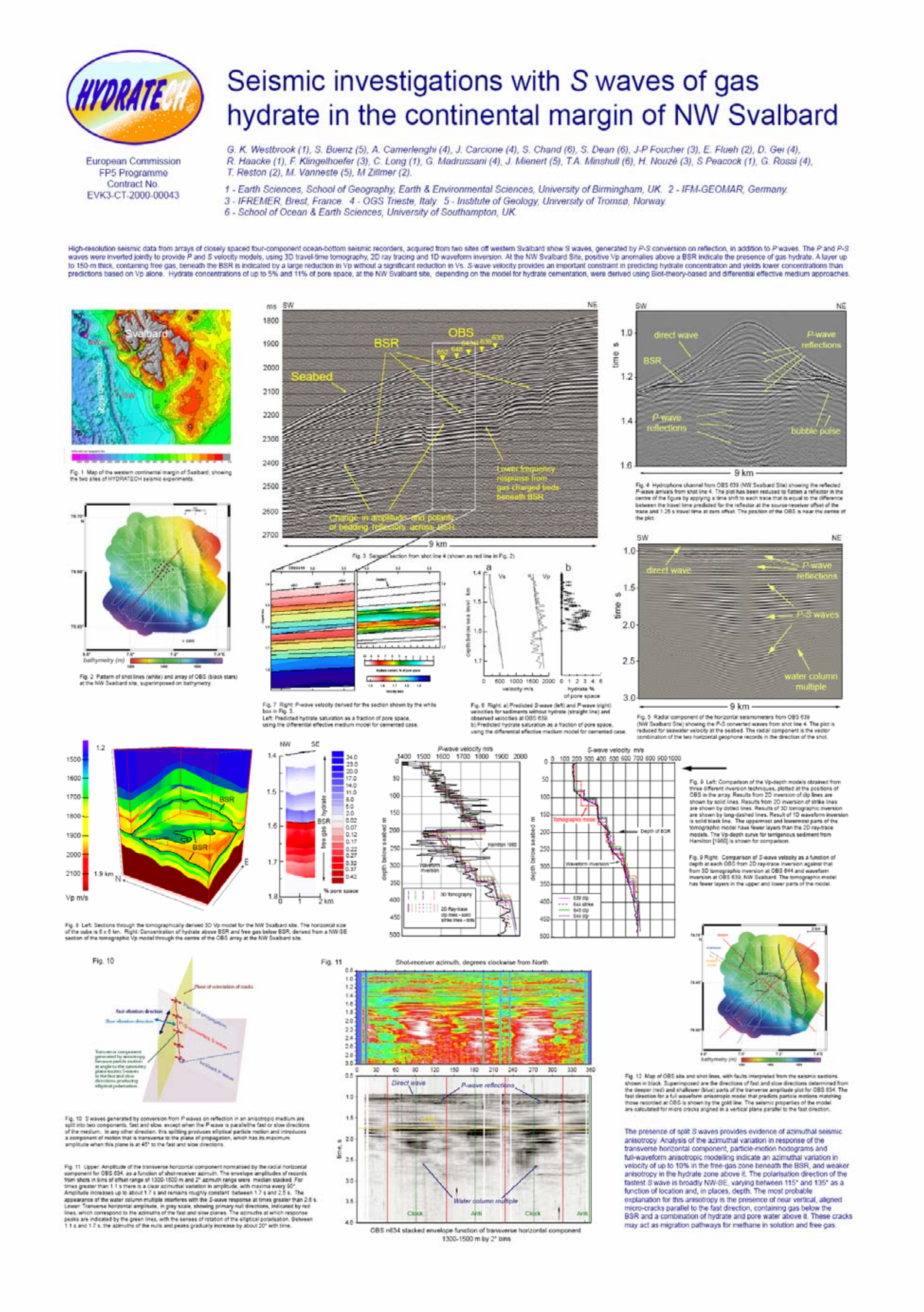
APPENDIX B



Seismic investigations with *S* waves of gas hydrate in the continental margin of NW Svalbard

European Commission
FP5 Programme
Contract No.
EVK3-CT-2000-00043

G. K. Westbrook (1), S. Buenz (5), A. Camerlenghi (4), J. Carcione (4), S. Chand (6), S. Dean (6), J-P Foucher (3), E. Flueh (2), D. Gei (4), R. Haacke (1), F. Klingelhoefer (3), C. Long (1), G. Madrussani (4), J. Mienert (5), T.A. Minshull (6), H. Nouzé (3), S Peacock (1), G. Rossi (4), T. Reston (2), M. Vanneste (5), M Zillmer (2).

1 - Earth Sciences, School of Geography, Earth & Environmental Sciences, University of Birmingham, UK. 2 - IFM-GEOMAR, Germany.
3 - IFREMER, Brest, France. 4 - OGS Trieste, Italy. 5 - Institute of Geology, University of Tromsø, Norway.
6 - School of Ocean & Earth Sciences, University of Southampton, UK.

High-resolution seismic data from arrays of closely spaced four-component ocean-bottom seismic recorders, acquired from two sites off western Svalbard show *S* waves, generated by *P-S* conversion on reflection, in addition to *P* waves. The *P* and *P-S* waves were inverted jointly to provide *P* and *S* velocity models, using 3D travel-time tomography, 2D ray tracing and 1D waveform inversion. At the NW Svalbard Site, positive Vp anomalies above a BSR indicate the presence of gas hydrate. A layer up to 150-m thick, containing free gas, beneath the BSR is indicated by a large reduction in Vp without a significant reduction in Vs. *S*-wave velocity provides an important constraint in predicting hydrate concentration and yields lower concentrations than predictions based on Vp alone. Hydrate concentrations of up to 5% and 11% of pore space, at the NW Svalbard site, depending on the model for hydrate cementation, were derived using Biot-theory-based and differential effective medium approaches.

Fig. 1 Map of the western continental margin of Svalbard, showing the two sites of HYDRATECH seismic experiments.

Fig. 2 Pattern of shot lines (white) and array of OBS (black stars) at the NW Svalbard site, superimposed on bathymetry.

Fig. 3 Seismic section from shot line 4 (shown as red line in Fig. 2)

Fig. 4 Hydrophone channel from OBS 639 (NW Svalbard Site) showing the reflected *P*-wave arrivals from shot line 4. The plot has been reduced to flatten a reflector in the centre of the figure by applying a time shift to each trace that is equal to the difference between the travel time predicted for the reflector at the source-receiver offset of the trace and 1.25 s travel time at zero offset. The position of the OBS is near the centre of the plot.

Fig. 5 Radial component of the horizontal seismometers from OBS 639 (NW Svalbard Site) showing the *P-S* converted waves from shot line 4. The plot is reduced for seawater velocity at the seabed. The radial component is the vector combination of the two horizontal geophone records in the direction of the shot.

Fig. 7 Right: *P*-wave velocity derived for the section shown by the white box in Fig. 3.
Left: Predicted hydrate saturation as a fraction of pore space, using the differential effective medium model for cemented case.

Fig. 6 Right: a) Predicted *S*-wave (left) and *P*-wave (right) velocities for sediments without hydrate (straight line) and observed velocities at OBS 639.
b) Predicted hydrate saturation as a fraction of pore space, using the differential effective medium model for cemented case.

Fig. 8 Left: Sections through the tomographically derived 3D Vp model for the NW Svalbard site. The horizontal size of the cube is 6 x 6 km. Right: Concentration of hydrate above BSR and free gas below BSR, derived from a NW-SE section of the tomographic Vp model through the centre of the OBS array at the NW Svalbard site.

Fig. 9 Left: Comparison of the Vp–depth models obtained from three different inversion techniques, plotted at the positions of OBS in the array. Results from 2D inversion of dip lines are shown by solid lines. Results from 2D inversion of strike lines are shown by dotted lines. Results of 3D tomographic inversion are shown by long-dashed lines. Result of 1D waveform inversion is solid black line. The uppermost and lowermost parts of the tomographic model have fewer layers than the 2D ray-trace models. The Vp-depth curve for terrigenous sediment from Hamilton [1980] is shown for comparison.

Fig. 9 Right: Comparison of *S*-wave velocity as a function of depth at each OBS from 2D ray-trace inversion against that from 3D tomographic inversion at OBS 644 and waveform inversion at OBS 639, NW Svalbard. The tomographic model has fewer layers in the upper and lower parts of the model.

Fig. 10

Fig. 10 *S* waves generated by conversion from *P* waves on reflection in an anisotropic medium are split into two components, fast and slow, except when the *P* wave is parallelthe fast or slow directions of the medium. In any other direction, this splitting produces elliptical particle motion and introduces a component of motion that is transverse to the plane of propagation, which has its maximum amplitude when this plane is at 45° to the fast and slow directions.

Fig. 11

Fig. 11 Upper: Amplitude of the transverse horizontal component normalised by the radial horizontal component for OBS 634, as a function of shot-receiver azimuth. The envelope amplitudes of records from shots in bins of offset range of 1300-1500 m and 2° azimuth range were median stacked. For times greater than 1.1 s there is a clear azimuthal variation in amplitude, with maxima every 90°. Amplitude increases up to about 1.7 s and remains roughly constant between 1.7 s and 2.5 s. The appearance of the water column multiple interferes with the *S*-wave response at times greater than 2.6 s. Lower: Tranverse horizontal amplitude, in grey scale, showing primary null directions, indicated by red lines, which correspond to the azimuths of the fast and slow planes. The azimuths at which response peaks are indicated by the green lines, with the senses of rotation of the elliptical polarisation. Between 1.1 s and 1.7 s, the azimuths of the nulls and peaks gradually increase by about 20° with time.

Fig. 12 Map of OBS site and shot lines, with faults interpreted from the seismic sections shown in black. Superimposed are the directions of fast and slow directions determined from the deeper (red) and shallower (blue) parts of the tranverse amplitude plot for OBS 634. The fast direction for a full waveform anisotropic model that predicts particle motions matching those recorded at OBS is shown by the gold line. The seismic properties of the model are calculated for micro cracks aligned in a vertical plane parallel to the fast direction.

The presence of split *S* waves provides evidence of azimuthal seismic anisotropy. Analysis of the azimuthal variation in response of the transverse horizontal component, particle-motion hodograms and full-waveform anisotropic modelling indicate an azimuthal variation in velocity of up to 10% in the free-gas zone beneath the BSR, and weaker anisotropy in the hydrate zone above it. The polarisation direction of the fastest *S* wave is broadly NW-SE, varying between 115° and 135° as a function of location and, in places, depth. The most probable explanation for this anisotropy is the presence of near vertical, aligned micro-cracks parallel to the fast direction, containing gas below the BSR and a combination of hydrate and pore water above it. These cracks may act as migration pathways for methane in solution and free gas.

APPENDIX B

Coordinated Mapping and Quantification of Ocean Floor Hydrate-associated Methane Sources With Manned Submersibles, AUVs and Moored Event-driven Sensor Arrays

POSTER NOT AVAILABLE

Jean Whelan, Richard Camilli, Oscar Pizarro, Norman Farr, Joanne Goudreau,
Christopher Martens, and Howard Mendlovitz

Recent evidence has shown that gases, particularly methane, are at high concentrations in many gas hydrate areas which actively vent methane-enriched cold fluids through the ocean floor. Occasionally episodes of massive bubble plume eruptions occur. More commonly, dissolved gases, sometimes along with small bubble streams, vent through small fissures in the ocean floor. This venting occurs in many locations worldwide and is important to the biology, chemistry and geology of the ocean. However, no standard strategy exists for systematic exploration and mapping of these highly localized vent features, and at the present time these methane vents continue to be found almost accidentally. Even after methane venting features are found and mapped, it is difficult to obtain reliable measurements of gas fluxes because venting tends to be very heterogeneous and episodic. As a result, the effects of a major source of gas venting to the oceans and its effects on seafloor and sub-seafloor gas hydrates are almost unknown. We describe a comprehensive approach being applied in the Gulf of Mexico (MC118) for seafloor monitoring of gas, oil and fluids venting from methane hydrate mounds in order to assess their influence on biogeochemistry and microbial communities in bottom waters surrounding the hydrate zone. This approach first utilizes AUVs as reconnaissance platforms to provide initial chemical and bathymetric surveys of the study area. This data is then processed into maps which are used to identify target sites of potential methane seep and exposed methane hydrate areas. Following the AUV survey, a manned submersible equipped with a Gemini in situ mass spectrometer is then used to localize the methane seep sources. The manned submersible is then used in conjunction with a surface ship to position a 50-meter-high tethered benthic boundary layer array (BBLA) near the methane seeps and hydrate features, and to place chimney sampling arrays (CSA) directly over target features. Initial results of the approach from recent cruises to North Carolina seafloor pockmarks, the Puerto Rico Trench and the Chile Margin are described.

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APPENDIX B

Thermodynamic and Kinetic Stability of Clathrate Hydrates

Mary Anne White

Through investigation of model hydrates, we have investigated aspects of both thermodynamic and kinetic stability of clathrate hydrates. Thermodynamic aspects have been studied for bulk samples. Kinetic aspects have been explored through studies of the influence of surfactant on nucleation of clathrate hydrates from emulsions of THF (tetrahydrofuran)/ water suspended in an immiscible fluid.

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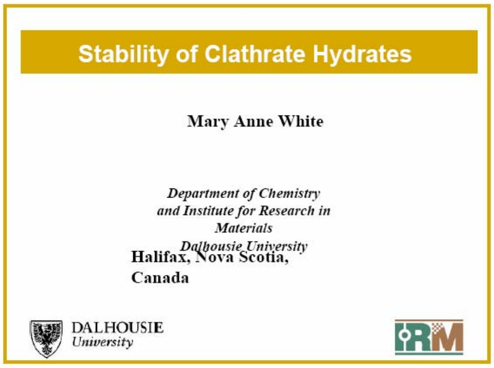

Stability of Clathrate Hydrates

Mary Anne White

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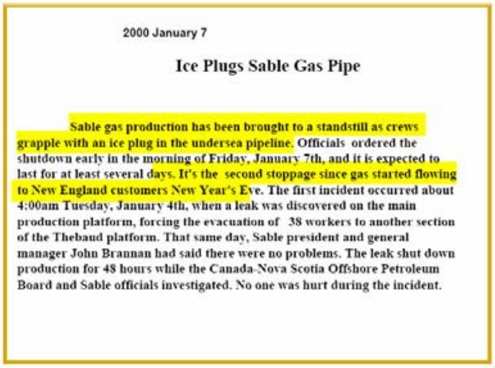
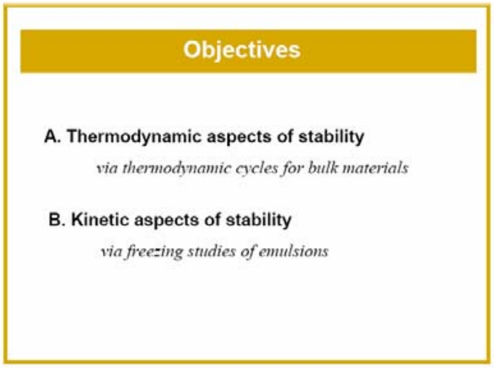
DALHOUSIE
University



2000 January 7

Ice Plugs Sable Gas Pipe

Sable gas production has been brought to a standstill as crews grapple with an ice plug in the undersea pipeline. Officials ordered the shutdown early in the morning of Friday, January 7th, and it is expected to last for at least several days. It's the second stoppage since gas started flowing to New England customers New Year's Eve. The first incident occurred about 4:00am Tuesday, January 4th, when a leak was discovered on the main production platform, forcing the evacuation of 38 workers to another section of the Thebaud platform. That same day, Sable president and general manager John Brannan had said there were no problems. The leak shut down production for 48 hours while the Canada-Nova Scotia Offshore Petroleum Board and Sable officials investigated. No one was hurt during the incident.



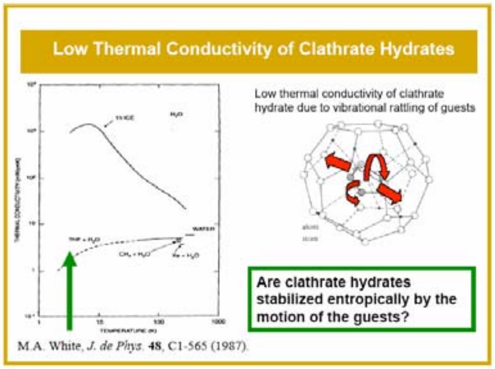
Objectives

A. Thermodynamic aspects of stability

via thermodynamic cycles for bulk materials

B. Kinetic aspects of stability

via freezing studies of emulsions



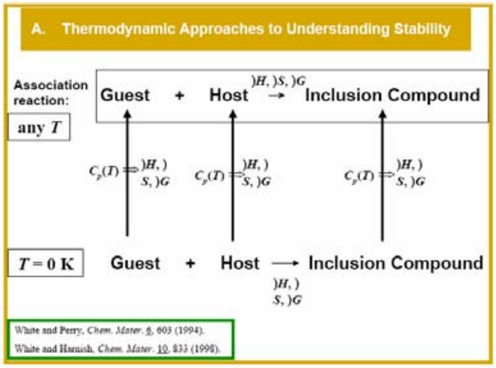
Low Thermal Conductivity of Clathrate Hydrates

M.A. White, *J. de Phys.* **48**, C1-565 (1987).

Low thermal conductivity of clathrate hydrate due to vibrational rattling of guests

Are clathrate hydrates stabilized entropically by the motion of the guests?

APPENDIX B



A. Thermodynamic Approaches to Understanding Stability

Association reaction:

any T

Guest + Host $\xrightarrow{)H,\ )S,\ )G}$ Inclusion Compound

$C_p(T) \Rightarrow)H,\ )S,\ )G$

$C_p(T) \Rightarrow)H,\ )S,\ )G$

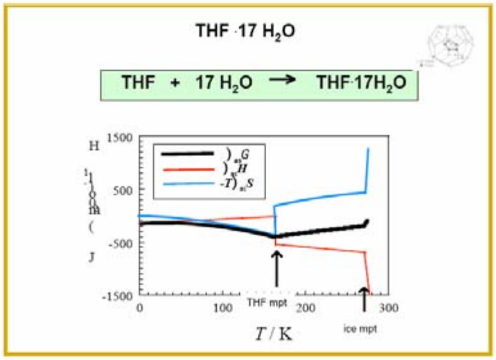
$C_p(T) \Rightarrow)H,\ )S,\ )G$

$T = 0$ K

Guest + Host $\xrightarrow[)H,\ )S,\ )G]{}$ Inclusion Compound

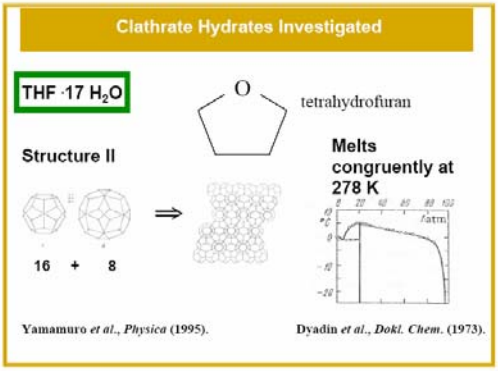
White and Perry, *Chem. Mater.* 6, 603 (1994).

White and Harnish, *Chem. Mater.* 10, 833 (1998).



THF ·17 H_2O

THF + 17 H_2O → THF·17H_2O



Clathrate Hydrates Investigated

THF ·17 H_2O

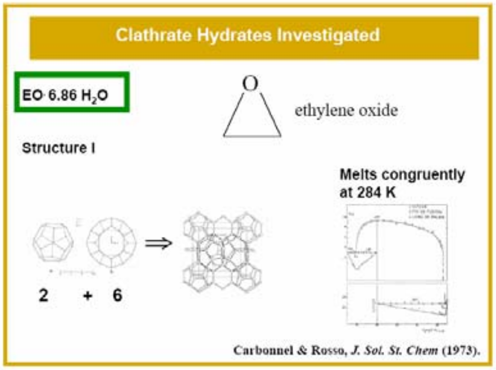
tetrahydrofuran

Structure II

Melts congruently at 278 K

Yamamuro *et al.*, *Physica* (1995).

Dyadin *et al.*, *Dokl. Chem.* (1973).



Clathrate Hydrates Investigated

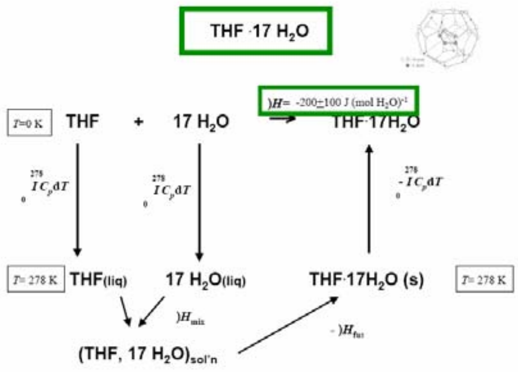
EO· 6.86 H_2O

ethylene oxide

Structure I

Melts congruently at 284 K

Carbonnel & Rosso, *J. Sol. St. Chem* (1973).



THF ·17 H_2O

$)H = -200 \pm 100$ J (mol H_2O)$^{-1}$

T=0 K THF + 17 H_2O → THF·17H_2O

$\underset{0}{\overset{278}{I}} C_p dT$

$\underset{0}{\overset{278}{I}} C_p dT$

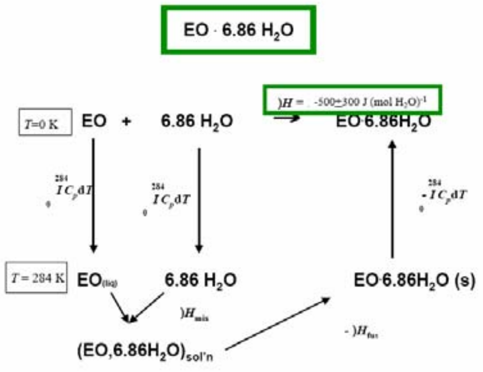
$- \underset{0}{\overset{278}{I}} C_p dT$

T= 278 K THF(liq) 17 H_2O(liq) THF·17H_2O (s) T= 278 K

$)H_{mix}$

$-)H_{fus}$

(THF, 17 H_2O)$_{sol'n}$



EO · 6.86 H_2O

$)H = -500 \pm 300$ J (mol H_2O)$^{-1}$

T=0 K EO + 6.86 H_2O → EO·6.86H_2O

$\underset{0}{\overset{284}{I}} C_p dT$

$\underset{0}{\overset{284}{I}} C_p dT$

$- \underset{0}{\overset{284}{I}} C_p dT$

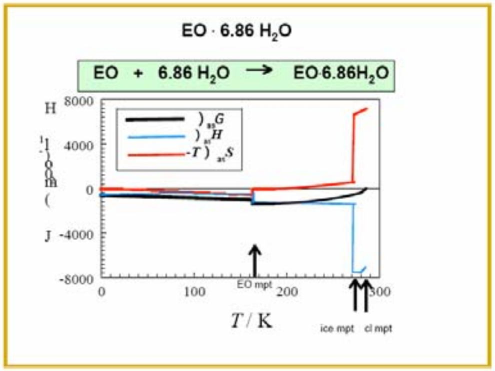
T = 284 K EO$_{(liq)}$ 6.86 H_2O EO·6.86H_2O (s)

$)H_{mix}$

$-)H_{fus}$

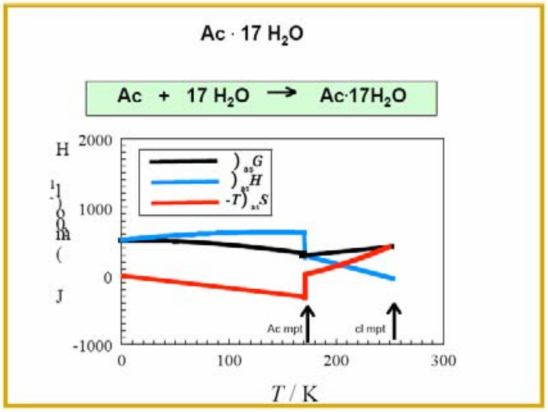
(EO,6.86H_2O)$_{sol'n}$

APPENDIX B



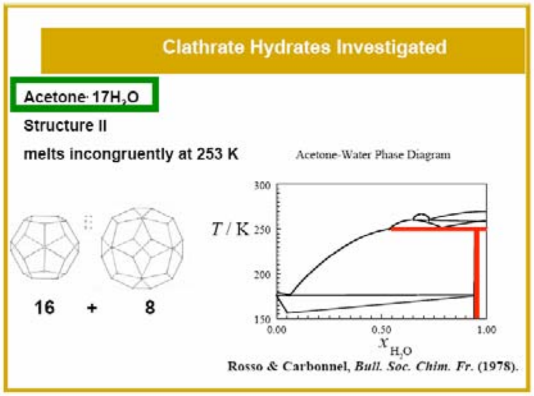
EO · 6.86 H_2O

EO + 6.86 H_2O ⟶ EO·6.86H_2O



Ac · 17 H_2O

Ac + 17 H_2O ⟶ Ac·17H_2O



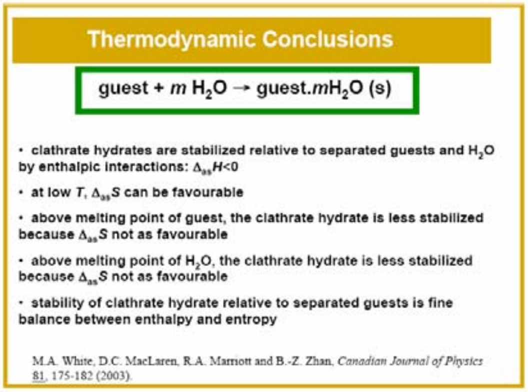
Clathrate Hydrates Investigated

Acetone·17H_2O

Structure II

melts incongruently at 253 K

Rosso & Carbonnel, *Bull. Soc. Chim. Fr.* (1978).

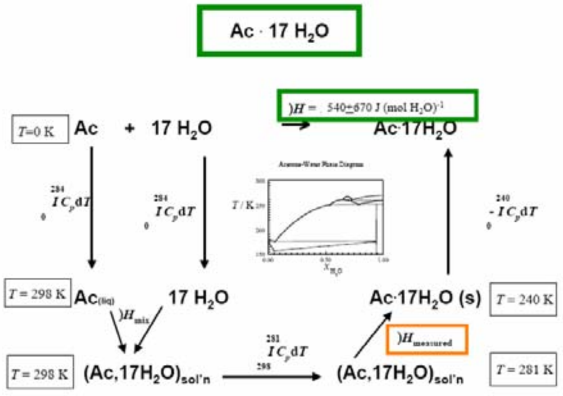


Thermodynamic Conclusions

guest + *m* H_2O → guest.*m*H_2O (s)

- clathrate hydrates are stabilized relative to separated guests and H_2O by enthalpic interactions: $\Delta_{as}H<0$
- at low *T*, $\Delta_{as}S$ can be favourable
- above melting point of guest, the clathrate hydrate is less stabilized because $\Delta_{as}S$ not as favourable
- above melting point of H_2O, the clathrate hydrate is less stabilized because $\Delta_{as}S$ not as favourable
- stability of clathrate hydrate relative to separated guests is fine balance between enthalpy and entropy

M.A. White, D.C. MacLaren, R.A. Marriott and B.-Z. Zhan, *Canadian Journal of Physics* 81, 175-182 (2003).



Ac · 17 H_2O

)H = . 540±670 J (mol H_2O)$^{-1}$

T=0 K Ac + 17 H_2O ⟶ Ac·17H_2O

$\int_0^{284} C_p\,dT$

$\int_0^{284} C_p\,dT$

$-\int_0^{240} C_p\,dT$

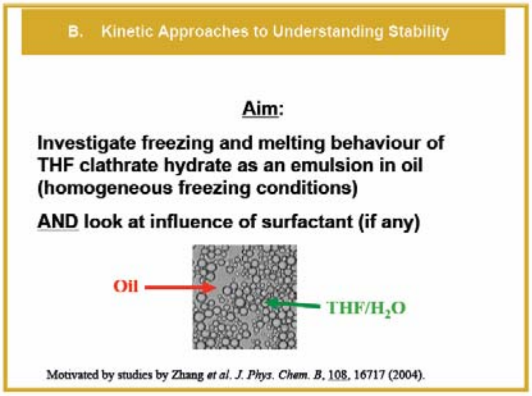
T = 298 K Ac$_{(liq)}$ 17 H_2O

)H_{mix}

Ac·17H_2O (s) T = 240 K

)$H_{measured}$

T = 298 K (Ac,17H_2O)$_{sol'n}$ $\xrightarrow{\int_{298}^{281} C_p\,dT}$ (Ac,17H_2O)$_{sol'n}$ T = 281 K



B. Kinetic Approaches to Understanding Stability

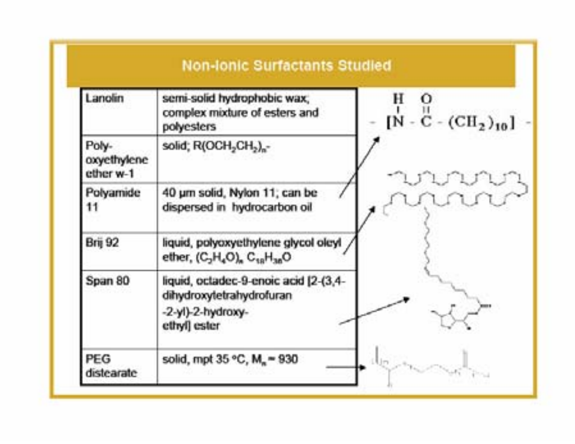
Aim:

Investigate freezing and melting behaviour of THF clathrate hydrate as an emulsion in oil (homogeneous freezing conditions)

AND look at influence of surfactant (if any)

Motivated by studies by Zhang *et al. J. Phys. Chem. B*, 108, 16717 (2004).

APPENDIX B



Non-Ionic Surfactants Studied

Lanolin	semi-solid hydrophobic wax; complex mixture of esters and polyesters
Poly-oxyethylene ether w-1	solid; $R(OCH_2CH_2)_n$-
Polyamide 11	40 µm solid, Nylon 11; can be dispersed in hydrocarbon oil
Brij 92	liquid, polyoxyethylene glycol oleyl ether, $(C_2H_4O)_n\ C_{18}H_{36}O$
Span 80	liquid, octadec-9-enoic acid [2-(3,4-dihydroxytetrahydrofuran -2-yl)-2-hydroxy-ethyl] ester
PEG distearate	solid, mpt 35 °C, M_n = 930

$$-[\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}]-$$

Acknowledgements

Co-workers:

D.C. MacLaren

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B.-Z. Zhan

H. Rafiee

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NSERC

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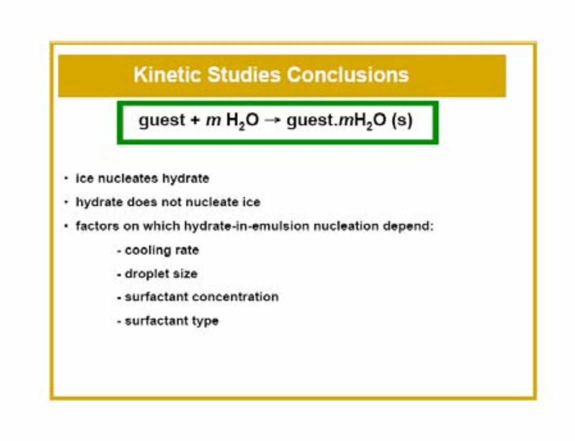

Kinetic Studies Conclusions

$$\boxed{\text{guest} + m\ H_2O \rightarrow \text{guest}.mH_2O\ (s)}$$

- ice nucleates hydrate
- hydrate does not nucleate ice
- factors on which hydrate-in-emulsion nucleation depend:
    - cooling rate
    - droplet size
    - surfactant concentration
    - surfactant type

APPENDIX B

A Comparative Study of Seismic, Electromagnetic and Seafloor Compliance Methods For The Assessment of Marine Gas Hydrate Deposits

E. C. Willoughby, K. Schwalenberg, R.N. Edwards, R. Mir, G.D. Spence and R.D. Hyndman

The existence, distribution and concentration of marine natural gas hydrate are mostly diagnosed using seismic data. The base of the hydrate stability zone marks an acoustic impedance contrast, which generally mimics seafloor topography and is associated with a bright, negative-polarity reflector, known as the Bottom Simulating Reflector (BSR). However, limitations of seismic methods include uncertainty in the origin of the BSR, which does not distinguish between low velocity gas and high velocity hydrate, blanking and lack of clear upper boundary reflections. Sufficiently accurate hydrate layer velocities have been obtained at few sites, and these could better evaluate hydrate content with reference to velocities in similar sediments without hydrate—a situation very difficult to find. Therefore, estimation of the total mass of a deposit is difficult using seismic data alone. We have developed two supplementary geophysical imaging techniques for the evaluation of marine hydrate: a deep-towed controlled-source electromagnetic (CSEM) and a seafloor compliance experiment. These methods are sensitive to physical properties of the sedimentary section, which are modified by the presence of gas hydrate, namely the resistivity and the bulk shear modulus depth profile, respectively. CSEM data are gathered by inline receivers towed behind an AC transmitter; high precision timing allows measurement of the EM field propagation time through marine sediments which is proportional to resistivity, which is increased by the presence of insulating hydrate. Seafloor compliance is the transfer function between pressure induced on the seafloor by surface gravity waves and the associated deformation of the seafloor. It is mostly sensitive to shear modulus anomalies. Shear modulus is increased by hydrates, which can cement grains together. Here we present field data at a gas hydrate site, south of ODP Hole 889B in northern Cascadia, over a proposed new IODP transect, where these three methodologies can be compared.

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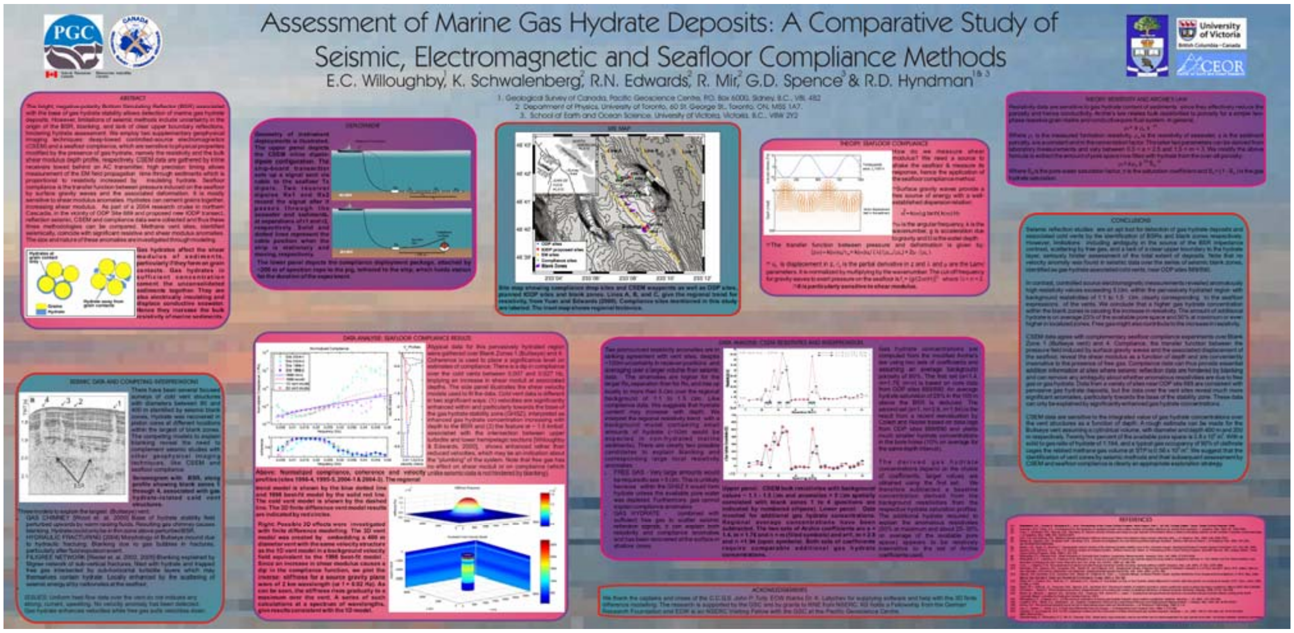

Assessment of Marine Gas Hydrate Deposits: A Comparative Study of Seismic, Electromagnetic and Seafloor Compliance Methods

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APPENDIX B

Marine Gas Hydrate Studies off Vancouver Is., W. Canada

ABSTRACT NOT AVAILABLE

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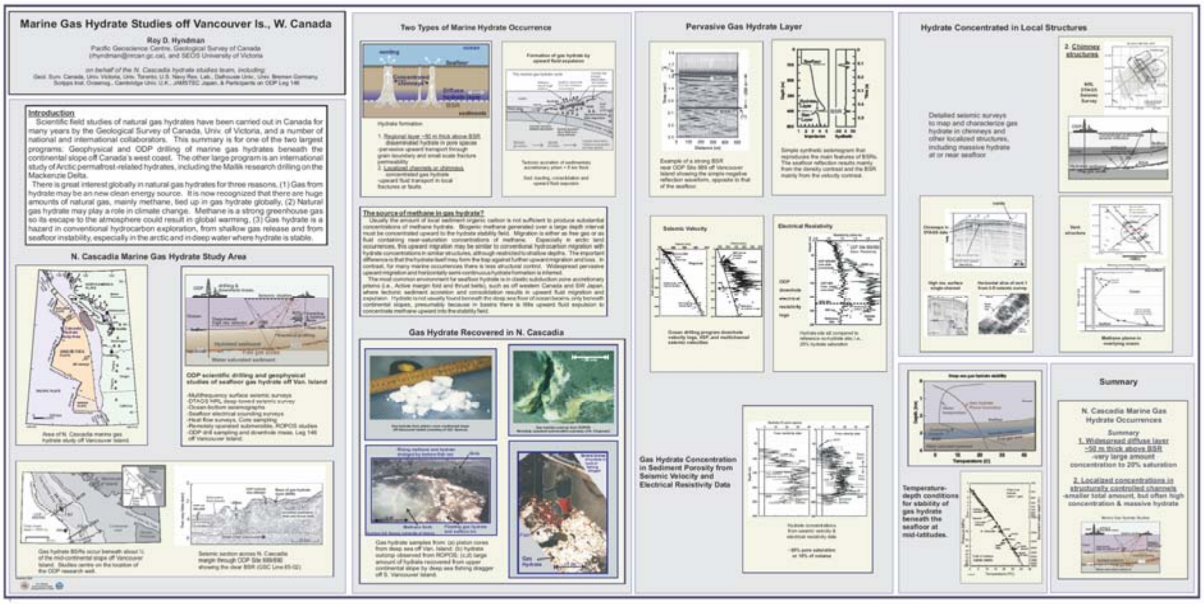

Marine Gas Hydrate Studies off Vancouver Is., W. Canada

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on behalf of the N. Cascadia hydrate studies team, including:
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Scripps Inst. Oceanog., Cambridge Univ. U.K., JAMSTEC Japan, & Participants on ODP Leg 146

Introduction

Scientific field studies of natural gas hydrates have been carried out in Canada for many years by the Geological Survey of Canada, Univ. of Victoria, and a number of national and international collaborators. This summary is for one of the two largest programs: Geophysical and ODP drilling of marine gas hydrates beneath the continental slope off Canada's west coast. The other large program is an international study of Arctic permafrost-related hydrates, including the Mallik research drilling on the Mackenzie Delta.

There is great interest globally in natural gas hydrates for three reasons. (1) Gas from hydrate may be an new clean energy source. It is now recognized that there are huge amounts of natural gas, mainly methane, tied up in gas hydrate globally. (2) Natural gas hydrate may play a role in climate change. Methane is a strong greenhouse gas so its escape to the atmosphere could result in global warming. (3) Gas hydrate is a hazard in conventional hydrocarbon exploration, from shallow gas release and from seafloor instability, especially in the arctic and in deep water where hydrate is stable.

N. Cascadia Marine Gas Hydrate Study Area

Area of N. Cascadia marine gas hydrate study off Vancouver Island.

ODP scientific drilling and geophysical studies of seafloor gas hydrate off Van. Island

-Multifrequency surface seismic surveys
-DTAGS NRL deep-towed seismic survey
-Ocean-bottom seismographs
-Seafloor electrical sounding surveys
-Heat flow surveys, Core sampling
-Remotely operated submersible, ROPOS studies
-ODP drill sampling and downhole meas. Leg 146 off Vancouver Island

Gas hydrate BSRs occur beneath about ½ of the mid-continental slope off Vancouver Island. Studies centre on the location of the ODP research well.

Seismic section across N. Cascadia margin through ODP Site 889/890 showing the clear BSR (GSC Line 85-02)

Two Types of Marine Hydrate Occurrence

Hydrate formation

1. Regional layer ~50 m thick above BSR
disseminated hydrate in pore spaces
-pervasive upward transport through grain boundary and small scale fracture permeability
2. Localized channels or chimneys
concentrated gas hydrate
-upward fluid transport in local fractures or faults

Formation of gas hydrate by upward fluid expulsion

Tectonic accretion of sedimentary accretionary prism > 5 km thick

Sed. loading, consolidation and upward fluid expulsion

The source of methane in gas hydrate?

Usually the amount of local sediment organic carbon is not sufficient to produce substantial concentrations of methane hydrate. Biogenic methane generated over a large depth interval must be concentrated upward to the hydrate stability field. Migration is either as free gas or as fluid containing near-saturation concentrations of methane. Especially in arctic land occurrences, this upward migration may be similar to conventional hydrocarbon migration with hydrate concentrations in similar structures, although restricted to shallow depths. The important difference is that the hydrate itself may form the trap against further upward migration and loss. In contrast, for many marine occurrences there is less structural control. Widespread pervasive upward migration and horizontally semi-continuous hydrate formation is inferred.

The most common environment for seafloor hydrate is in clastic subduction zone accretionary prisms (i.e., Active margin fold and thrust belts), such as off western Canada and SW Japan, where tectonic sediment accretion and consolidation results in upward fluid migration and expulsion. Hydrate is not usually found beneath the deep sea floor of ocean basins, only beneath continental slopes, presumably because in basins there is little upward fluid expulsion to concentrate methane upward into the stability field.

Gas Hydrate Recovered in N. Cascadia

Gas hydrate samples from: (a) piston cores from deep sea off Van. Island, (b) hydrate outcrop observed from ROPOS, (c,d) large amount of hydrate recovered from upper continental slope by deep sea fishing dragger off S. Vancouver Island.

Pervasive Gas Hydrate Layer

Example of a strong BSR near ODP Site 889 off Vancouver Island showing the simple negative reflection waveform, opposite to that of the seafloor.

Simple synthetic seismogram that reproduces the main features of BSRs. The seafloor reflection results mainly from the density contrast and the BSR mainly from the velocity contrast.

Seismic Velocity

Ocean drilling program downhole velocity logs, VSP and multichannel seismic velocities

Electrical Resistivity

ODP downhole electrical resistivity logs

Gas Hydrate Concentration in Sediment Porosity from Seismic Velocity and Electrical Resistivity Data

Hydrate Concentrated in Local Structures

Detailed seismic surveys to map and characterize gas hydrate in chimneys and other localized structures, including massive hydrate at or near seafloor

2. Chimney structures

Methane plume in overlying ocean

Temperature-depth conditions for stability of gas hydrate beneath the seafloor at mid-latitudes.

Summary

N. Cascadia Marine Gas Hydrate Occurrences

Summary
1. Widespread diffuse layer ~50 m thick above BSR
-very large amount
concentration to 20% saturation

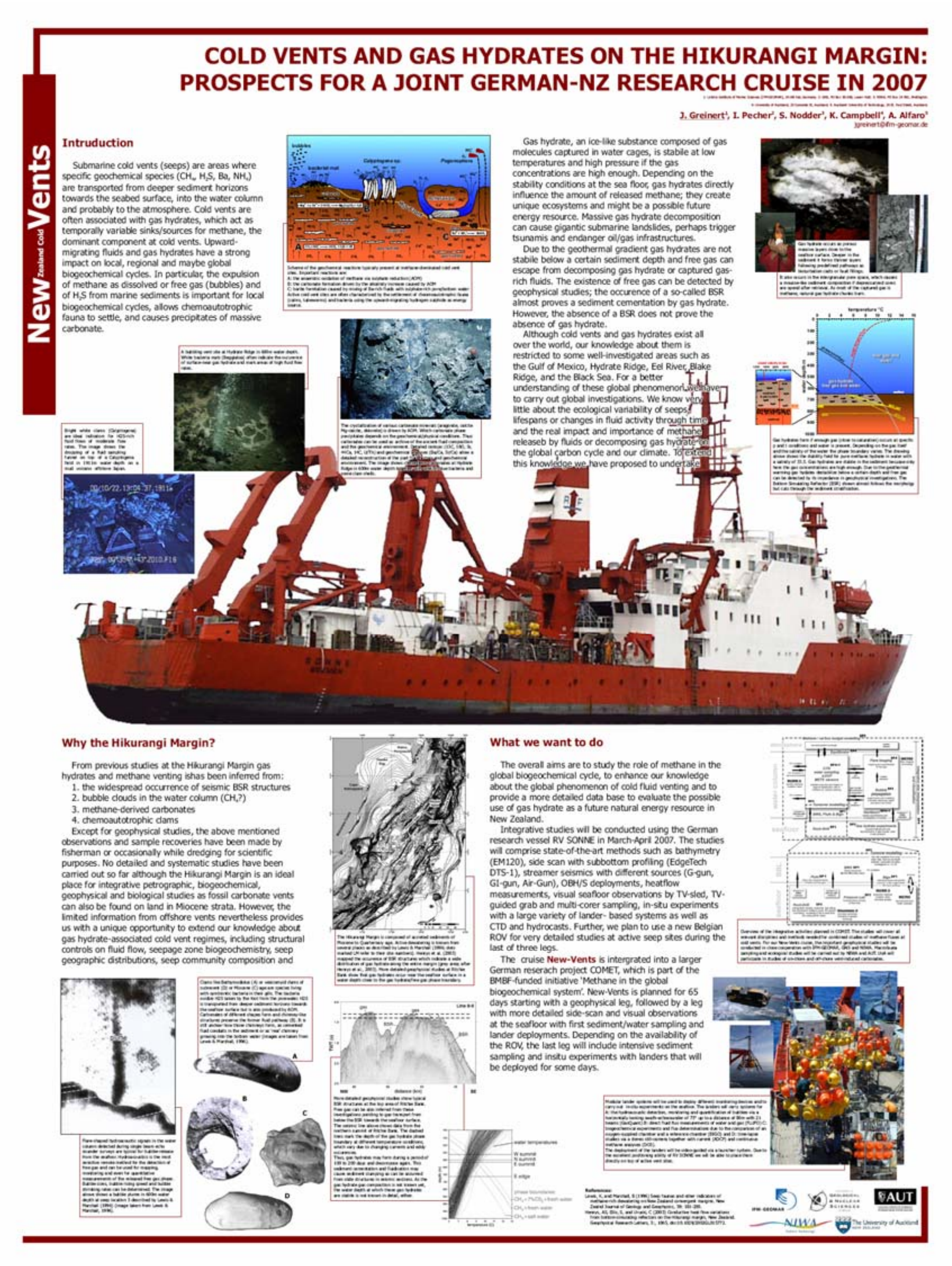
2. Localized concentrations in structurally controlled channels
-smaller total amount, but often high concentration & massive hydrate

APPENDIX B

Cold Vents and Gas Hydrates on the Hikurangi Margin: Prospects for a Joint German-NZ Research Cruise in 2007

ABSTRACT NOT AVAILABLE

J. Greinert, I. Pecher, S. Noddler, K. Campbell, and A. Alfano.



New Zealand Cold Vents

COLD VENTS AND GAS HYDRATES ON THE HIKURANGI MARGIN: PROSPECTS FOR A JOINT GERMAN-NZ RESEARCH CRUISE IN 2007

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Intruduction

Submarine cold vents (seeps) are areas where specific geochemical species (CH_4, H_2S, Ba, NH_4) are transported from deeper sediment horizons towards the seabed surface, into the water column and probably to the atmosphere. Cold vents are often associated with gas hydrates, which act as temporally variable sinks/sources for methane, the dominant component at cold vents. Upward-migrating fluids and gas hydrates have a strong impact on local, regional and maybe global biogeochemical cycles. In particular, the expulsion of methane as dissolved or free gas (bubbles) and of H_2S from marine sediments is important for local biogeochemical cycles, allows chemoautotrophic fauna to settle, and causes precipitates of massive carbonate.

Gas hydrate, an ice-like substance composed of gas molecules captured in water cages, is stabile at low temperatures and high pressure if the gas concentrations are high enough. Depending on the stability conditions at the sea floor, gas hydrates directly influence the amount of released methane; they create unique ecosystems and might be a possible future energy resource. Massive gas hydrate decomposition can cause gigantic submarine landslides, perhaps trigger tsunamis and endanger oil/gas infrastructures.

Due to the geothermal gradient gas hydrates are not stabile below a certain sediment depth and free gas can escape from decomposing gas hydrate or captured gas-rich fluids. The existence of free gas can be detected by geophysical studies; the occurence of a so-called BSR almost proves a sediment cementation by gas hydrate. However, the absence of a BSR does not prove the absence of gas hydrate.

Although cold vents and gas hydrates exist all over the world, our knowledge about them is restricted to some well-investigated areas such as the Gulf of Mexico, Hydrate Ridge, Eel River, Blake Ridge, and the Black Sea. For a better understanding of these global phenomenon we have to carry out global investigations. We know very little about the ecological variability of seeps, lifespans or changes in fluid activity through time and the real impact and importance of methane releaseb by fluids or decomposing gas hydrate on the global carbon cycle and our climate. To extend this knowledge we have proposed to undertake

Why the Hikurangi Margin?

From previous studies at the Hikurangi Margin gas hydrates and methane venting ishas been inferred from:

1. the widespread occurrence of seismic BSR structures
2. bubble clouds in the water column (CH_4?)
3. methane-derived carbonates
4. chemoautotrophic clams

Except for geophysical studies, the above mentioned observations and sample recoveries have been made by fisherman or occasionally while dredging for scientific purposes. No detailed and systematic studies have been carried out so far although the Hikurangi Margin is an ideal place for integrative petrographic, biogeochemical, geophysical and biological studies as fossil carbonate vents can also be found on land in Miocene strata. However, the limited information from offshore vents nevertheless provides us with a unique opportunity to extend our knowledge about gas hydrate-associated cold vent regimes, including structural controls on fluid flow, seepage zone biogeochemistry, seep geographic distributions, seep community composition and

What we want to do

The overall aims are to study the role of methane in the global biogeochemical cycle, to enhance our knowledge about the global phenomenon of cold fluid venting and to provide a more detailed data base to evaluate the possible use of gas hydrate as a future natural energy resource in New Zealand.

Integrative studies will be conducted using the German research vessel RV SONNE in March-April 2007. The studies will comprise state-of-the-art methods such as bathymetry (EM120), side scan with subbottom profiling (EdgeTech DTS-1), streamer seismics with different sources (G-gun, GI-gun, Air-Gun), OBH/S deployments, heatflow measurements, visual seafloor observations by TV-sled, TV-guided grab and multi-corer sampling, in-situ experiments with a large variety of lander- based systems as well as CTD and hydrocasts. Further, we plan to use a new Belgian ROV for very detailed studies at active seep sites during the last of three legs.

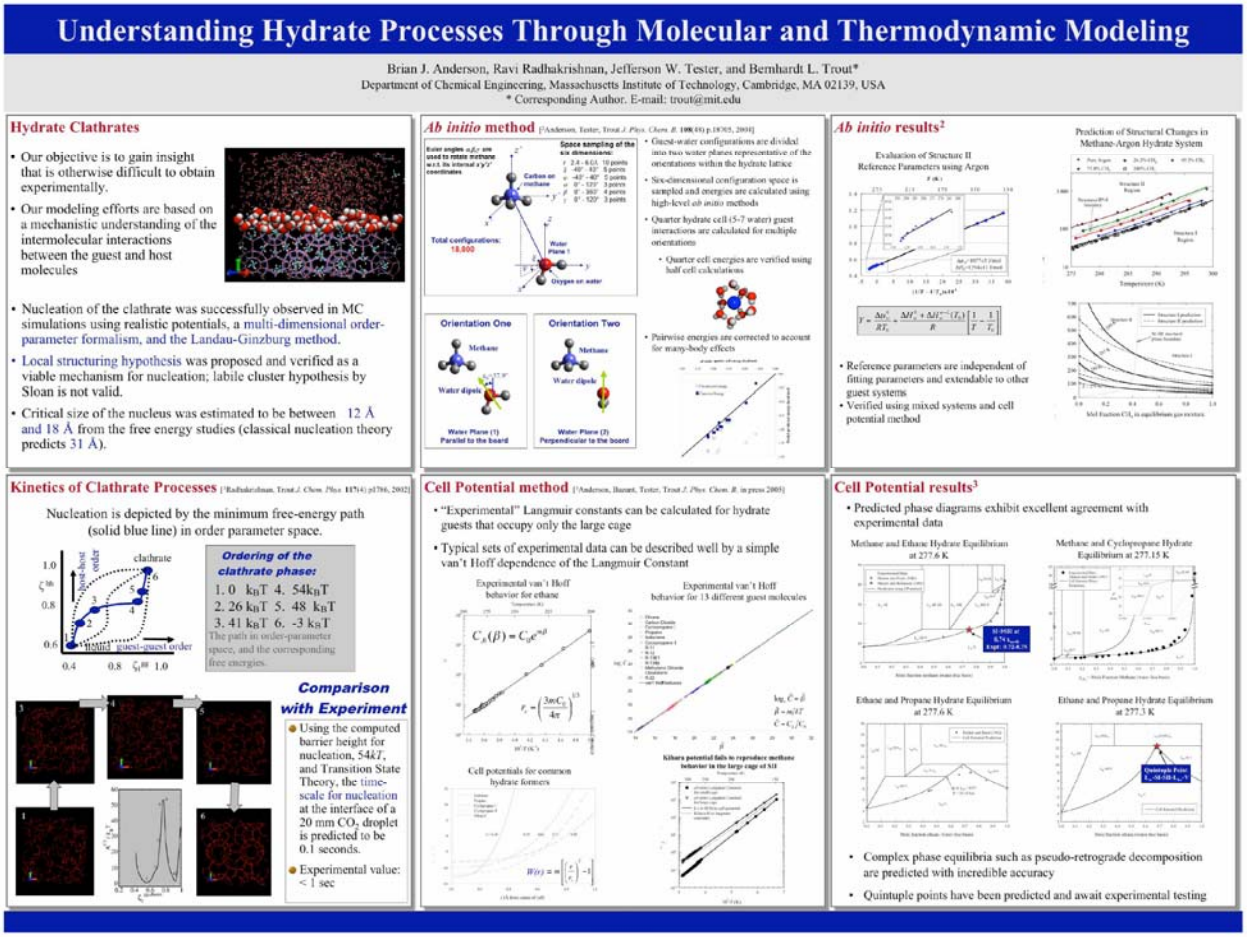
The cruise **New-Vents** is intergrated into a larger German reserach project COMET, which is part of the BMBF-funded initiative 'Methane in the global biogeochemical system'. New-Vents is planned for 65 days starting with a geophysical leg, followed by a leg with more detailed side-scan and visual observations at the seafloor with first sediment/water sampling and lander deployments. Depending on the availability of the ROV, the last leg will include intensive sediment sampling and insitu experiments with landers that will be deployed for some days.

APPENDIX B

Understanding Hydrate Processes Through Molecular and Thermodynamic Modeling

ABSTRACT NOT AVAILABLE

C. J. Anderson, R. Rakrishnan, J. W. Tester, and B. L. Trout



Understanding Hydrate Processes Through Molecular and Thermodynamic Modeling

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Hydrate Clathrates

- Our objective is to gain insight that is otherwise difficult to obtain experimentally.
- Our modeling efforts are based on a mechanistic understanding of the intermolecular interactions between the guest and host molecules
- Nucleation of the clathrate was successfully observed in MC simulations using realistic potentials, a multi-dimensional order-parameter formalism, and the Landau-Ginzburg method.
- Local structuring hypothesis was proposed and verified as a viable mechanism for nucleation; labile cluster hypothesis by Sloan is not valid.
- Critical size of the nucleus was estimated to be between 12 Å and 18 Å from the free energy studies (classical nucleation theory predicts 31 Å).

Ab initio method [¹Anderson, Tester, Trout J. Phys. Chem. B. 108(48) p.18705, 2004]

Euler angles α,β,γ are used to rotate methane w.r.t. its internal x′y′z′ coordinates

Space sampling of the six dimensions:

Carbon on methane

Total configurations: 18,000

Water Plane 1

Oxygen on water

Orientation One

Orientation Two

Methane

Water dipole

Water Plane (1) Parallel to the board

Water Plane (2) Perpendicular to the board

- Guest-water configurations are divided into two water planes representative of the orientations within the hydrate lattice
- Six-dimensional configuration space is sampled and energies are calculated using high-level *ab initio* methods
- Quarter hydrate cell (5-7 water) guest interactions are calculated for multiple orientations
  - Quarter cell energies are verified using half cell calculations
- Pairwise energies are corrected to account for many-body effects

Ab initio results²

Evaluation of Structure II Reference Parameters using Argon

Prediction of Structural Changes in Methane-Argon Hydrate System

$$Y = \frac{\Delta\mu_w^0}{RT_0} - \frac{\Delta H_w^0 + \Delta H_w^{L-I}(T_0)}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

- Reference parameters are independent of fitting parameters and extendable to other guest systems
- Verified using mixed systems and cell potential method

Kinetics of Clathrate Processes [²Radhakrishnan, Trout J. Chem. Phys. 117(4) p1786, 2002]

Nucleation is depicted by the minimum free-energy path (solid blue line) in order parameter space.

Ordering of the clathrate phase:

1. 0 k_BT
2. 26 k_BT
3. 41 k_BT
4. 54k_BT
5. 48 k_BT
6. -3 k_BT

The path in order-parameter space, and the corresponding free energies.

Comparison with Experiment

- Using the computed barrier height for nucleation, 54*kT*, and Transition State Theory, the time-scale for nucleation at the interface of a 20 mm CO_2 droplet is predicted to be 0.1 seconds.
- Experimental value: < 1 sec

Cell Potential method [³Anderson, Bazant, Tester, Trout J. Phys. Chem. B. in press 2005]

- "Experimental" Langmuir constants can be calculated for hydrate guests that occupy only the large cage
- Typical sets of experimental data can be described well by a simple van't Hoff dependence of the Langmuir Constant

Experimental van't Hoff behavior for ethane

$$C_{\beta}(\beta) = C_0 e^{m\beta}$$

$$r_c = \left(\frac{3mC_0}{4\pi}\right)^{1/3}$$

Experimental van't Hoff behavior for 13 different guest molecules

Cell potentials for common hydrate formers

Kihara potential fails to reproduce methane behavior in the large cage of SII

Cell Potential results³

- Predicted phase diagrams exhibit excellent agreement with experimental data

Methane and Ethane Hydrate Equilibrium at 277.6 K

Methane and Cyclopropane Hydrate Equilibrium at 277.15 K

Ethane and Propane Hydrate Equilibrium at 277.6 K

Ethane and Propane Hydrate Equilibrium at 277.3 K

- Complex phase equilibria such as pseudo-retrograde decomposition are predicted with incredible accuracy
- Quintuple points have been predicted and await experimental testing

APPENDIX C

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Victoria, B.C., CANADA May 9–11, 2005

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APPENDIX C

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APPENDIX D

QUESTIONAIRE

International Database for Collaborative Research on Gas Hydrates

Data Collection Form

The purpose of this electronic data collection form is to compile a database of expertise in gas hydrate research in order to assist the development of international collaboration. Please take the time to complete this form 'on-line' and on completion, please return it via email to Ross Chapman < chapman@uvic.ca >, who is convening the next international Workshop in Victoria, BC (9 – 11 May 2005). Those agreeing to complete this form will be given full access to the database and its continuing up-dates.

Thank you for your cooperation.

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Data Source Identification

Click in the grey shaded field areas ‘ ’ below to enter details

Full name of the Principal Investigator: Title, First & Last names	
The full title and address of your organization	

Your contact details:	Tel:	Fax:	Email:

Questionnaire

1. Research Motivation

Please score <u>every</u> item (1.a to 1.h) using a scale of 1 – 5 (5 = strong interest, 1= no interest)

and add any relevant information in the grey shaded area opposite.

1.a. Future Energy	0	Additional information?
1.b. Seabed Stability	0	Additional information?
1.c. Climate Change	0	Additional information?
1.d. Chemosynthetics	0	Additional information?
1.e. Sequestration	0	Additional information?
1.f. Basic Science	0	Additional information?
1.g. Defense	0	Additional information ?

1.h. Other, *please specify here*:

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2. Technical Expertise		
Please click in the Grey Box to make a selection from the drop-down list to score:		***Unique*** ***World-class****,* *or* ***Significant***
2.a. Seismics	Click here	Additional information?
2.b. Electromagnetics	Click here	Additional information?
2.c. Seabed Mapping	Click here	Additional information?
2.d. OBS	Click here	Additional information?
2.e. Sound Speed	Click here	Additional information?
2.f. Drilling (including IODP)	Click here	Additional information?
2.g. Coring	Click here	Additional information?
2.h. Source Characterization	Click here	Additional information?
2.i. Material Characterization	Click here	Additional information?
2.j. Heat-flow	Click here	Additional information?
2.k. Vent & Flares	Click here	Additional information?
2.l. Seabed Dynamics & Slope Stability	Click here	Additional information?
2.m. Radio Carbon Isotopes	Click here	Additional information?
2.n. Modelling	Click here	Additional information?
2.o. Lab Techniques & - Synthetics	Click here	Additional information?
2.p. Geochemistry	Click here	Additional information?
2.q. Fluid Flow Chemistry (*pore water, water column & hydrate*)	Click here	Additional information?
2.r. Biological & Chemosynthetics	Click here	Additional information?
2.s. Additional information?		

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3. Availability of Equipment, Laboratory and Test Facilities

*For each criterion (**Equipment, Laborator**y, and **Test Facilities)** please click in the grey boxes to make a selection from the drop-down list to score as appropriate:*

Specific in-house development

Commercially available with in-house modifications or

Commercially available

	Equipment	Laboratory Modeling	Test Facilities
3.a. Seismics	Click here to select	Click here to select	Click here to select
3.b. Electromagnetics	Click here to select	Click here to select	Click here to select
3.c. Seabed Mapping	Click here to select	Click here to select	Click here to select
3.d. OBS	Click here to select	Click here to select	Click here to select
3.e. Sound Speed	Click here to select	Click here to select	Click here to select
3.f. Drilling	Click here to select	Click here to select	Click here to select
3.g. Coring	Click here to select	Click here to select	Click here to select
3.h. Source Characterization	Click here to select	Click here to select	Click here to select
3.i. Material Characterization	Click here to select	Click here to select	Click here to select
3.j. Heat Flow	Click here to select	Click here to select	Click here to select
3.k. Vent & Flares	Click here to select	Click here to select	Click here to select
3.l. Seabed Dynamics & Slope Stability	Click here to select	Click here to select	Click here to select
3.m. Radio Carbon Isotopes	Click here to select	Click here to select	Click here to select
3.n. Modelling	Click here to select	Click here to select	Click here to select
3.o. Lab Techniques & Synthetics	Click here to select	Click here to select	Click here to select
3.p. Geochemistry	Click here to select	Click here to select	Click here to select
3.q. Fluid Flow Chemistry (pore-water, water-column & hydrate)	Click here to select	Click here to select	Click here to select
3.r. Biological & Chemosynthetics	Click here to select	Click here to select	Click here to select
3.s. Additional information?			

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4. Current or Planned ‘Operating Environment’

Please click in the Grey box to make a selection from the drop-down list in each section

4.a. Ship Click here to select *Other? Specify below in 4.d*	4.b. Permafrost Click here to select *Other? Specify below in 4.d*	4.c. Laboratory& Modeling Click here to select *Other? Specify below in 4.d*

4.d. Additional information?

5. Details of Existing Program/s (submit more than one questionnaire if necessary)

5.a. Full title of your program			
5.b. Click to check a box if your program is planned, or confirmed	Planned ☐ Confirmed ☐	Other? Please specify	
5.c. Program start date:		5d. Program end date:	
5.d. State Funding Authority:			
5.e. Program collaborators (*incl. details of their technical input*)			
5.f. Budget (*optional*)			
5.g. Location for field work			
5.h. Modeling/Laboratory studies			
5.i. Details of future proposals			
5.j. Additional information?			

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6. Willingness & scope to make changes to your program in order to enhance collaboration:		
To indicate a positive response, please click in the grey box next to your selection/s to check it. :		
6.a. To work in an additional (*or other*) area/s outside your national EEZ	☐	Additional information?
6.b. To incorporate additional objectives and techniques in your program	☐	Additional information?
6.c. To seek complimentary technologies to augment your program	☐	Additional information?
6.d. To seek collaborative funding	☐	Additional information?
6.e. Additional information?		
7. Please add any further comments which you feel would be beneficial		
Thank you for completing this questionnaire. **Please send your response to** Ross Chapman < chapman@uvic.ca >		