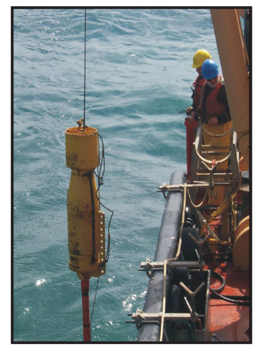
Naval Research Laboratory
Washington, DC 20375-5320

NRL/MR/6114--03-8696

FIERY ICE FROM THE SEAS

2nd International Workshop on Methane Hydrate R&D

29-31 October 2002
Washington Plaza Hotel, Washington, DC



Chaired By:

Richard B. Coffin
Marine Biogeochemistry Section, Chemistry Division
Naval Research Laboratory, Washington, DC

Stephen M. Masutani
School of Ocean and Earth Science and Technology
Hawaii Natural Energy Institute, Honolulu, Hawaii

Tsutomu Uchida
Gas Hydrate Research Group
AIST, Sapporo, Japan

Bjørn Kvamme
Department of Physics
University of Bergen, Bergen, Norway

November 14, 2003

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Chaired by:
Richard B. Coffin, Stephen M. Masutani,* Tsutomu Uchida,† and Bjørn Kvamme‡

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*School of Ocean and Earth Science and Technology, Hawaii Natural Energy Institute, Honolulu, Hawaii
†Gas Hydrate Research Group, AIST, Sapporo, Japan
‡Department of Physics, University of Bergen, Bergen, Norway

14. ABSTRACT

The Second Workshop of the International Committee on Methane Hydrates was held in Washington, DC, at the Washington Plaza Hotel on 29-31 October 2002**.** This workshop was organized by the Marine Biogeochemistry Section, Code 6114, of the U.S. Naval Research Laboratory (NRL), Hawaii Natural Energy Institute of the University of Hawaii (HNEI), Agency of Industrial Science and Technology (AIST), and the Department of Physics at the University of Bergen (UB). Grants of $10,000 each were awarded by the Office of Naval Research-International Field Office and the National Energy Technology Laboratory of U.S. Department of Energy to support the event. Additional funds were provided through the Hawaii Energy and Environmental Technologies (HEET) initiative sponsored by the U.S. Department of Defense through the efforts of U.S. Senator Daniel K. Inouye of Hawaii. Participants, including 99 people from the United States, Japan, Egypt, Chile, Canada, Norway, Russia, and the United Kingdom, attended the workshop. Participation was by invitation only. Attendees included some of the world's leading researchers in methane hydrates and representatives from government agencies and the private sector.

The principal workshop objectives were: (1) review past, ongoing, and planned methane hydrates R&D projects and programs; (2) share information on budgets and research resources and priorities in different countries; (3) establish linkages for domestic and international partnering; and (4) develop international laboratory and field collaborations. The program of the 2-1/2 day workshop included plenary lectures, panel discussions, small group breakout meetings, and a poster session. It was conducted as a working event where all participants conferred to develop a roadmap for future collaborative studies of methane hydrates.

15. SUBJECT TERMS

Methane hydrates; International collaboration; NRL; UH

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INTRODUCTION

Gas hydrates, ice-like mixtures of hydrocarbon gas (mostly methane) and water are found within arctic permafrost and ocean sediments located along the margins of most landmasses. Methane hydrates form when water and methane are brought in contact within a specific pressure-temperature regime. In the oceanic environment, this generally occurs in seafloor sediments at locations where water depths range from 300 meters to 2000 meters. Hydrates in these sediments are stable in the zone extending approximately 300 to 600 meters below the seafloor. Depending on the vertical migration and in situ production of methane, hydrates may be found up to the water-sediment interface.

The discovery of the methane hydrate reservoir has generated considerable excitement since it is estimated to contain at least twice the energy in all known reserves of fossil fuels. Although methane has the lowest ratio of carbon to hydrogen of all hydrocarbon fuels, exploitation and oxidation of this massive methane pool for energy production will undoubtedly exacerbate the ongoing build up of greenhouse gases in the atmosphere and may seriously impact global climate. Moreover, the methane hydrate component constitutes a significant fraction of the sediment volume in certain locales and serves to stabilize the continental slopes. Commercial mining of methane hydrates could negatively impact slope stability and result in underwater landslides and slumps which, in turn, have the potential to generate tsunamis.

The energy, environmental, and safety implications of methane hydrates have led to the initiation of major research programs in a number of countries over the past decade. Although national interests will need to be protected in certain areas of development, international collaboration is a logical and effective means to pursue the basic science and technology of methane hydrates. The rationale behind this approach is apparent when one considers that the environmental consequences associated with purposeful or inadvertent hydrate destabilization and methane release, such as global climate change and underwater landslides and the tsunamis that may result, do not respect national borders. Furthermore, exploitation of the hydrate resource for energy, may have profound global economic and political implications.

In concert with growing national and world interest in methane hydrates, the Naval Research Laboratory (NRL) initiated an R&D program designed to improve understanding and develop models of the formation and dissociation of natural gas hydrates. This 5 year program that began in FY'99, is funded at a level of $1 million per year using in-house NRL funds. The specific research goal of this effort is to quantify the impacts of hydrates on the geophysical and geotechnical properties of marine sediments in littoral regions. The results of this study have potential to contribute significantly to general understanding of issues related to resource characterization, commercial availability of the resource, the global carbon cycle, and sea floor stability. A subsequent 5-year research program, starting in FY'04, is being planned at a similar funding level to investigate the influence of biogeochemical cycles on hydrate formation, stability and lattice saturation. The NRL program will support broad international and U.S. objectives.

Against the backdrop of heightened research activity on oceanic methane hydrates, NRL and the Hawaii Natural Energy Institute (HNEI) of the University of Hawaii (UH) agreed to cooperate to establish an international research partnership which could offer extensive cross-disciplinary technical resources and expertise that could be applied to determine methane hydrate resource distribution and availability; develop viable recovery technologies; establish safety procedures for offshore commercial and military installations in hydrate sediment zones; and evaluate the impact of methane hydrates on global climate and the marine environment. HNEI and NRL began contacting potential foreign research partners at the beginning of 1999, and groups from Korea, Japan, and Norway agreed to collaborate on methane hydrate projects. Partners include the Hokkaido National Industrial Research Institute of the Agency of Industrial Science and Technology of the Government of Japan, the Korea Research Institute of Chemical Technology, University of Korea, Norwegian Institute for Water Research, and University of Bergen, also of Norway. This effort has expanded to other national laboratories and universities in Chile, Canada, New Zealand and Australia.

As a major first step to implement the international research partnership, a workshop was held at the University of Hawaii in March 2000 to define R&D priorities and initiate cooperative projects. Participants to the workshop included representatives from academic, government and industry from 7 countries. Several projects were identified at the workshop that would integrate the capabilities of universities and government agencies from a number of countries:

1) Japanese (AIST-Sapporo) and UH/NRL scientist to provide a natural system database to assist in developing a hydrate dissociation simulator.
2) Japanese (AIST-Tskuba) and NRL exploration of hydrates off the coast of Japan on the Nankai Trough.
3) Research cruises on the Cascadia Margin off the coast of Victoria, British Columbia operating seismic systems and remote operated vehicles (ROV) and conducting deep piston coring on methane hydrate rich sediment beds.
4) Research planning for work in the Norwegian and North Sea to explore hydrate beds for prediction of hydrates on the petroleum platform stability.

A subsequent workshop was held on 29-31 October 2002 in Washington, D.C. with participants from 11 nations. The Hokkaido National Industrial Research Institute of Japan's Agency of Industrial Science and Technology and University of Bergen cooperated with HNEI and NRL to organize this workshop. Grants of $10,000 each were awarded by the Office of Naval Research-International Field Office and the U.S. Department of Energy to help support the event.

The principal workshop objectives were:

(1) Review past, ongoing, and planned methane hydrates research and development projects and programs.

(2) Share information on budgets and research resources and priorities in different countries.

(3) Establish linkages for domestic and international partnering.

The program of the two and a half day workshop included plenary lectures, panel discussions, small group break-out meetings, and a poster session. One of the primary products of this workshop was the development of a plan for hydrate research off the mid coast of Chile that would be conducted by U.S. (UH/NRL), Canadian, Japanese, German and Chilean researchers. Representatives from UH/NRL started the preliminary planning for this cruise in November 2002.

TOPICS AND FORMAT

Workshop Chairs:

Dr. Richard Coffin, Biogeochemistry Section, Naval Research Laboratory, USA, rcoffin@ccf.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, USA, Masutan@wiliki.eng.hawaii.edu

Dr. Tsutomu Uchida, Institute for Energy Utilization, AIST-Hokkaido, Sapporo, Japan, t.uchida@aist.go.jp

Date: October, 29-31, 2002

Location: Washington, DC, USA

Participating Nations:
Japan, Norway, United States, Canada, Korea, Russia, Egypt, Taiwan, China, India, Germany, United Kingdom

Research Topics:

I. Methane Hydrate Resource Characterization and Distribution
II. Biological Influence on Hydrate Formation, Stability, Content and Lattice Saturation
III. Kinetics of Hydrate Formation and Dissociation
IV. Environmental Concern: Seabed Stability and Ecosystem Health
V. Methane Storage and Shipping
VI. International Interdisciplinary Scientific Network

Expected Products:

I. International Interdisciplinary Scientific Network
II. Ship Time Sharing
III. Site Data Integration
IV. Laboratory and Field Technology Information
V. Preliminary Hydrate Dissociation Strategies

The following presentations and abstracts are the result of the 2002 workshop.

SESSION I

Methane Hydrate Resource Characterization and Distribution

Chairman: Dr. Joseph F. Gettrust
Naval Research Laboratory
Stennis Space Center, Mississippi

Rapporteur: Dr. Manabu Tanahashi
Fuel Resource Geology Research Group, AIST
Tsukuba, Japan

Some recent results of the gas hydrate monitoring project in the northern Gulf of Mexico

Thomas M. McGee

Center for Marine Resources and Environmental Technology
University of Mississippi

ABSTRACT

A number of results have been produced by those members of the Gulf of Mexico Hydrate Research Consortium who have been involved with developing equipment and techniques for use in a sea-floor monitoring station. These results will be presented and discussed.

CMRET CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY

SOME RECENT RESULTS OF THE GAS HYDRATE MONITORING PROJECT IN THE NORTHERN GULF OF MEXICO

The Second Workshop of the
International Committee on Methane Hydrates
Washington Plaza Hotel, Washington, D.C.
October 29-31, 2002

The University of Mississippi

CMRET CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY

OBJECTIVE OF THE PROJECT

To establish a remote, multisensor monitoring station at a selected location within the hydrate stability zone of the northern Gulf of Mexico

The University of Mississippi

CMRET CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY

BRIEF OVERVIEW OF FY 2002

During FY 2002, significant progress was made in several aspects of the research activities leading to installation of the gas hydrate monitoring station.

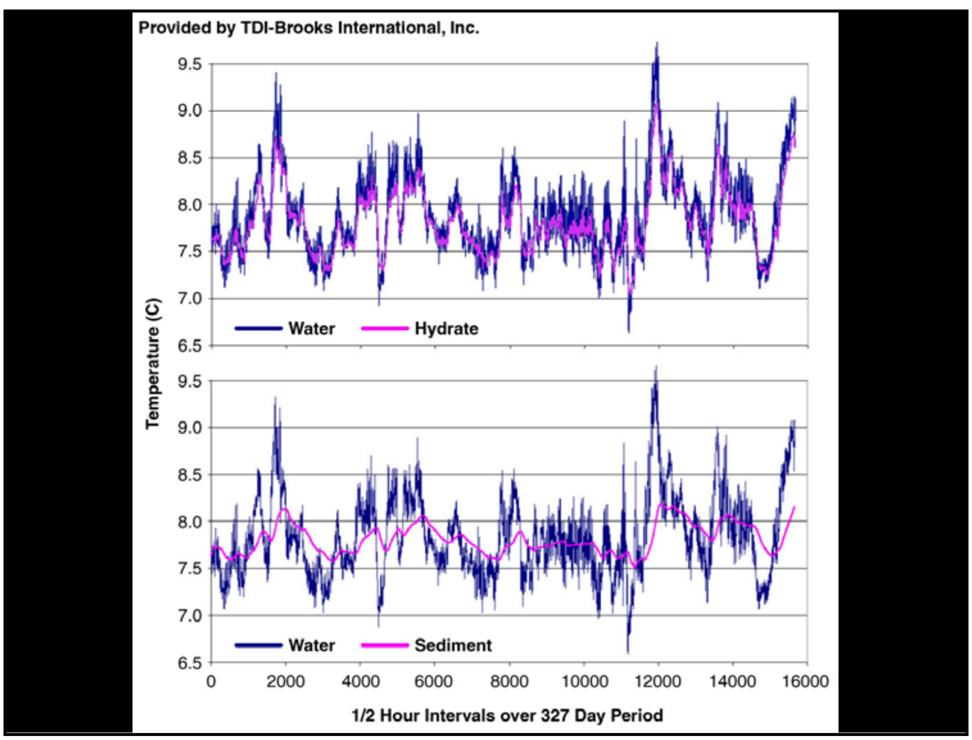
These aspects included:
building and testing equipment,
deploying equipment at sea,
and laboratory experiments.

Several involved use of the Johnson Sea Link manned submersible.

All were funded by DoE-NETL and/or MMS-Herndon.

The University of Mississippi


© Ian MacDonald
Exposed Hydrate Mound with Johnson Sea Link
Submersible in Background


Provided by TDI-Brooks International, Inc.
Temperature (C)
Water
Hydrate
Water
Sediment
1/2 Hour Intervals over 327 Day Period

CMRET CENTER FOR MARINE RESOURCES AND ENVIRONMENTAL TECHNOLOGY

Re: I. MacDonald, M. Vardaro, B. Bernard, J. Brooks

Preliminary Results:

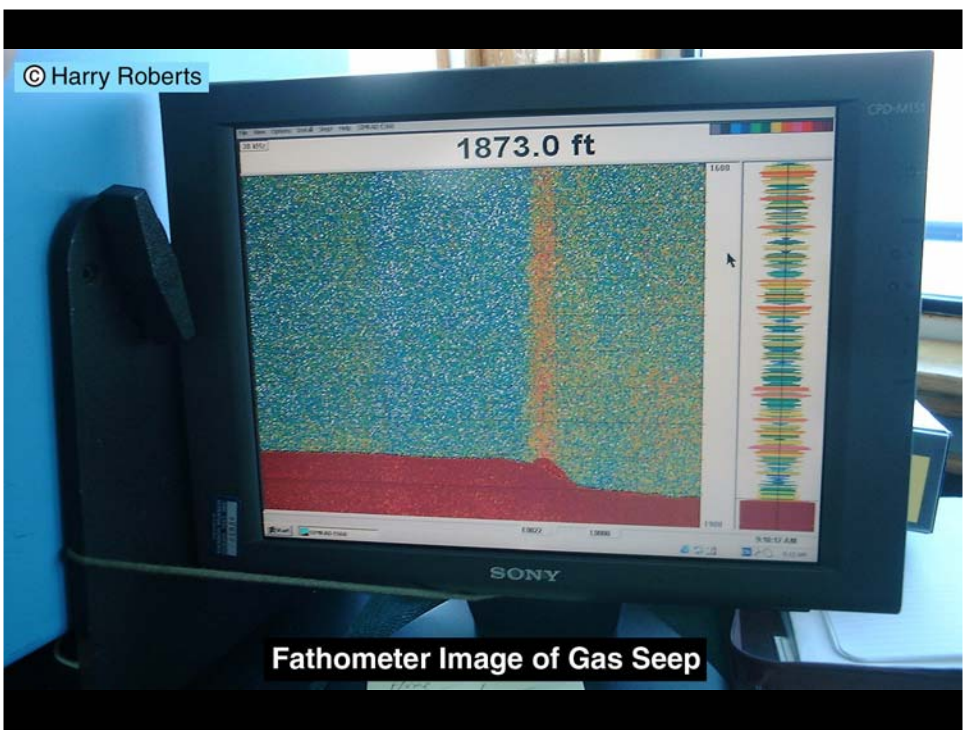
1) No dramatic changes in size, shape or amount of gas being venting.

2) Mean temperatures 7.87 °C in water
7.81 °C in both hydrate and sediment.

3) subbottom temperatures lag behind water temperatures.

Further analysis is expected to advance efforts to model and understand thermal response (i.e. thermal conductivity) of exposed hydrate deposits.

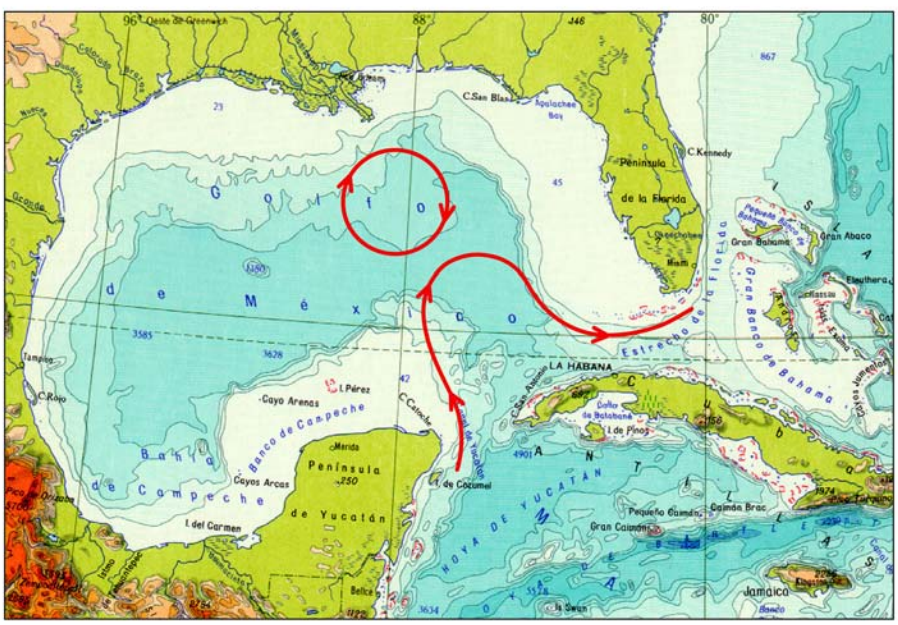
The University of Mississippi



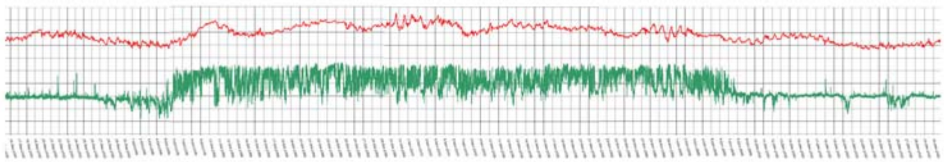
Fathometer Image of Gas Seep

© Harry Roberts

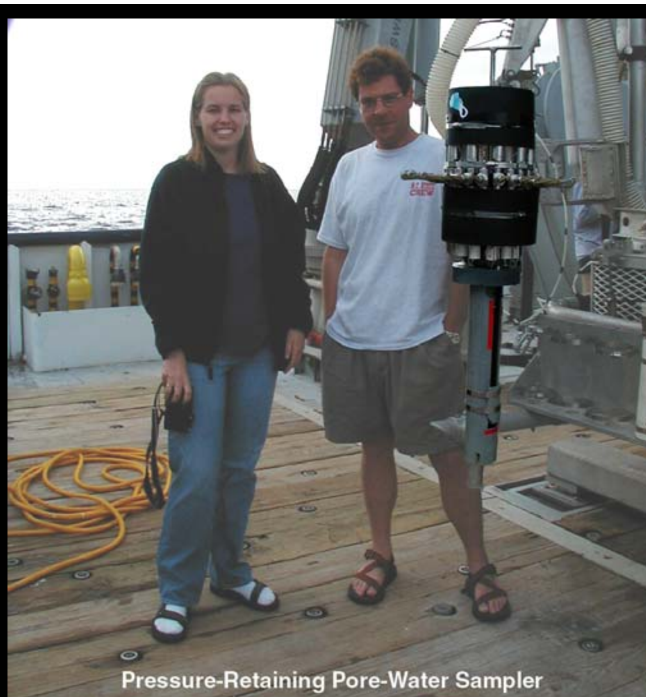
Device for Measuring Gas from Seeps



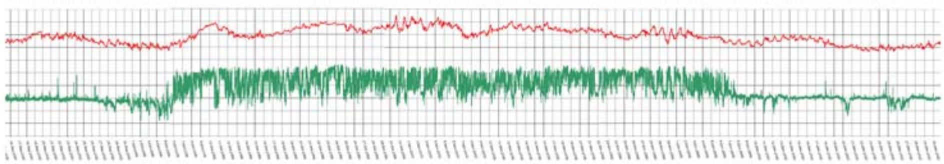
Loop Current and Detached Eddy



Temperature and Gas Activity
During Loop Current Passage (Re: Harry Roberts)



Pressure-Retaining Pore-Water Sampler



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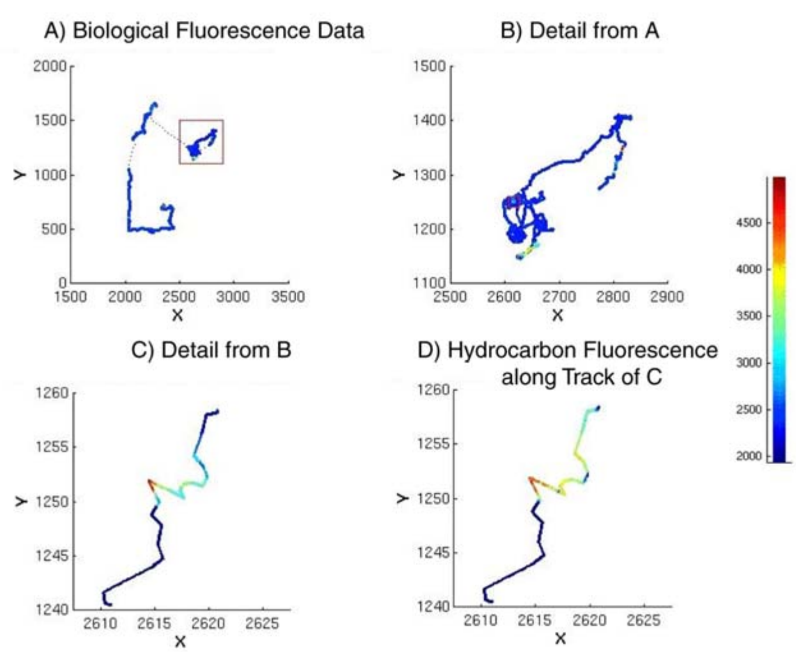
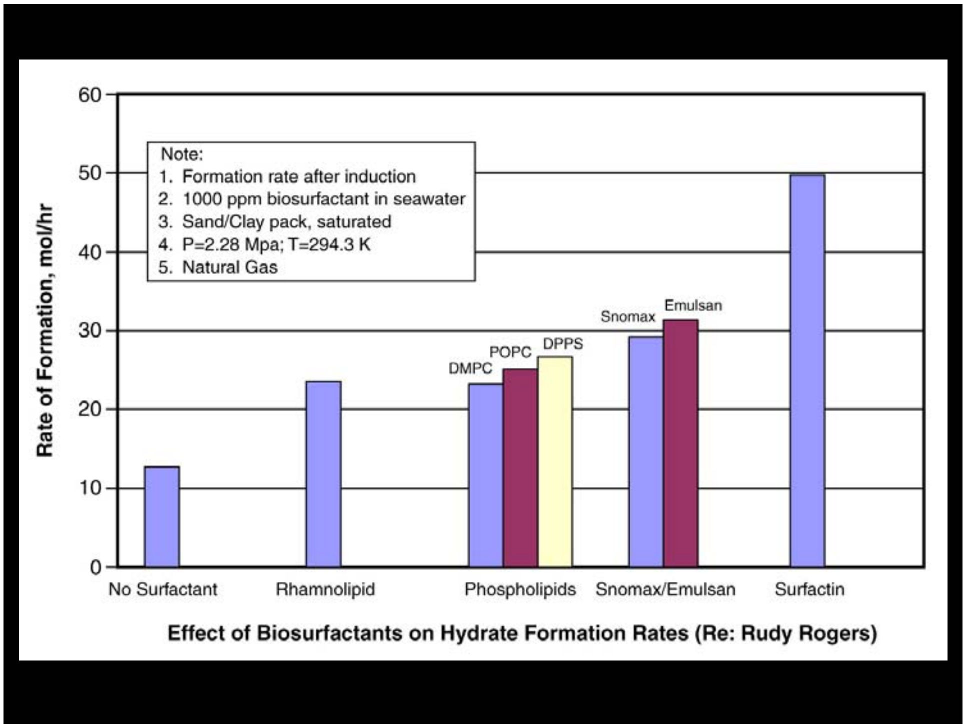
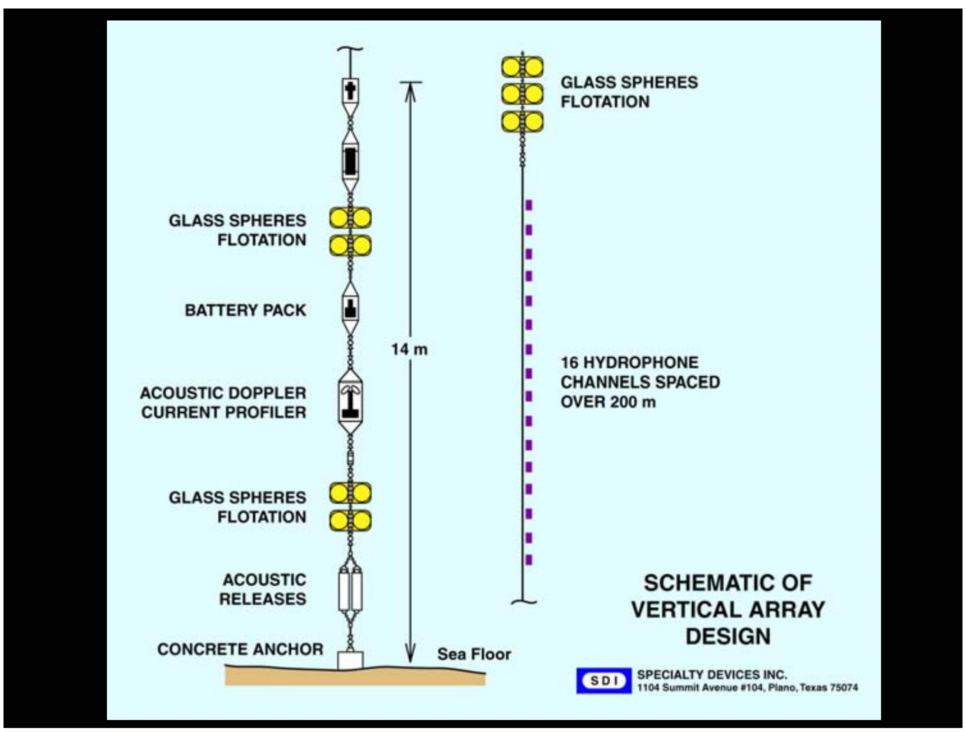


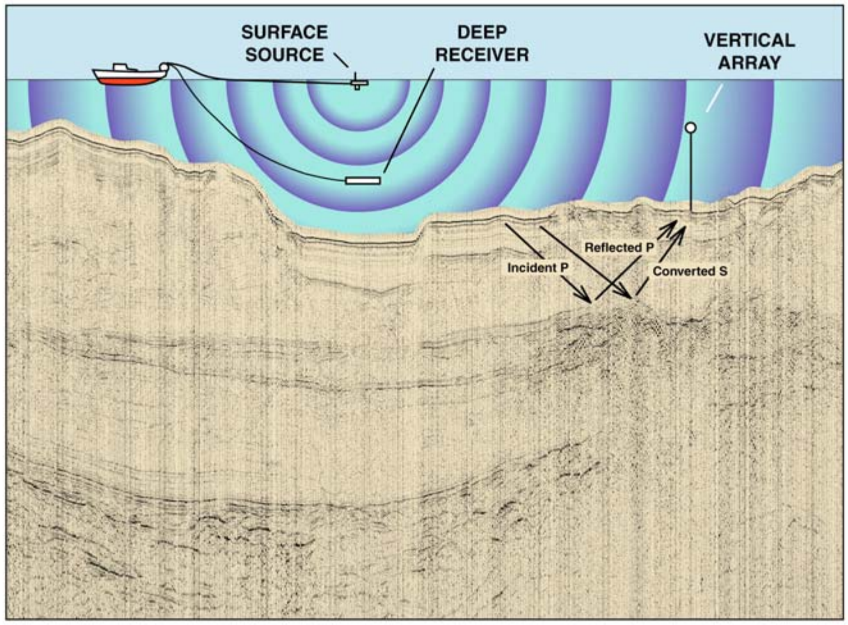
Scale Comparison of Fluorometer Measurements (Re: Jean Whelan)



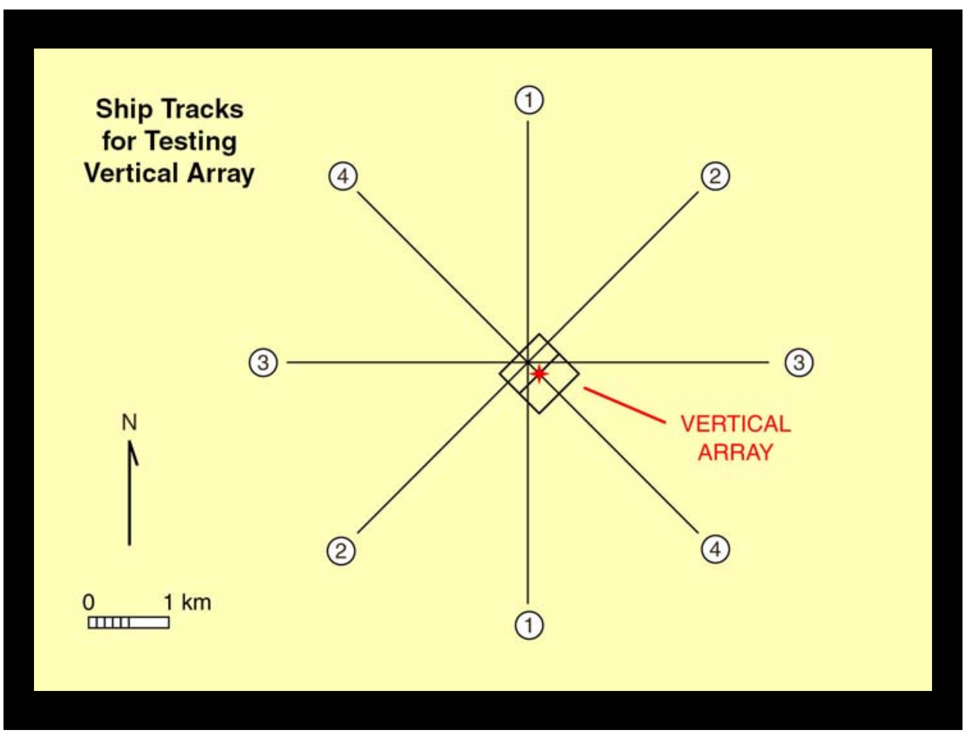
Rate of Formation, mol/hr
60
50
40
30
20
10
0
Note:
1. Formation rate after induction
2. 1000 ppm biosurfactant in seawater
3. Sand/Clay pack, saturated
4. P=2.28 Mpa; T=294.3 K
5. Natural Gas
DMPC
POPC
DPPS
Snomax
Emulsan
No Surfactant
Rhamnolipid
Phospholipids
Snomax/Emulsan
Surfactin
Effect of Biosurfactants on Hydrate Formation Rates (Re: Rudy Rogers)

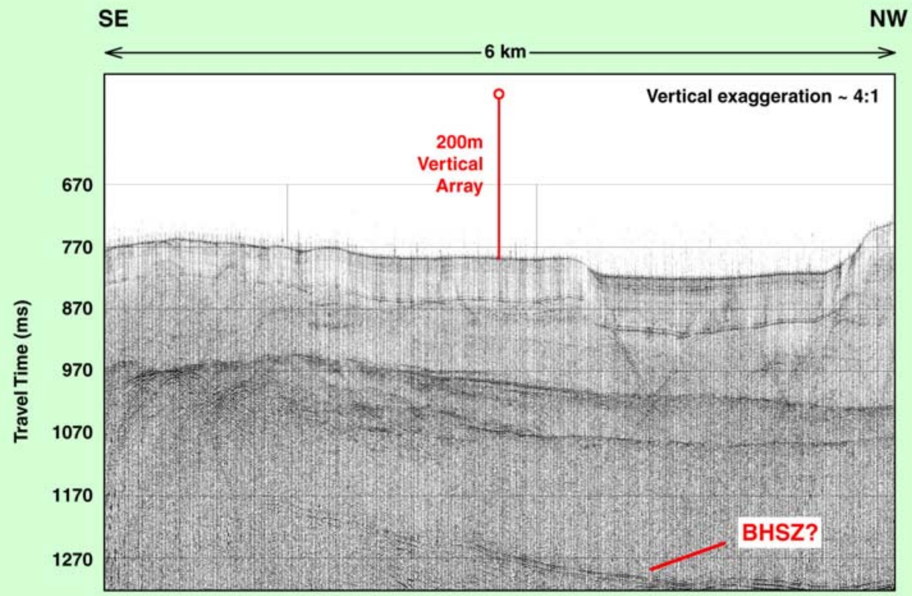


GLASS SPHERES FLOTATION
BATTERY PACK
ACOUSTIC DOPPLER CURRENT PROFILER
GLASS SPHERES FLOTATION
ACOUSTIC RELEASES
CONCRETE ANCHOR
14 m
Sea Floor
GLASS SPHERES FLOTATION
16 HYDROPHONE CHANNELS SPACED OVER 200 m
SCHEMATIC OF VERTICAL ARRAY DESIGN
SDI
SPECIALTY DEVICES INC.
1104 Summit Avenue #104, Plano, Texas 75074

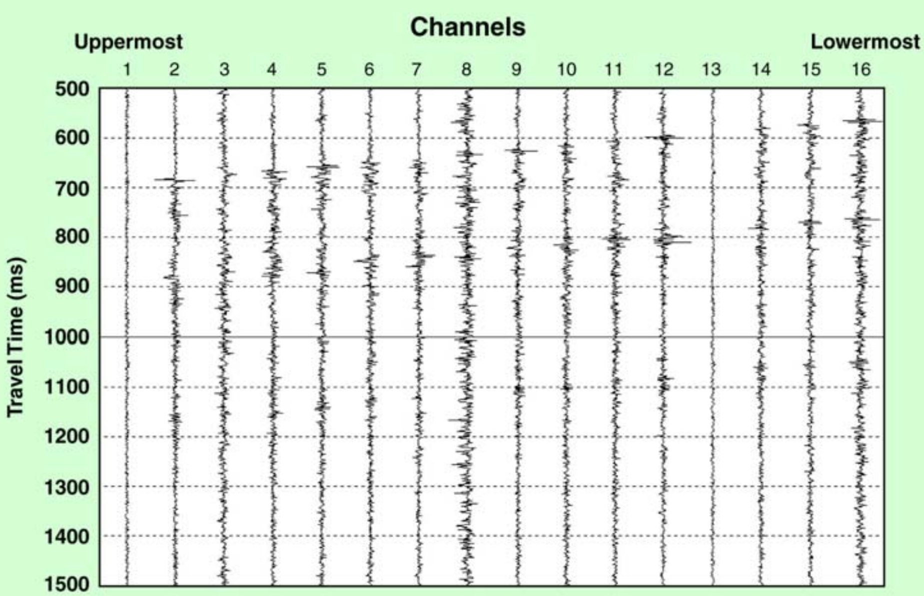


VERTICAL ARRAY TESTING WITH SS/DR HORIZONTAL PROFILING

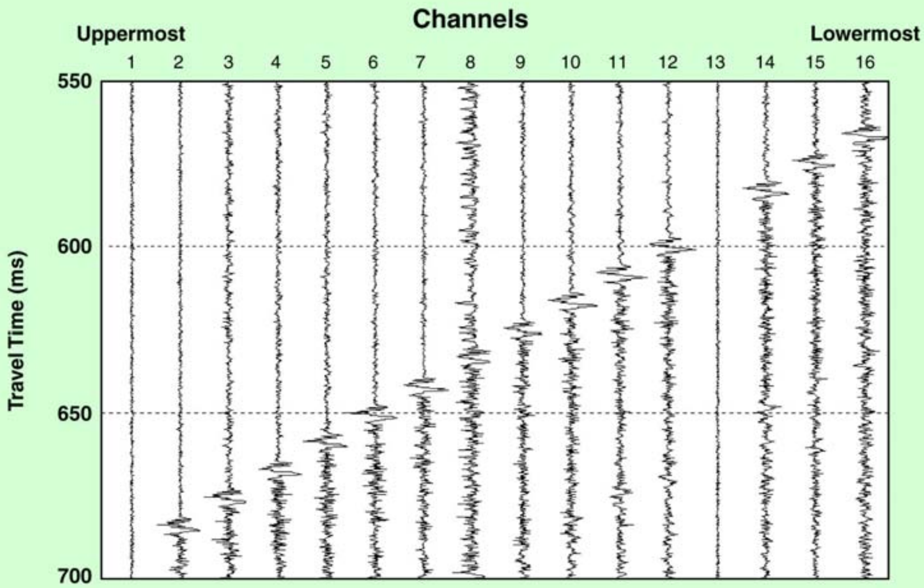




SS/DR Profile over Vertical Array Site

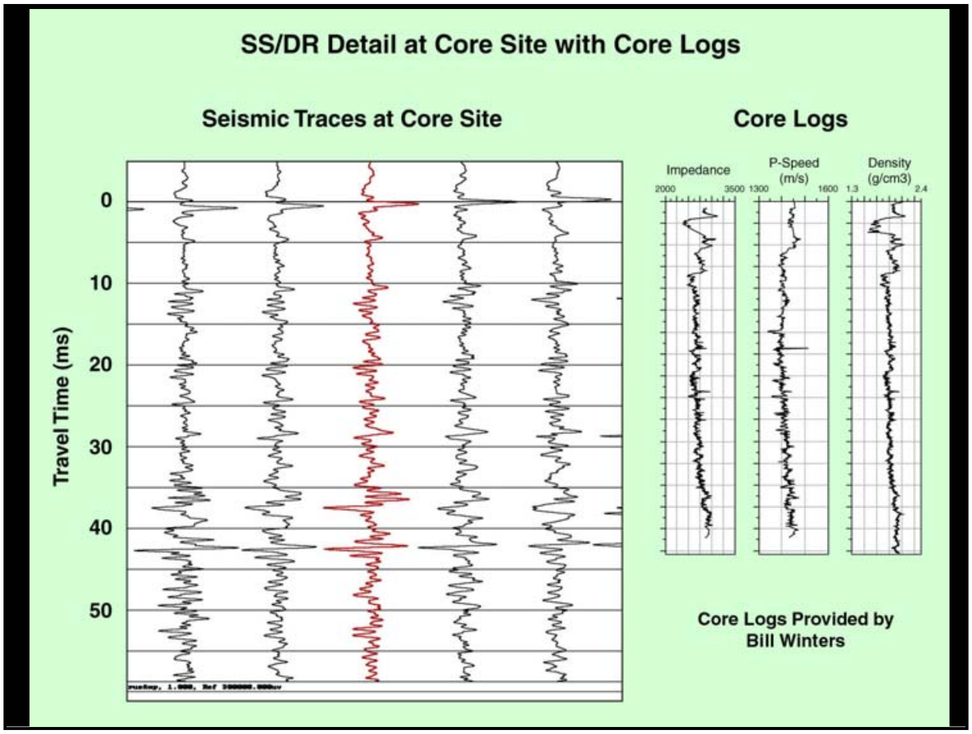


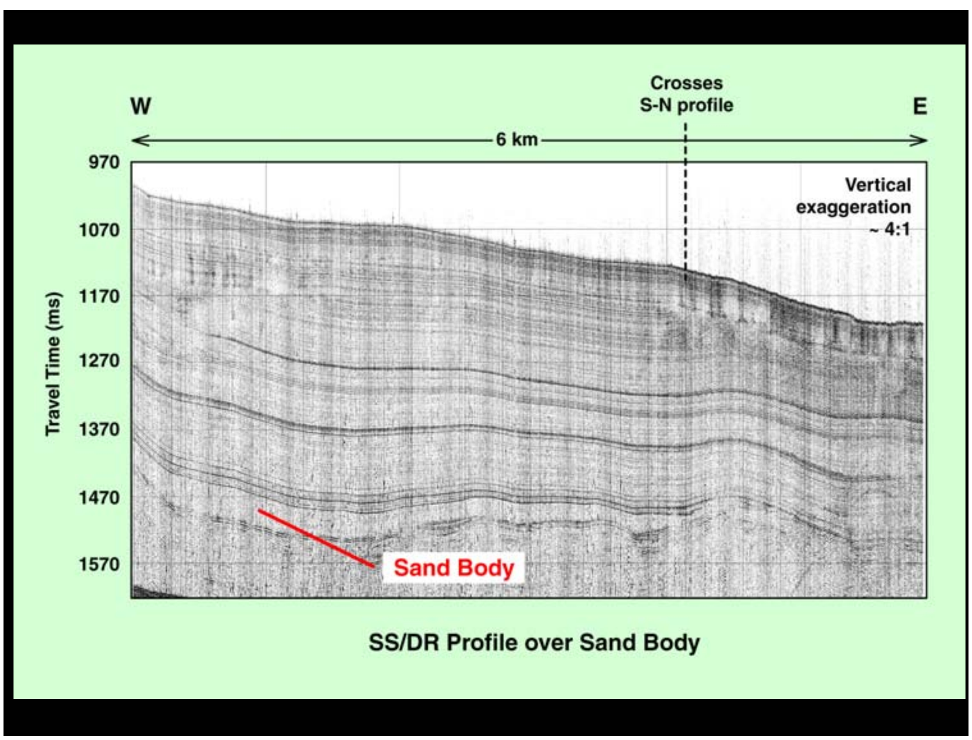
Example of Vertical Array Data

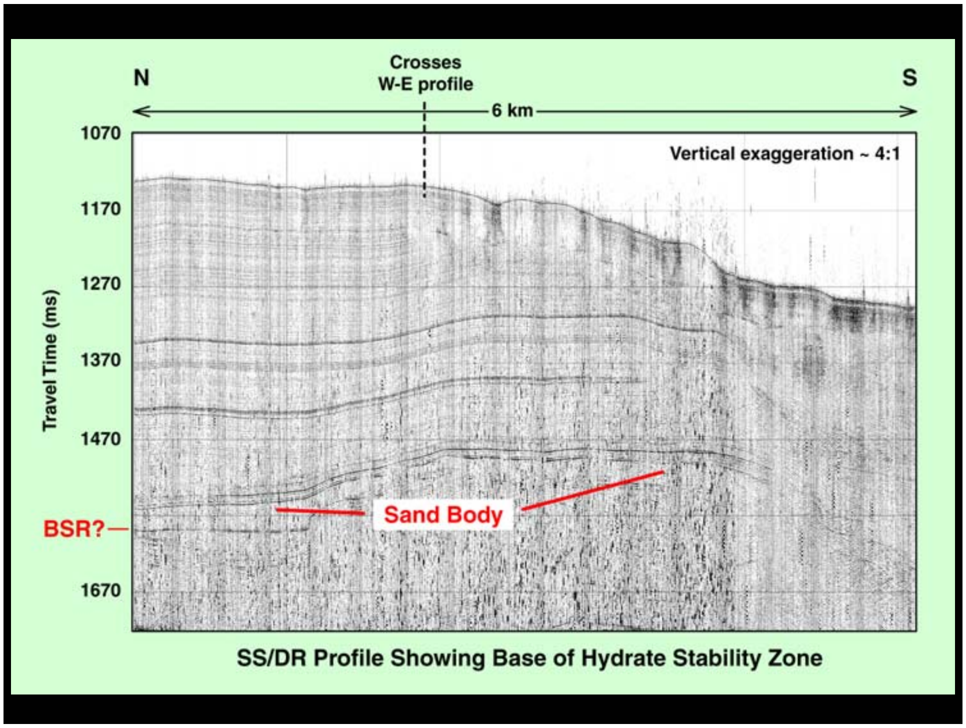


Example of Upward Traveling Wavefront

SS/DR Profile over Core Site


SS/DR Detail at Core Site with Core Logs
Seismic Traces at Core Site
Core Logs
Travel Time (ms)
0
10
20
30
40
50
Impedance
2000
3500
P-Speed
(m/s)
1300
1600
Density
(g/cm3)
1.3
2.4
Core Logs Provided by
Bill Winters

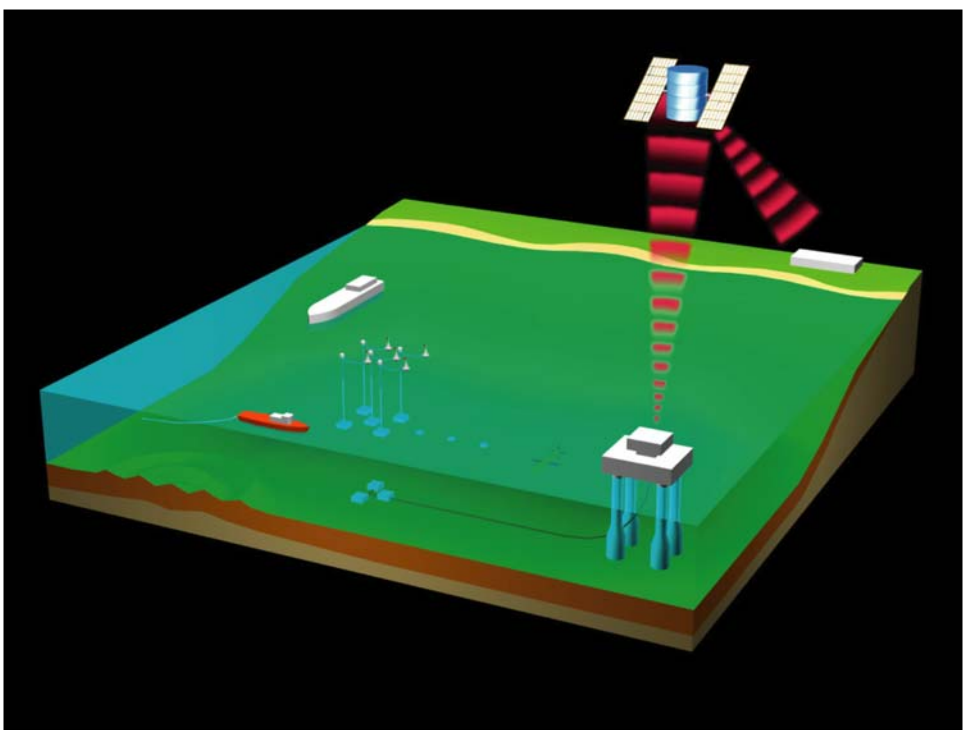

W
Crosses
S-N profile
E
6 km
970
1070
1170
1270
1370
1470
1570
Travel Time (ms)
Vertical
exaggeration
~ 4:1
Sand Body
SS/DR Profile over Sand Body

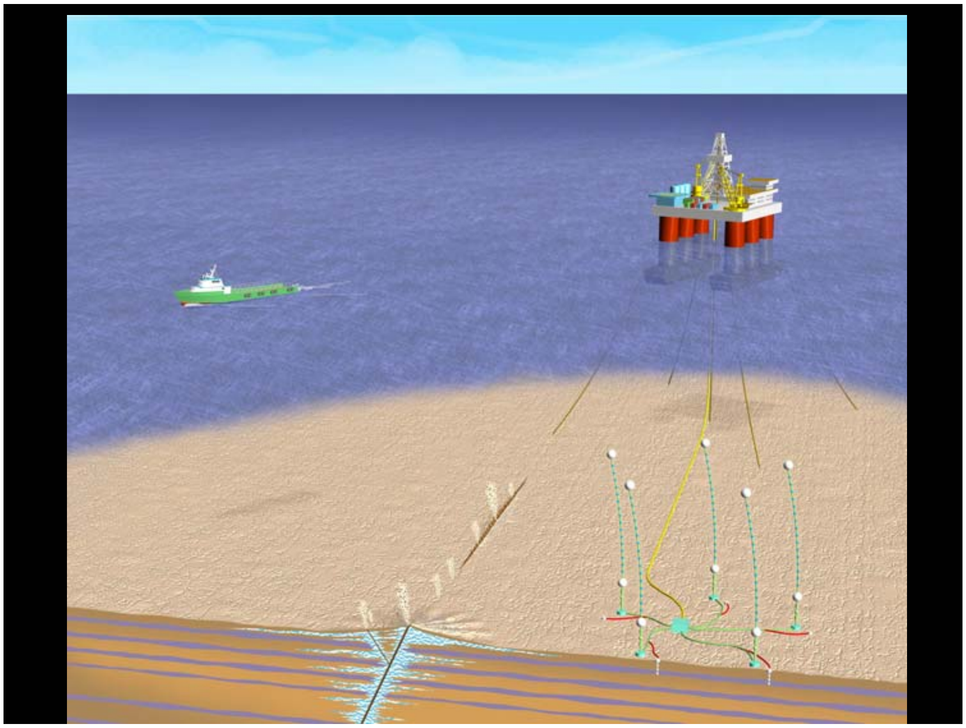


N
Crosses
W-E profile
S
6 km
Vertical exaggeration ~ 4:1
1070
1170
1270
1370
1470
1670
Travel Time (ms)
Sand Body
BSR?
SS/DR Profile Showing Base of Hydrate Stability Zone

© Jeff Chanton
Probe Sensor (Hydrophone and 3-Component Accelerometer)


© Jeff Chanton
Mechanism for Pushing Probe into Sea Floor





Strategies for Gas Production From Hydrate Accumulations Under Various Geological and Reservoir Conditions

George J. Moridis [(1)], *Timothy S. Collett* [(2)], *Scott Digert*[(3)], *and Robert Hunter*[(3)]

[(1)] Lawrence Berkeley National Laboratory;[(2)] United States Geological Survey;
[(3)] BP Exploration (Alaska), Inc.

ABSTRACT

The objective of this study is the analysis and development of appropriate strategies for gas production from a wide range of natural hydrate accumulations. These strategies involve the three main hydrate dissociation mechanisms (depressurization, thermal stimulation, inhibitor effects) either individually or in combination. Selection of the appropriate strategy is strongly influenced by the geological setting and the conditions prevailing in the hydrate accumulation. The TOUGH2 general-purpose simulator with the EOSHYDR2 module was used for the analysis. EOSHYDR2 models the non-isothermal gas release, phase behavior and flow in binary hydrate-bearing porous and fractured media (involving methane and another hydrate-forming gas) by solving the coupled equations of mass and heat balance, and can describe any combination of mechanisms of hydrate dissociation.

In terms of production strategy and behavior, hydrate accumulations are divided into three main classes. In Class 1 the permeable formation includes two zones: the hydrate interval and an underlying two-phase fluid zone with free (mobile) gas. In this class, the bottom of the hydrate stability zone occurs above the bottom of the permeable formation. Class 2 features a hydrate-bearing interval overlying a mobile water zone (e.g., an aquifer). Class 3 is characterized by the absence of a hydrate-free zone, and the permeable formation is thus composed of a single zone, the hydrate interval. In Classes 2 and 3, the entire hydrate interval may be well within the hydrate stability zone (i.e., the bottom of the hydrate interval does not necessarily indicate hydrate equilibrium).

We study gas production from several accumulations that span the spectrum of realistic representations within and across the three hydrate classes. The numerical simulations indicate that, in general, the appeal of depressurization decreases from Class 1 to Class 3, while that of thermal stimulation increases. Thus, simple depressurization appears to enjoy an advantage over other production strategies in Class 1 hydrate deposits. The most promising production strategy in Class 2 hydrates involves combinations of depressurization and thermal stimulation, and is clearly enhanced by multi-well production-injection systems, e.g., a five-spot configuration. Because of the very low permeability of hydrate-bearing sediments, the effectiveness of depressurization in Class 3 hydrates is limited, and thermal stimulation through single well systems seems to be the strategy of choice in such deposits (and especially so in high hydrate saturation regimes). These observations should only be viewed as general principles because the significant variability within each class, the case sensitivity and the insufficient body of prior experience on hydrates do not allow the outright dismissal of any production strategy in any class. The sensitivity of production to important parameters and conditions is investigated, and the limitations of the various production strategies are discussed.

Well Log Evaluation of Marine and Permafrost Associated Gas Hydrate Accumulations

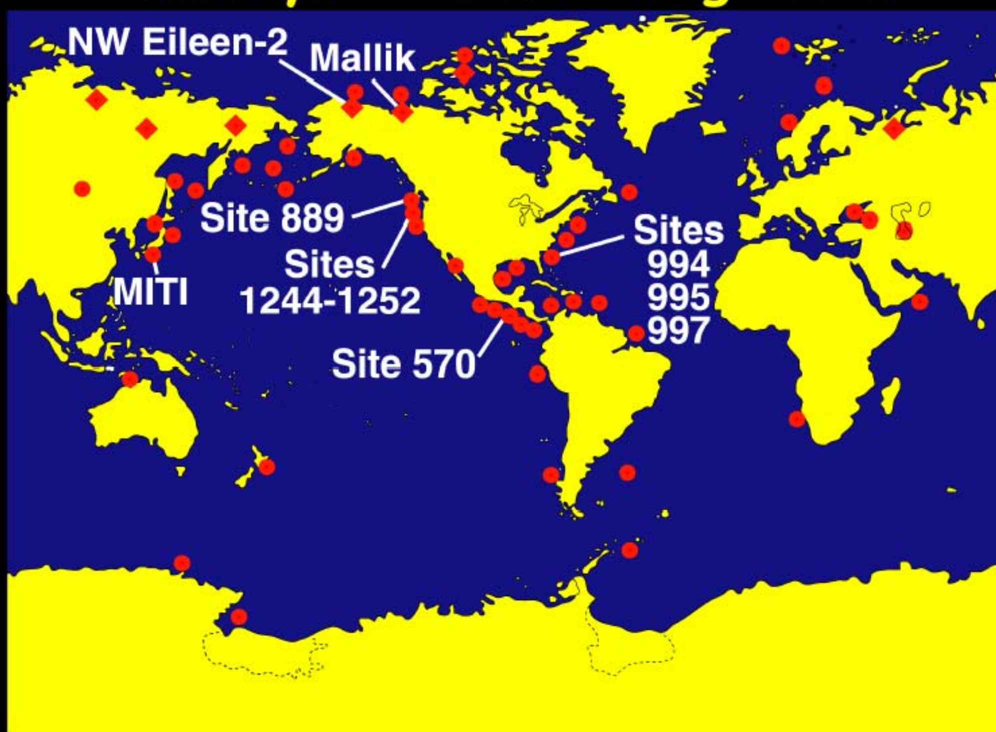
Second Workshop of the International Committee on Gas Hydrates
October 29-31, 2002, Washington, DC

Timothy S. Collett
U.S. Geological Survey

Outline of Presentation

- Gas Hydrate Reservoir Models
- Quantitative Well-Log Analysis of in-situ Gas Hydrates
- Arctic Case Study – Mallik
- Marine Case Study – Hydrate Ridge
- Summary

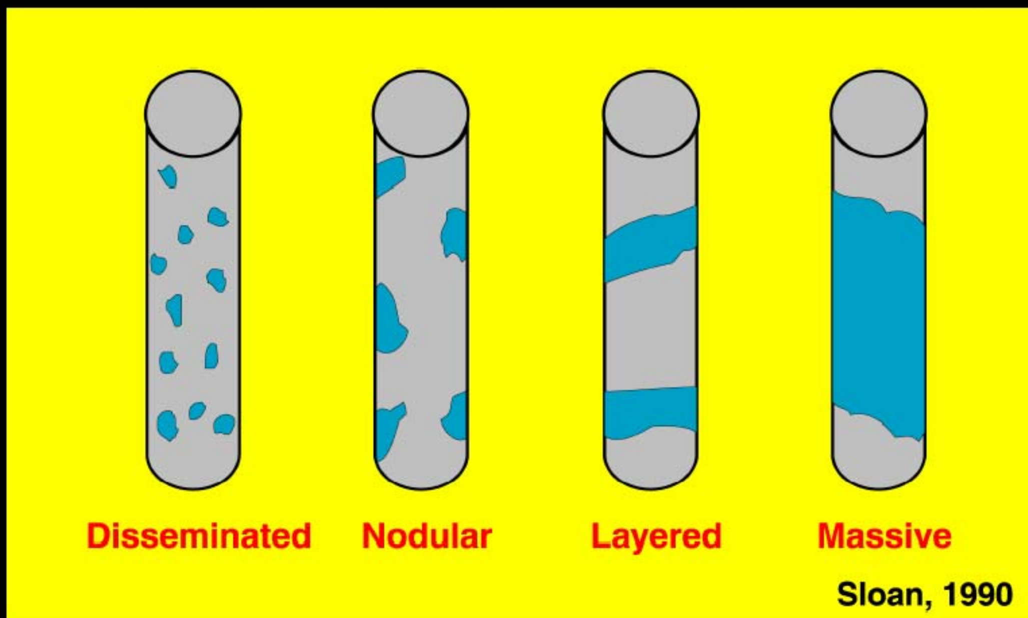
Gas Hydrate Well Log Sites



Outline of Presentation

- Gas Hydrate Reservoir Models
- Quantitative Well-Log Analysis of in-situ Gas Hydrates
- Arctic Case Study – Mallik
- Marine Case Study – Hydrate Ridge
- Summary

Gas Hydrate Occurrences
-Macroscopic Scale-

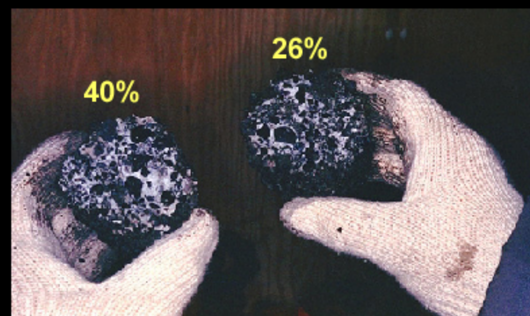


Mallik 2L-38 Science Program

Field Observations of Gas Hydrates Granular Sands and Gravel - 897-952m

Gas hydrate forms

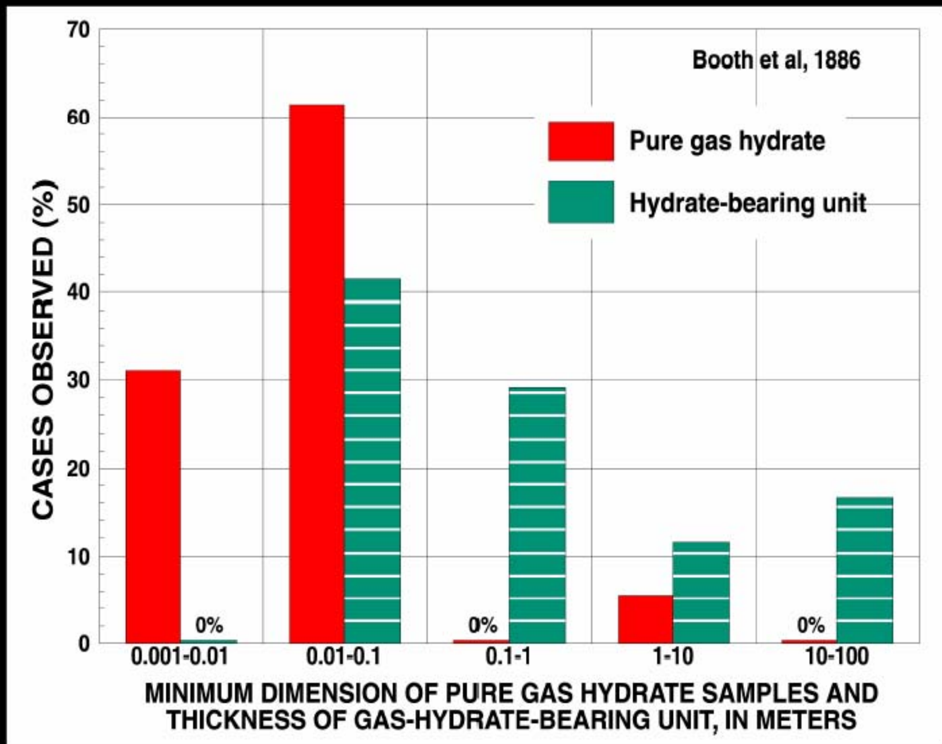
- pore space within granular sands
- intergranular fill forming matrix
- particle coatings
- nodules/clasts (<2cm)



Mallik 2L-38 Science Program

Field Observations of Gas Hydrates Sands - 897-952m

- pore space hydrate
- hydrate coating sand grains (<2mm)
- vein hydrate (<2mm)
- nodule/clast hydrate (<5mm)
- porosity 30-40%



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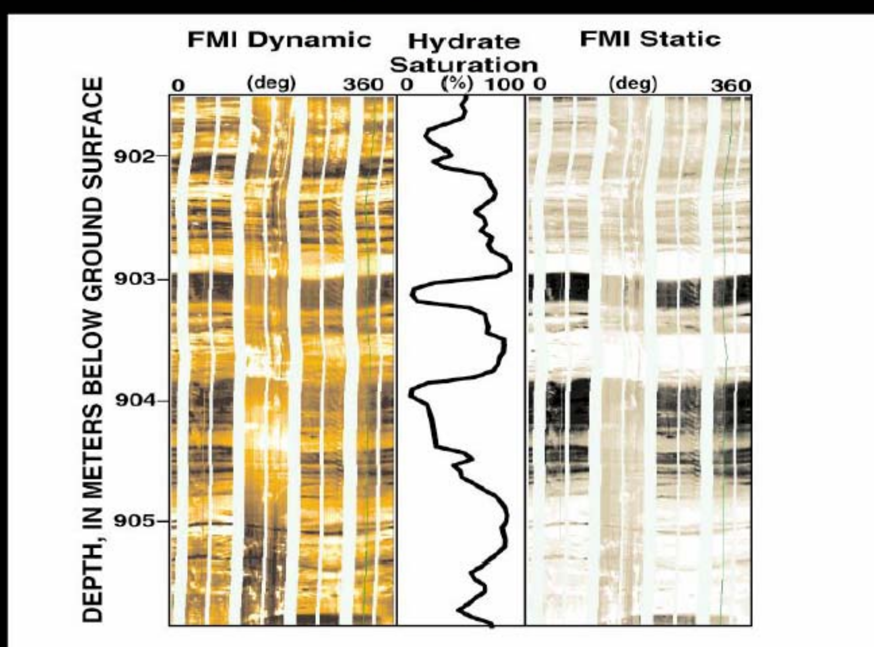
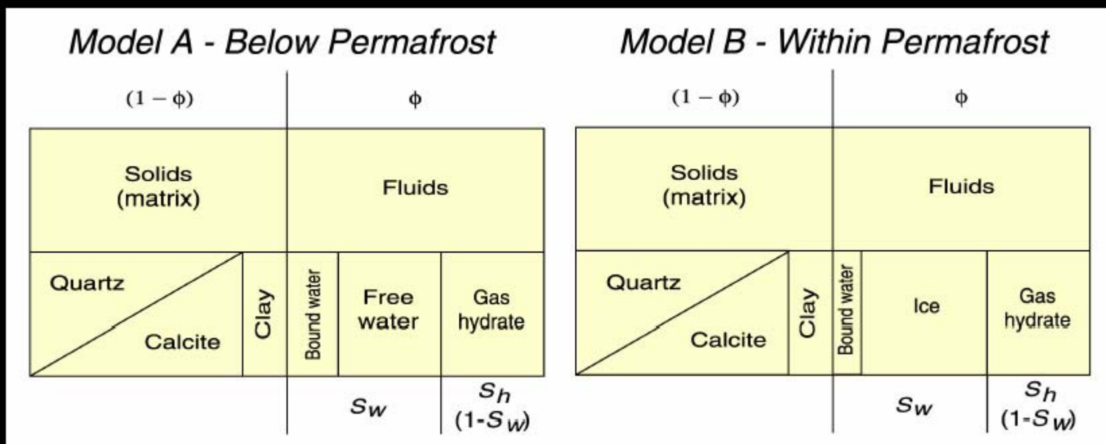
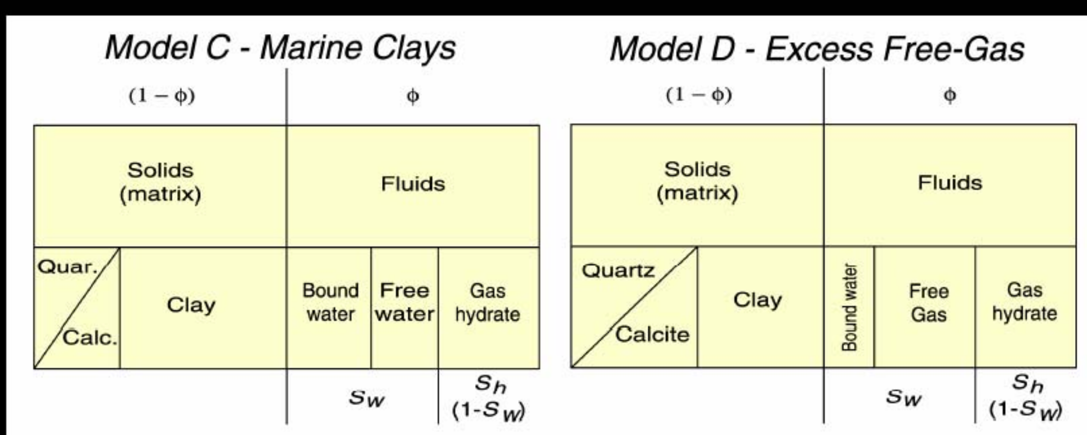
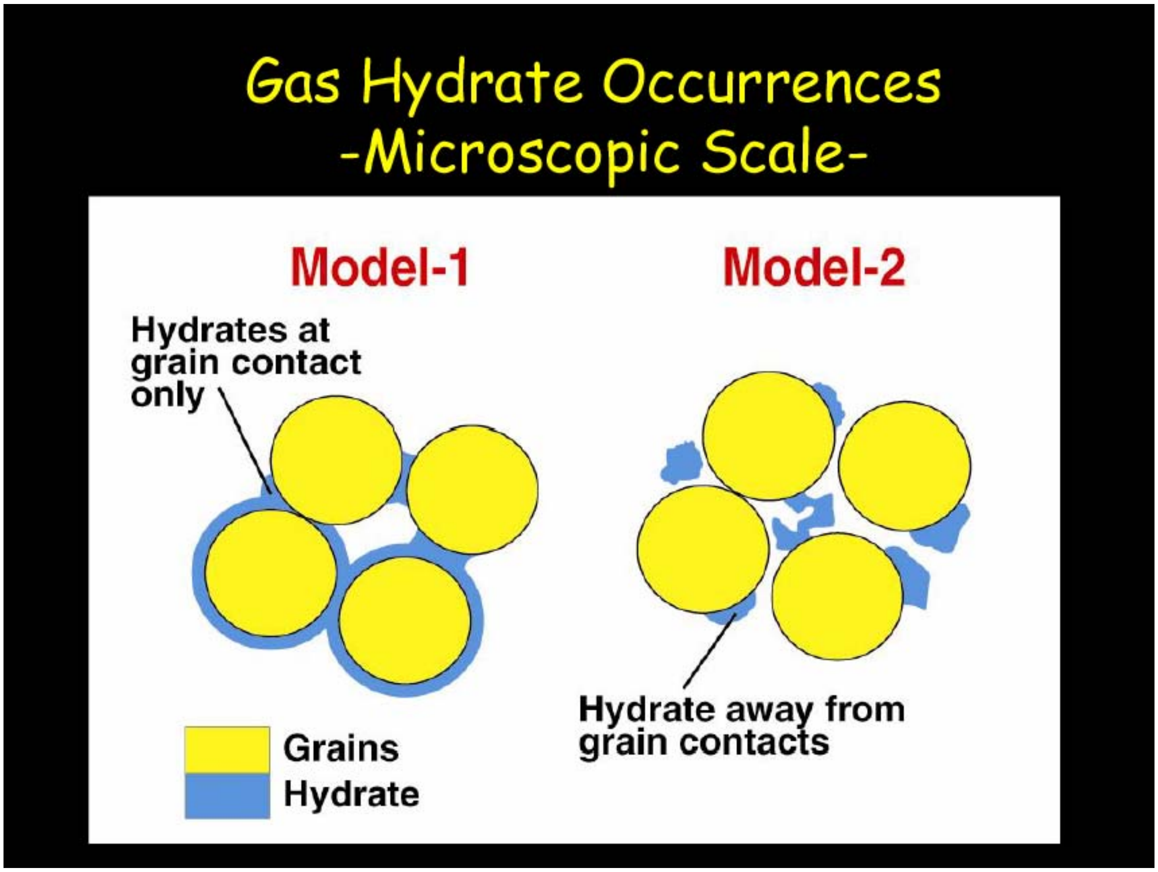


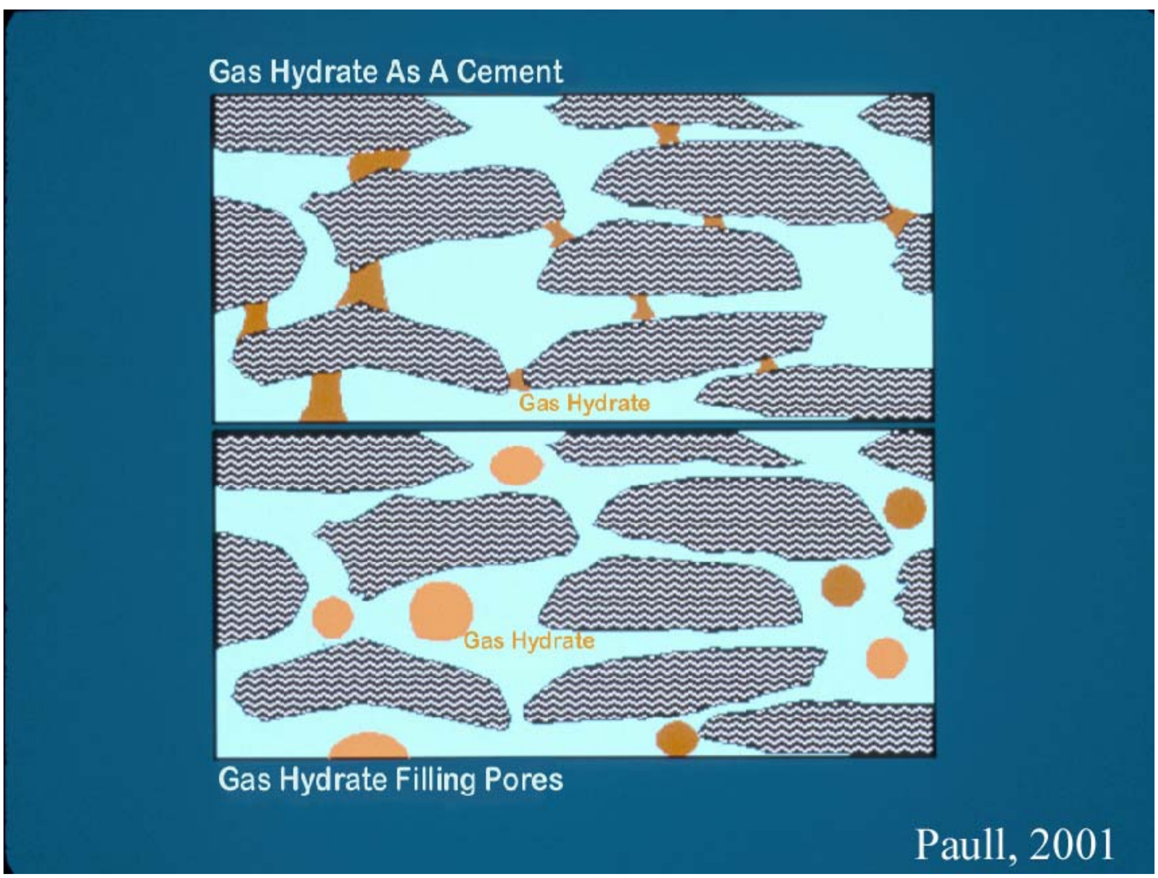
Gas Hydrate Reservoir Models



Gas Hydrate Reservoir Models




Gas Hydrate Occurrences
-Microscopic Scale-
Model-1
Model-2
Hydrates at
grain contact
only
Hydrate away from
grain contacts
Grains
Hydrate


Gas Hydrate As A Cement
Gas Hydrate
Gas Hydrate
Gas Hydrate Filling Pores
Paull, 2001

Outline of Presentation

- Gas Hydrate Reservoir Models
- Quantitative Well-Log Analysis of in-situ Gas Hydrates
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GAS HYDRATE ASSESSMENT TECHNOLOGIES

1. Hydrate stability
   Pressure (MDT, other downhole tools)
   Temperature (DAVIS, Villinger, downhole logs)
   Gas chemistry (cores, downhole spectroscopy)
   Water chemistry (cores, downhole spectroscopy)

2. Hydrate occurrence/concentration/amount
   Core monitoring (TPC)
   Core characterization
   - Simple X-ray
   - CT scan
   - NMR imaging

   Core analysis
   - Core temperatures (IR & direct measurement methods)
   - Water content (Cl, ions/cations)
   - Water chemistry (oxygen isotopes, etc.)
   - Gas chemistry (compositional/isotopic fractionation)
   - Gas content (volume)
   - Microbiologic analysis (population, ID, activity)

GAS HYDRATE ASSESSMENT TECHNOLOGIES

2. Hydrate occurrence/concentration/amount - Continued

Downhole logs (wireline and LWD)

- Neutron/Density porosity
- Electrical resistivity
- Acoustic velocity (Vp and Vs)
- Neutron spectroscopy (C/O)
- NMR (in-situ, laboratory)
- Raman spectroscopy (research)
- VSP
- Tomography

Downhole Tools

- Physical/Geothechnical properties
- Water/gas sampling tools (MDT, RFT)
- Pore-water pressure analysis (MDT, RFT)

Geophysics

- Seismic (low/high frequency, 2D-3D)
- Side-scan
- Electromagnetic surveys
- OBS
- Seafloor compliance

GAS HYDRATE ASSESSMENT TECHNOLOGIES

3. Hydrate dynamics

CORKs

Repeat surveys – time series

Gas Hydrate Well Log Evaluation

Well log	Application	Measurement
Density	Porosity	Electron density
Neutron Porosity	Porosity	Hydrogen content
Electrical Resistivity	Saturation/text.	Resistivity
Acoustic Velocity	Saturation/text.	Acoustic transit-time
Neutron Spect.	Saturation	C/O
NMR	Saturation/text.	Atomic interactions

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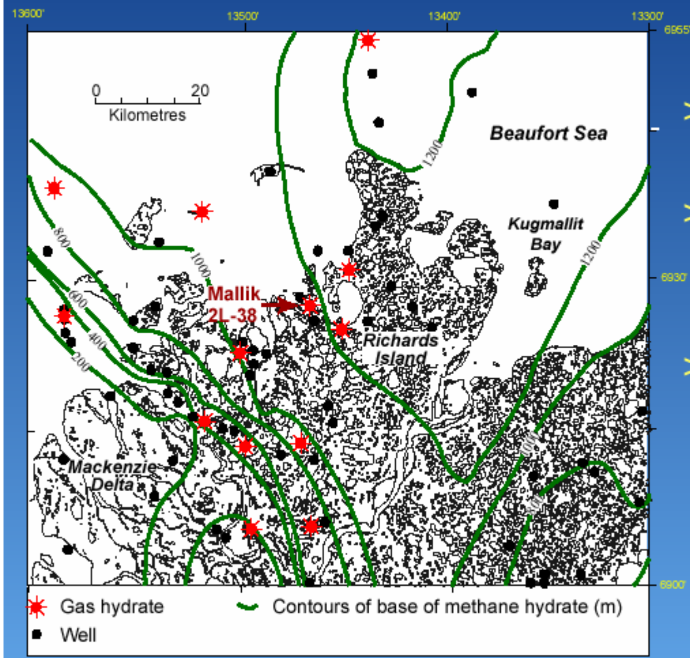
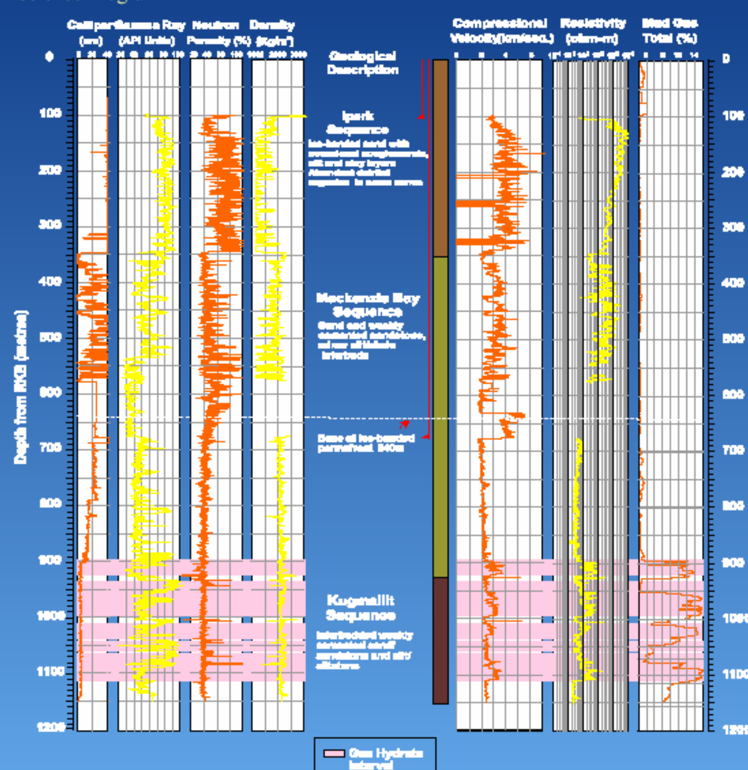
Gas Hydrates in the Mackenzie Delta

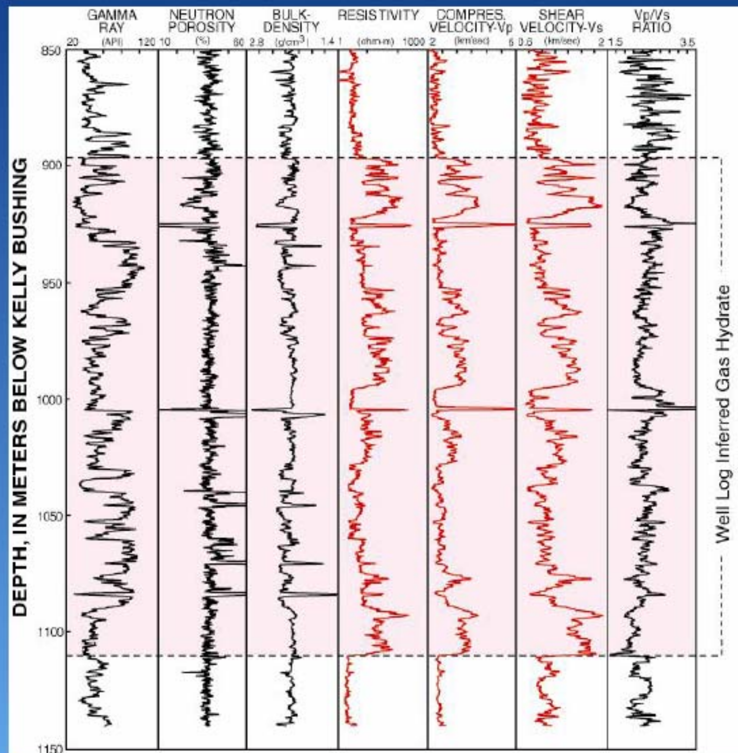


- >600m permafrost
- >1200m to base of methane hydrate stability field
- >20% of onshore wells drilled in 70's and 80's encountered hydrates

Mallik 2L-38 Science Program

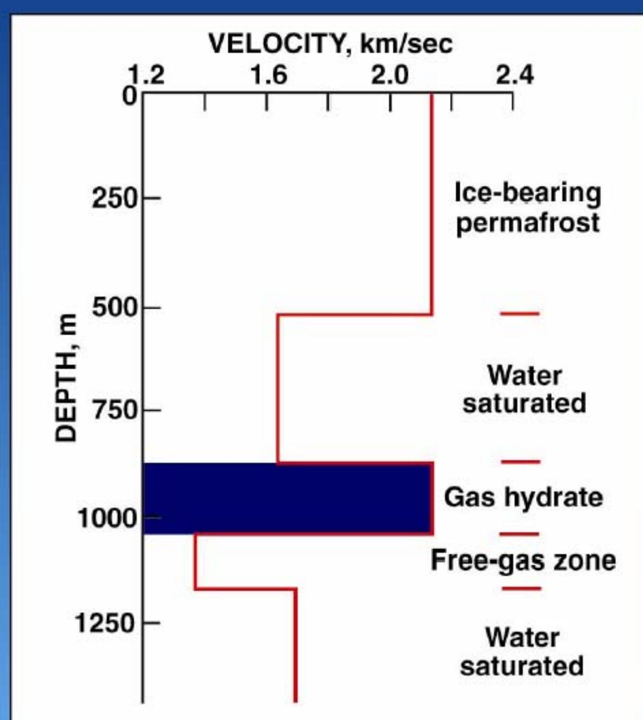


Mallik 2L-38 Science Program

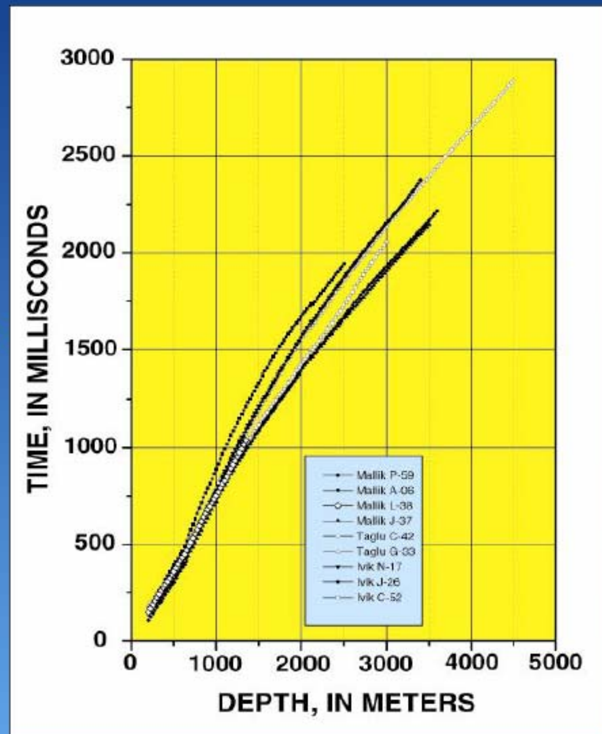


Mallik 2L-38 Science Program

- **Permafrost and Gas Hydrate Acoustic Velocity Model**

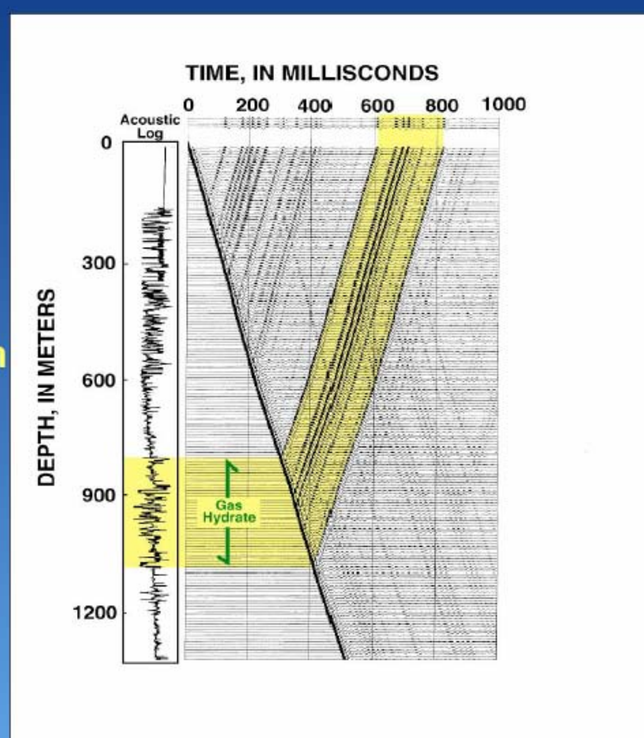


- **Well-Log Derived Time-Depth Acoustic Travel-Time Model**



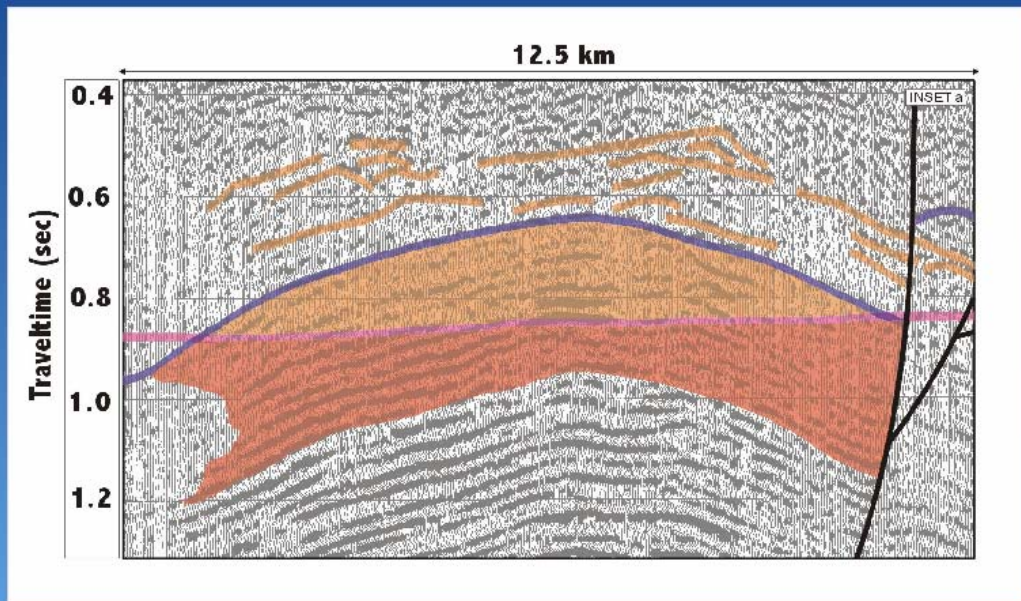
Mallik 2L-38 Science Program

- **Well-Log Derived Synthetic Seismogram**

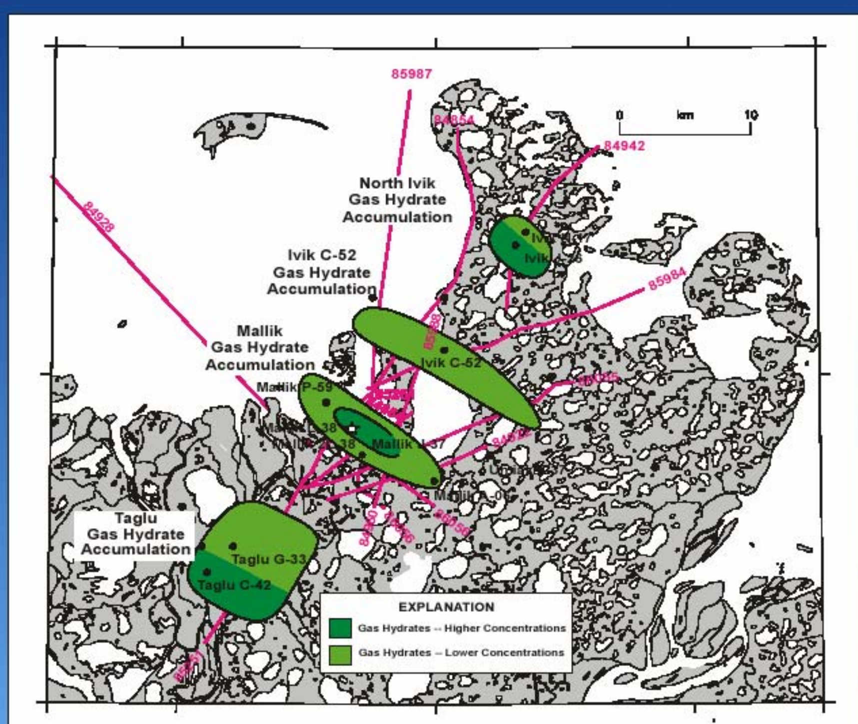


Mallik 2L-38 Science Program

Mallik Seismic Line



Mallik 2L-38 Science Program



Mallik 2L-38 Science Program

Regional Gas Hydrate Accumulations

Four structures mapped using well log and regional seismic data

	Total volume of gas
Mallik	$110{,}003 \times 10^{6}$ m^3
Ivik C-52	$42{,}928 \times 10^{6}$ m^3
North Ivik	$22{,}851 \times 10^{6}$ m^3
Taglu	$11{,}396 \times 10^{6}$ m^3

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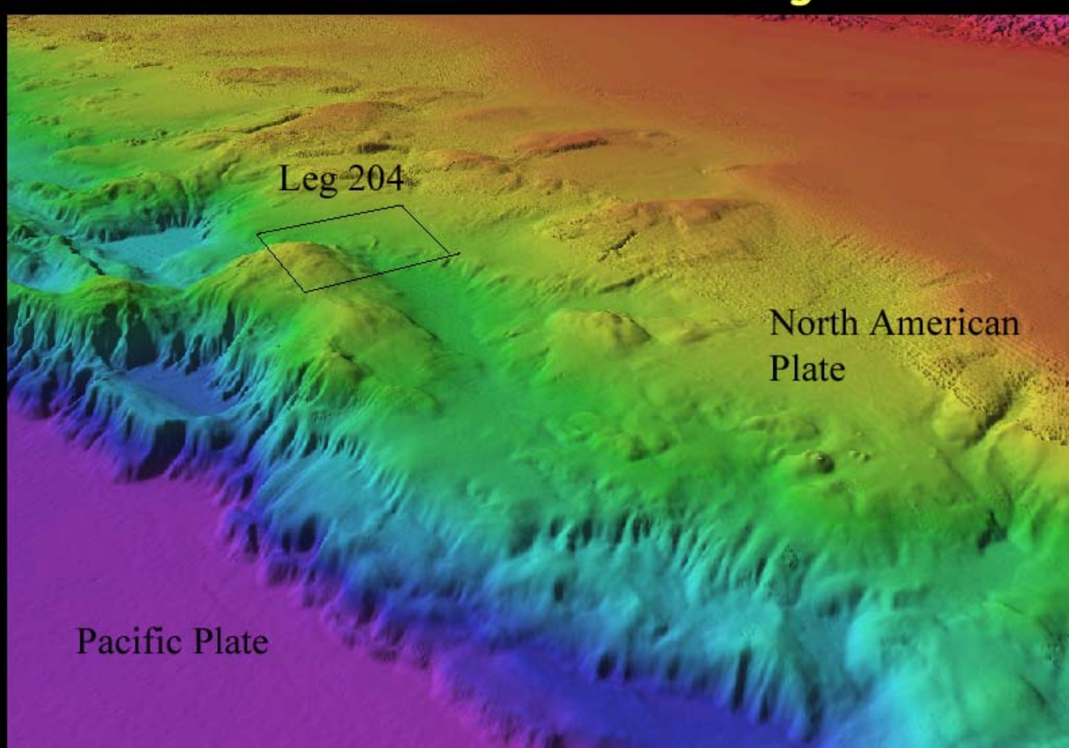
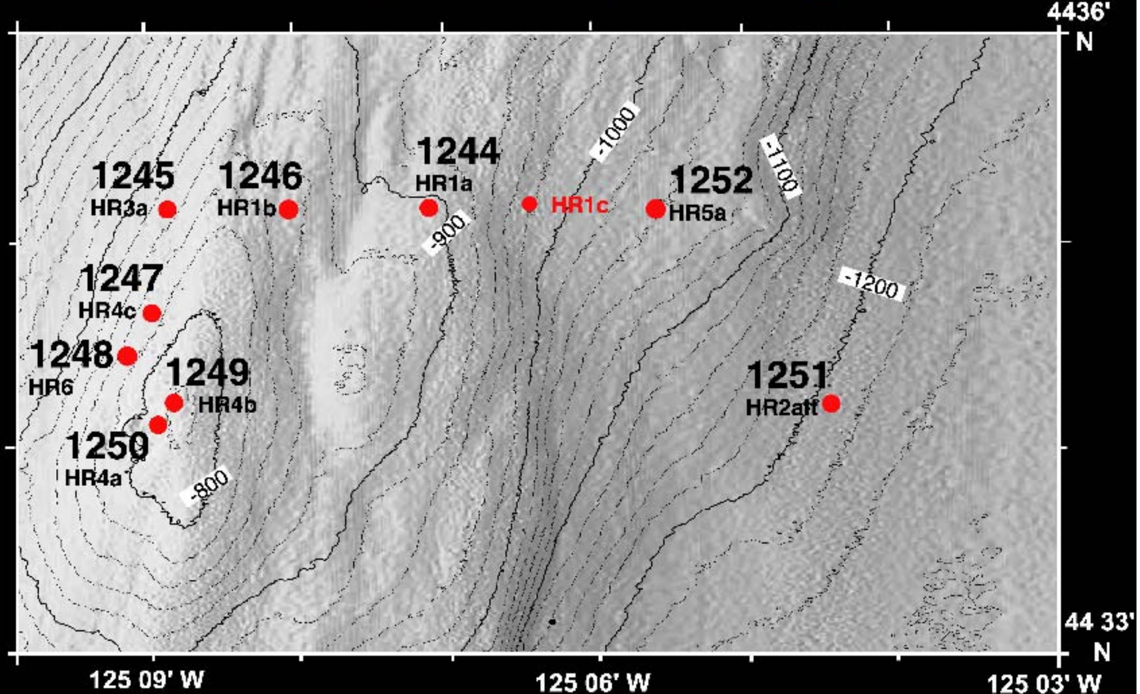
- **ODP Leg 146**

Cascadia Continental Margin

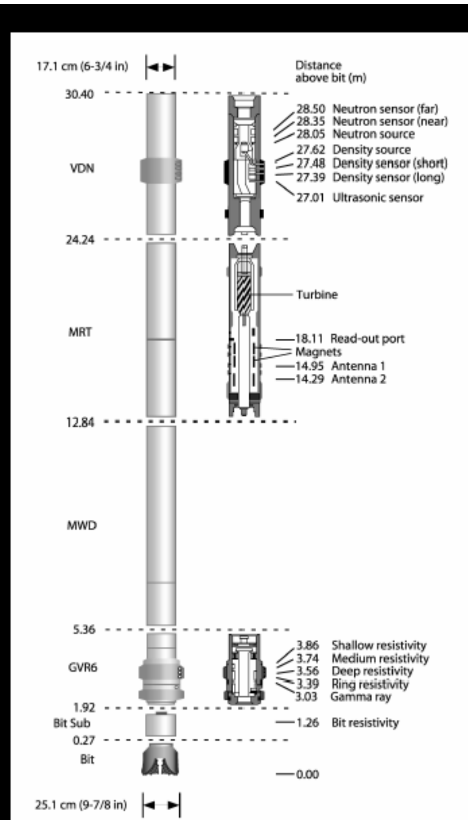


ODP Leg 204 – Hydrate Ridge



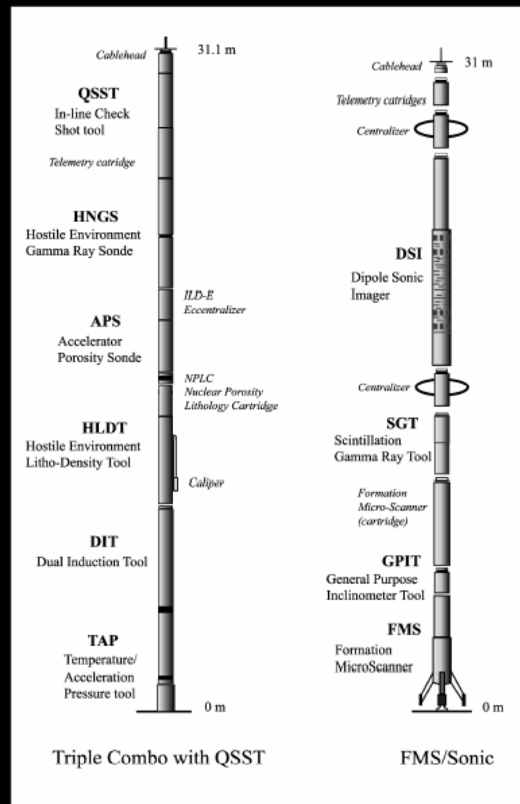
- **ODP Leg 204 – LWD tool string: VDN, MRT, GVR6, & MWD**

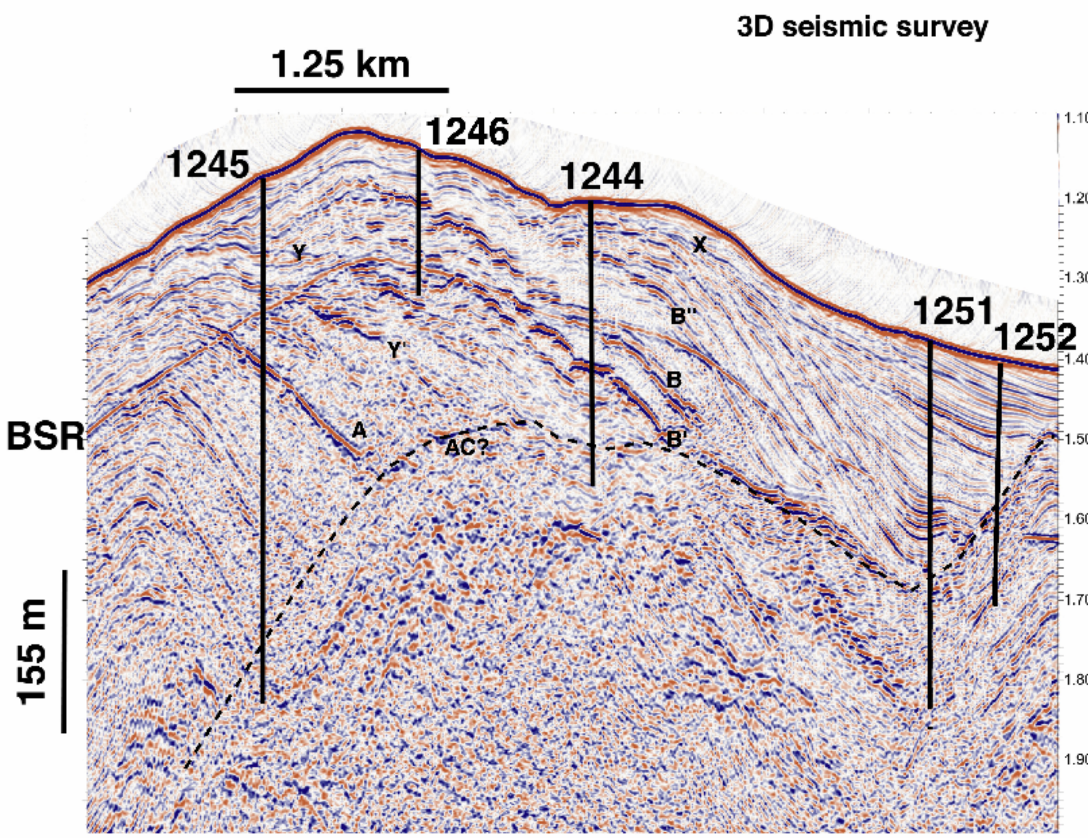
  - 8 Sites, 10 Holes

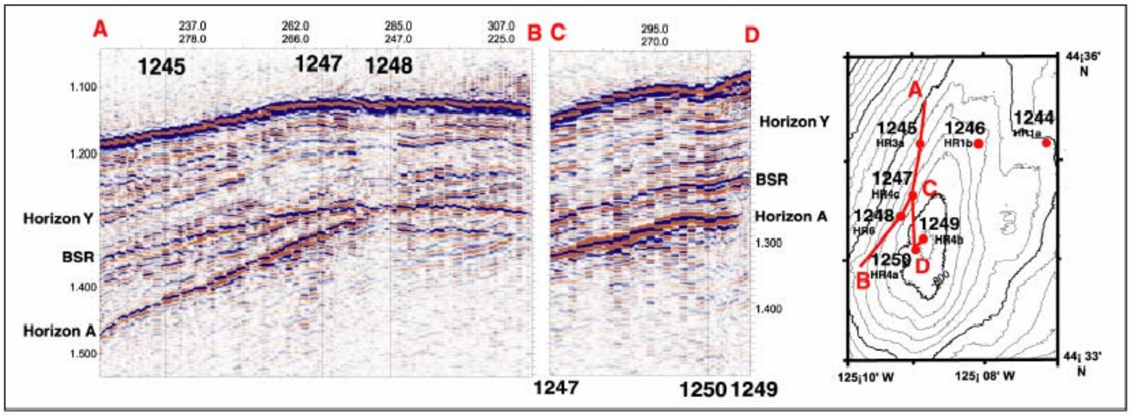


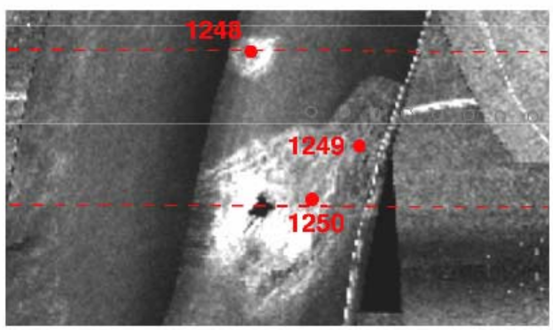
- **ODP Leg 204 – CWL tool strings: Triple Combination & FMS/Sonic**

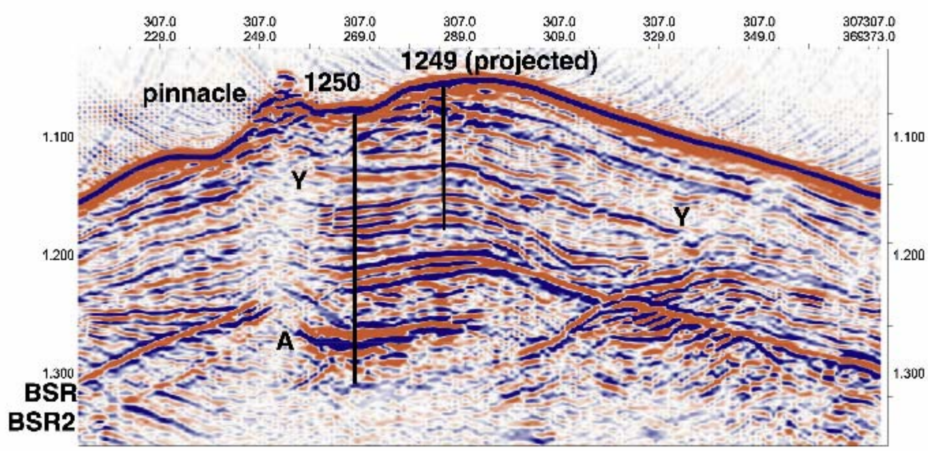
  - 6 Sites, 6 Holes



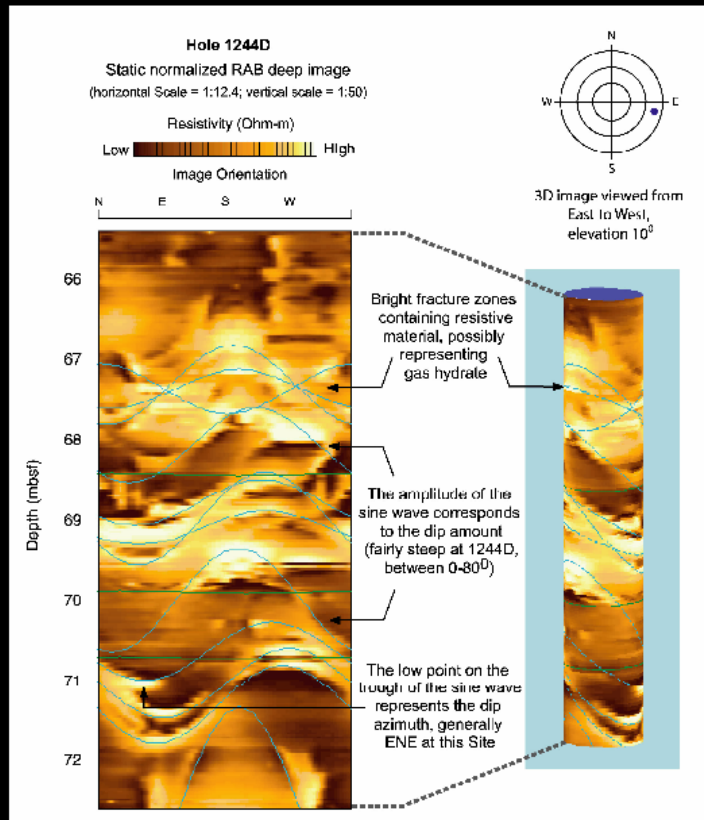



A
237.0
278.0
262.0
266.0
285.0
247.0
307.0
225.0
B
C
295.0
270.0
D
1245
1247
1248
1.100
1.200
Horizon Y
BSR
Horizon A
1.300
1.400
1.500
1247
1250
1249
44¡36'
N
1245
HR3a
1246
HR1b
1244
HR1a
1247
HR4c
1248
HR6
1249
HR4b
1250
HR4a
125¡10' W
125¡ 08' W
44¡ 33'
N

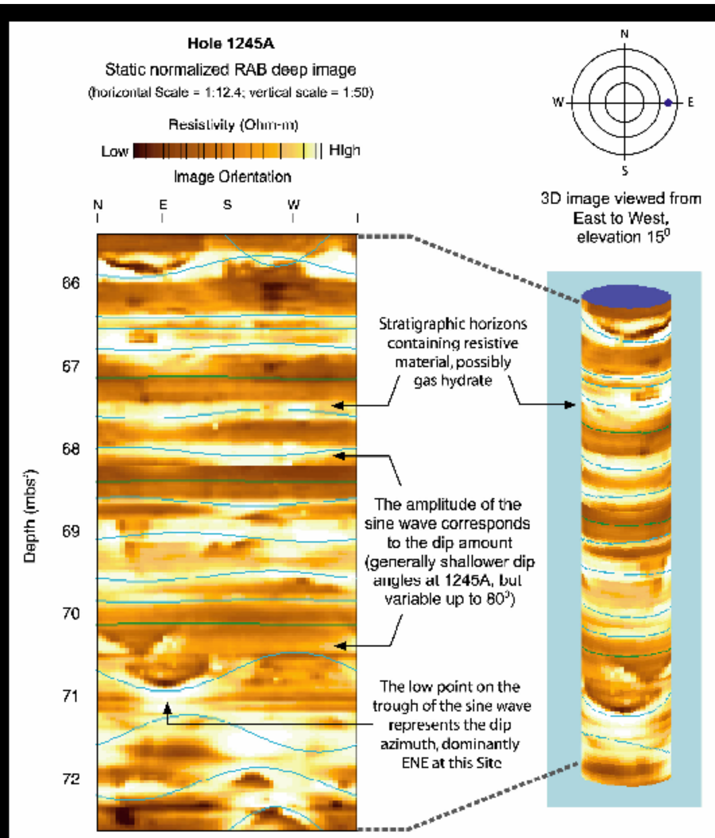

1248
1249
1250


307.0
229.0
307.0
249.0
307.0
269.0
307.0
289.0
307.0
309.0
307.0
329.0
307.0
349.0
1249 (projected)
pinnacle
1250
1.100
1.200
1.300
Y
Y
A
BSR
BSR2

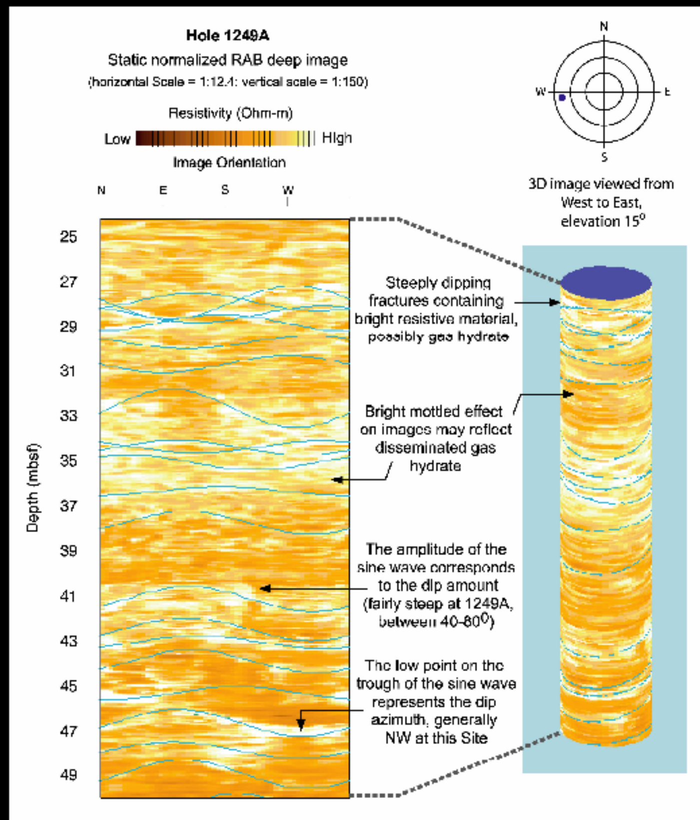
- **ODP Hole 1244D – RAB Image**



- **ODP Hole 1245A – RAB Image**



- **ODP Hole 1249A – RAB Image**



ODP Leg 204 – MRT Deployments

ODP Site	ODP Hole (mbrf)	Water Depth (mbsf)	LWD Interval	MRT sliding test
1244	1244D	906.0	0-380	YES
1245	1245A	882.0	0-380	No
1246	1246A	859.0	0-180	YES
1247	1247A	837.0	0-270	No
1248	1248A	839.0	0-194	No
1249	1249A	787.0	0-90	No
1250	1250A	806.0	0-210	No
1250	1250B	806.0	0-180	YES
1251	1251A	1216.5	0-380	No

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Gas Hydrate Well Log Evaluation

Well log	Application	Measurement
Density	Porosity	Electron density
Neutron Porosity	Porosity	Hydrogen content
Electrical Resistivity	Saturation/text.	Resistivity
Acoustic Velocity	Saturation/text.	Acoustic transit-time
Neutron Spect.	Saturation	C/O
NMR	Saturation/text.	Atomic interactions

The Second Workshop of the International Committee on Gas Hydrates 28-31 October 2002 Washington DC.

Sediment-hosted hydrates: pore morphology, geophysical characterisation, and geotechnical behaviour.

Mike Lovell[1], Peter Jackson[2], Dave Gunn[2], Chris Rochelle[2], Keith Bateman[2], Lavinia Nelder[2], Martin Culshaw[2], John Rees[2], David Long[2], Tim Francis[3], John Roberts[3], Peter Schultheiss[3]

[1]Department of Geology, University of Leicester, Leicester, LE1 7RH, UK
[2]British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK
[3]GeotekLtd., 3 Faraday Close, Daventry, NN11 5RD,UK

ABSTRACT

The ability to geophysically characterise gas hydrates remotely while stabilised in a pressurised core barrel may provide a route to detailing their physical extent and nature. Changes in the geophysical character of sediment-hosted gas hydrates during formation and dissociation processes should provide a means of improving our estimation and evaluation of natural hydrate resources.

Experiments to manufacture a range of gas hydrate morphologies in a range of sediments in the laboratory are in progress. To date we have succeeded in manufacturing both pure and sediment-hosted hydrates (Ar, THF & CO_2). Continuing experiments are developing a range of geometrical and internal structures and fabrics (from massive to disseminated) using different sediment-hosts. These generic hydrate groups provide a basis for non-invasive geophysical characterisation of hydrate morphologies. Controls on formation and dissociation of a wide range of gas hydrates have been studied visually in glass micro-models* hydrate being seen to grow mainly at the centre of pores.

Novel laboratory cells have been designed and constructed allowing both internal geophysical measurements and external geophysical logging. These measurements include P- and S-wave, and electrical resistivity measurements. One cell allows visual observation of the sediment-hosted hydrate during formation-dissociation. In parallel with these developments we are investigating fine scale monitoring of hydrate formation and dissociation at the pore scale.

Initial observations of compressional wave velocity during formation and dissociation* indicate the method has considerable potential as a monitoring tool, the velocity increasing with the presence of hydrate. Also the frequency content of the sonic pulses is diagnostic of the presence of hydrate, suggesting high frequencies are less attenuated when hydrate acts as a cement between grains.

From these results we aim to establish protocols to guide the geophysical logging of natural sediment-hydrate core maintained under pressure in lab transfer chambers on board the drillship, using the hyperbaric Geotek Core Logger. While new insight will be gained into geophysical modelling of hydrate behaviour, it will also guide the development of sampling programs, prior to depressurising and initiating dissociation. In addition, these studies will better constrain the variability and range of geotechnical properties associated with sediment hosted hydrates, in particular shear strength and S-wave velocity, both key to submarine slope stability analyses under earthquake loading.

* Observations made by Dr B Tohidi's group at HW

University of Leicester
British Geological Survey
GEO TEK

SEDIMENT-HOSTED HYDRATES:

pore morphology, geophysical characterisation, and geotechnical behaviour

SEDIMENT-HOSTED HYDRATES:

- OCEAN MARGINS LINK Project (NERC)
- Background
- Hydrate synthesis
- Sediment-hosted hydrate synthesis
- Geophysical Measurements on synthetic samples
- SEM images
- Implications for slope stability
- Current Interests

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University of Leicester

British Geological Survey

GEO TEK

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Co-funded by the Natural Environment Research Council

Ocean Margins LINK programme

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University of Leicester   British Geological Survey   GEOTEK

Background:

Physical Properties:

(inc. Geotechnical and Geophysical Properties)

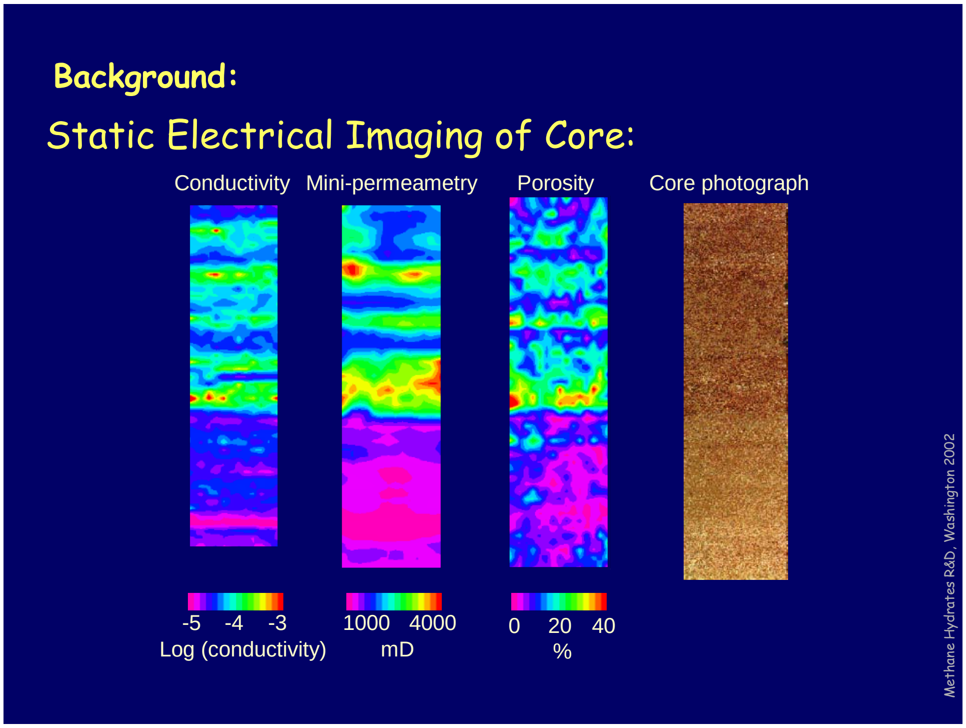
Laboratory Measurements

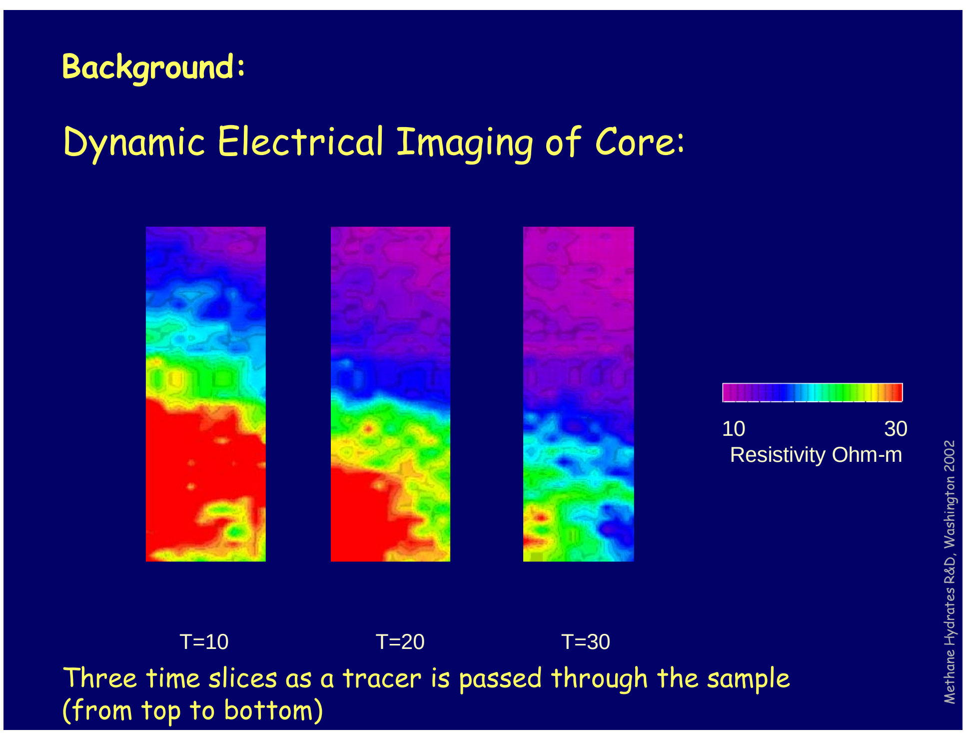
Borehole Logs – Core Logging

Geophysical and Geotechnical Field Measurements

Chemical Properties & Behaviour:

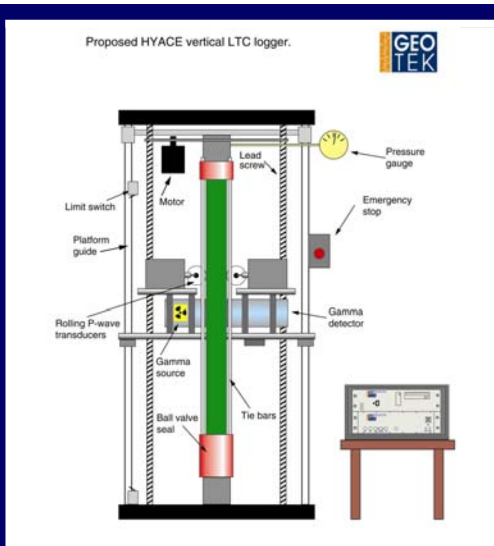
CO_2 sequestration and hydrothermal work

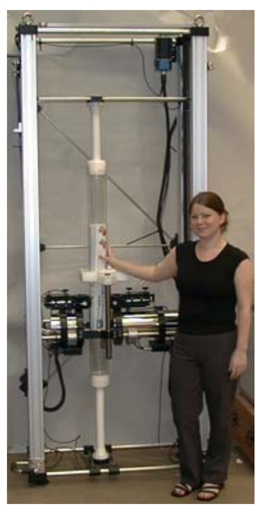

Background:
Static Electrical Imaging of Core:
Conductivity
Mini-permeametry
Porosity
Core photograph
-5 -4 -3
Log (conductivity)
1000 4000
mD
0 20 40
%
Methane Hydrates R&D, Washington 2002


Background:
Dynamic Electrical Imaging of Core:
10 30
Resistivity Ohm-m
T=10
T=20
T=30
Three time slices as a tracer is passed through the sample
(from top to bottom)
Methane Hydrates R&D, Washington 2002

Background:

Acoustic measurements:
shear wave transducers





Background:
HYACE/HYACINTH coring & laboratory characterisation

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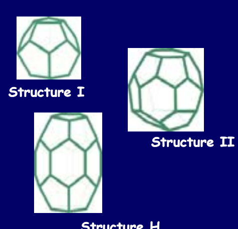
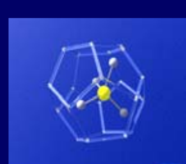
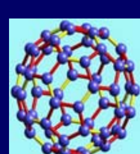
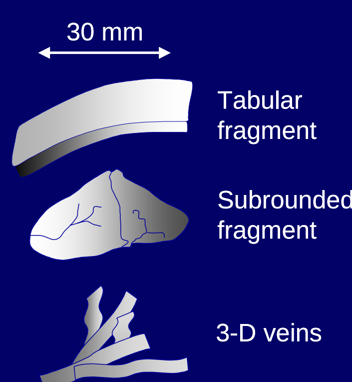
chemical & physical properties

Pure gas hydrate ⟷ **Sediment-hosted gas hydrate**

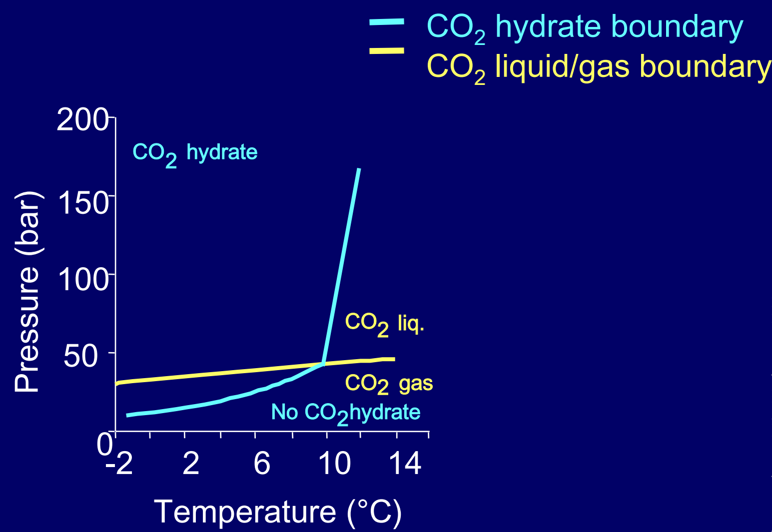








chemical & physical properties



Methane Hydrates R&D, Washington 2002

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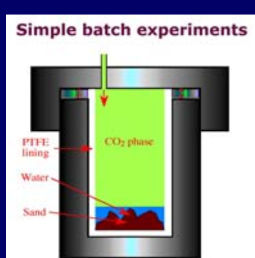
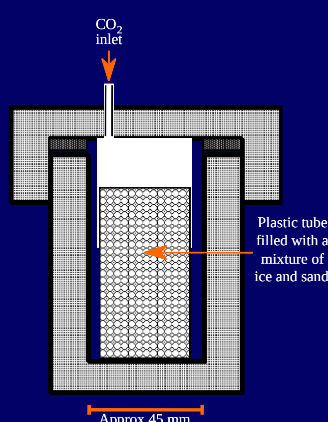
Methane Hydrates R&D, Washington 2002

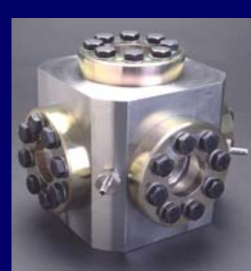
coring & laboratory characterisation

Methane Hydrates R&D, Washington 2002

coring & laboratory characterisation







Methane Hydrates R&D, Washington 2002

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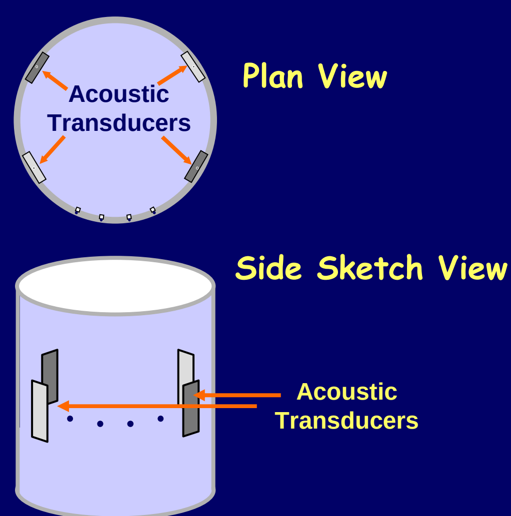
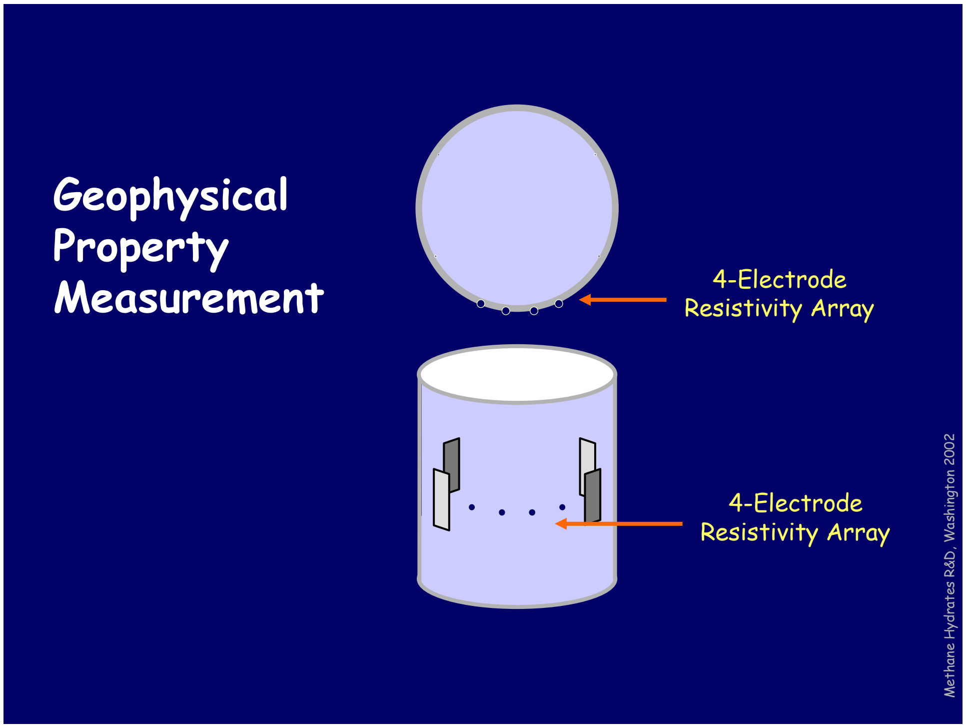
Geophysical Property Measurement




Geophysical Property Measurement
4-Electrode Resistivity Array
4-Electrode Resistivity Array
Methane Hydrates R&D, Washington 2002


CO_2 hydrate cementation in sand
cm 1 2 3 4 5 6 7 8 9 10
TENTHS 1 2 3 4
Methane Hydrates R&D, Washington 2002

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SEM Images

- 3 experiments to date:

  – CO_2 hydrate from de-ionized water in 2 'batch' experiments

  – THF hydrate at ambient P, low T

- Aims to improve understanding of hydrate formation-dissociation and pore morphology considerations for synthetic sediment-hosted hydrates

Methane Hydrates R&D, Washington 2002

SEM details

- Variable pressure SEM, with a cryogenic sample handling and cold stage facility.
- Backscatter mode enhances hydrate/ice/sediment contrast.
- Observed CO_2 hydrate and THF hydrate
- Details enhanced by 'developing' the sample using etching (destabilizing hydrate by warming).
- Time-lapse imaging of hydrate destabilization.

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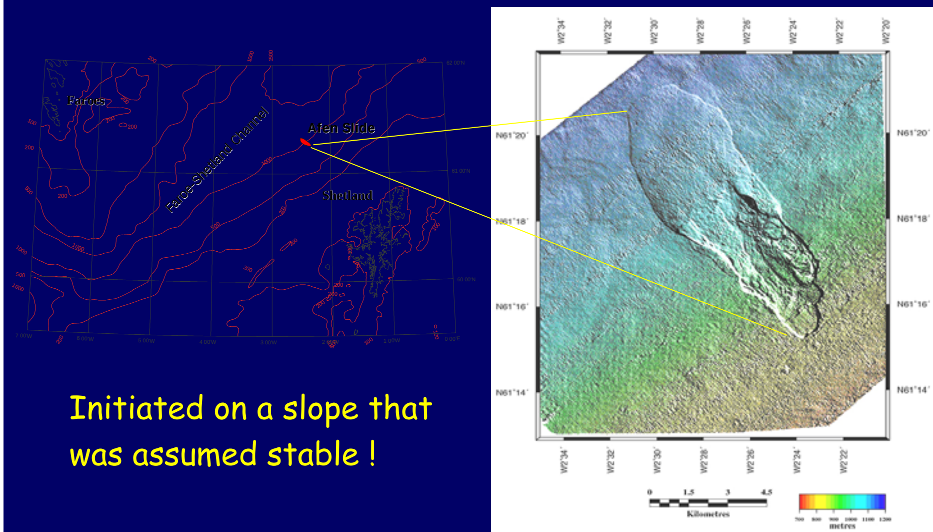
Methane Hydrates R&D, Washington 2002

Ground Models for Slope Instability

Are Slopes Stable ? - The Afen Landslide

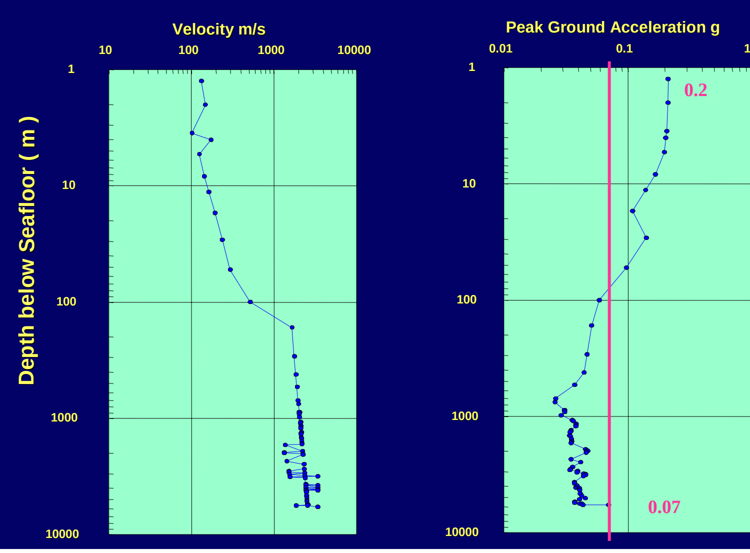


Initiated on a slope that was assumed stable !

Methane Hydrates R&D, Washington 2002

Ground Models for Slope Instability

Ground Motion Amplification



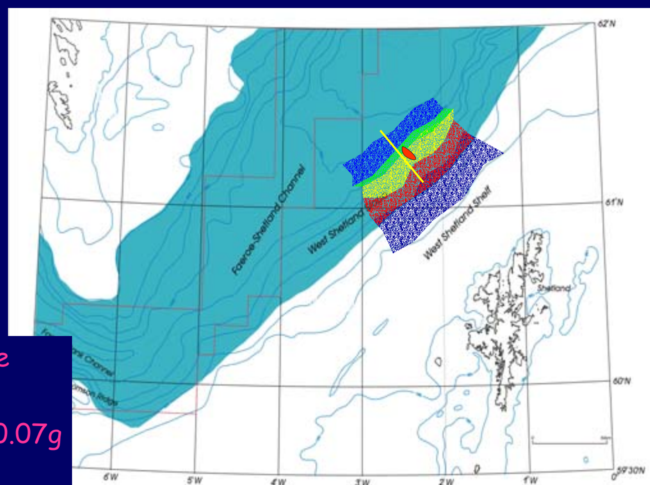
Methane Hydrates R&D, Washington 2002

Ground Models for Slope Instability

Slope Instability Susceptibility Maps

- but how does hydrate dissociation affect these analyses?

Scheme for a Simple Instability Susceptibility Map



10, 000 Yr Earthquake

Ground Acceleration 0.07g

SEDIMENT-HOSTED HYDRATES:

- OCEAN MARGINS LINK Project (NERC)
- Background
- Hydrate synthesis
- Sediment-hosted hydrate synthesis
- Geophysical Measurements on synthetic samples
- SEM images
- Implications for slope stability
- Current Interests

Current Interests:
Sediment-Hosted Hydrate Properties

- Dissociation Processes
  - Geophysical - Geotechnical Character
  - Pressure - Temperature Cycling
  - Salinity - Cohesion Relationship
- 'Natural' synthetic samples
  - Grain-pore properties
  - Hydrate distribution
- Geotechnical – Geophysical Models
  - Pore Pressure - Effective Stress Effects
  - Dissociation By-Products
  - Chemistry (Gas and Liquid)
  - Fabric Disruption

Acknowledgements:

- Natural Environment Research Council
  - Ocean Margins LINK programme
  - industry supported
- HYACE/HYACINTH partners
  - (EU Framework 5 programme)

University of Leicester

British Geological Survey

GEO TEK

High Resolution Seismic Studies of the Distribution of Gas Hydrates

Warren T. Wood
Naval Research Laboratory

ABSTRACT

Recent association of gas hydrate accumulations with sites of seafloor porewater seepage suggests that seeps may be responsible for a significant fraction of the global transfer of methane (and its associated carbon) from the seafloor to the ocean-atmosphere system. Many of these fluid flux conduits exist in deep water and extend laterally on a scale of meters to tens or hundreds of meters. Although features of this size and distance from the sea surface can frequently be detected in by surface towed seismic systems, deep-towed, high frequency systems offer significantly improved resolution. The seismic data presented here were acquired using DTAGS (Deep-Towed Acoustics Geophysics System) over areas known to contain gas hydrate. Although gas hydrate distribution is extremely difficult to quantify through seismic data alone, the high resolution images allow detailed examination of faults, diapirs, and anomalous amplitudes created by gas, gas hydrate or carbonate mineralization. Modeling the extents of the anomalies helps constrain the fluid and heat flux needed to determine gas hydrate distribution. In the summer, and again in the fall of 2002, additional DTAGS data were acquired in gas hydrate provinces, and co-located with piston cores so that the physical constraints of DTAGS and the chemical constraints acquired via coring could be applied to precisely the same conduits. The DTAGS data from 2002 were acquired with a new system with a broader frequency range than the old system, yielding even higher resolution images.

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Recent association of gas hydrate accumulations with sites of seafloor porewater seepage suggests that seeps may be responsible for a significant fraction of the global transfer of methane (and its associated carbon) from the seafloor to the ocean-atmosphere system. Many of these fluid flux conduits exist in deep water and extend laterally on a scale of meters to tens or hundreds of meters. Although features of this size and distance from the sea surface can frequently be detected in by surface towed seismic systems, deep-towed, high frequency systems offer significantly improved resolution. The seismic data presented here were acquired using DTAGS (Deep-Towed Acoustics Geophysics System) over areas known to contain gas hydrate. Although gas hydrate distribution is extremely difficult to quantify through seismic data alone, the high resolution images allow detailed examination of faults, diapirs, and anomalous amplitudes created by gas, gas hydrate or carbonate mineralization. Modeling the extents of the anomalies helps constrain the fluid and heat flux needed to determine gas hydrate distribution. In the summer, and again in the fall of 2002, additional DTAGS data were acquired in gas hydrate provinces, and co-located with piston cores so that the physical constraints of DTAGS and the chemical constraints acquired via coring could be applied to precisely the same conduits. The DTAGS data from 2002 were acquired with a new system with a broader frequency range than the old system, yielding even higher resolution images.

High Resolution Seismic Studies of the Distribution of Gas Hydrates

Warren T. Wood

Naval Research Laboratory, Stennis Space Center, MS

High Resolution:
Deep-Tow 220-820 Hz

Distribution of Gas Hydrates:
10s to 100s of meters

Deep Towed Acoustic/Geophysics System (DTAGS)

A. Helmholz Resonator

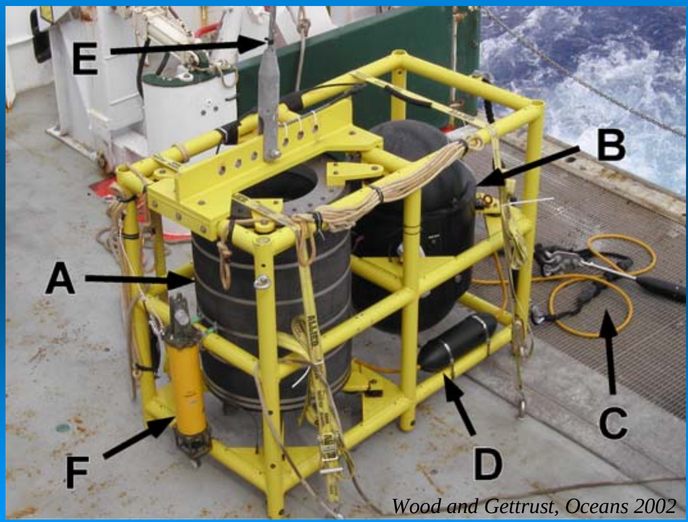
B. Electronics Egg

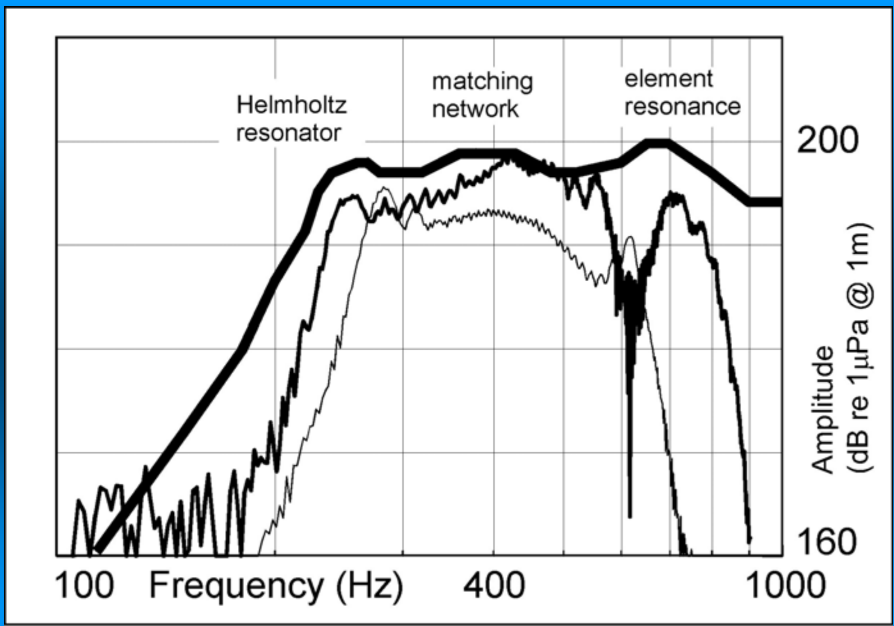
C. 48 Channel array

D. Orientation node

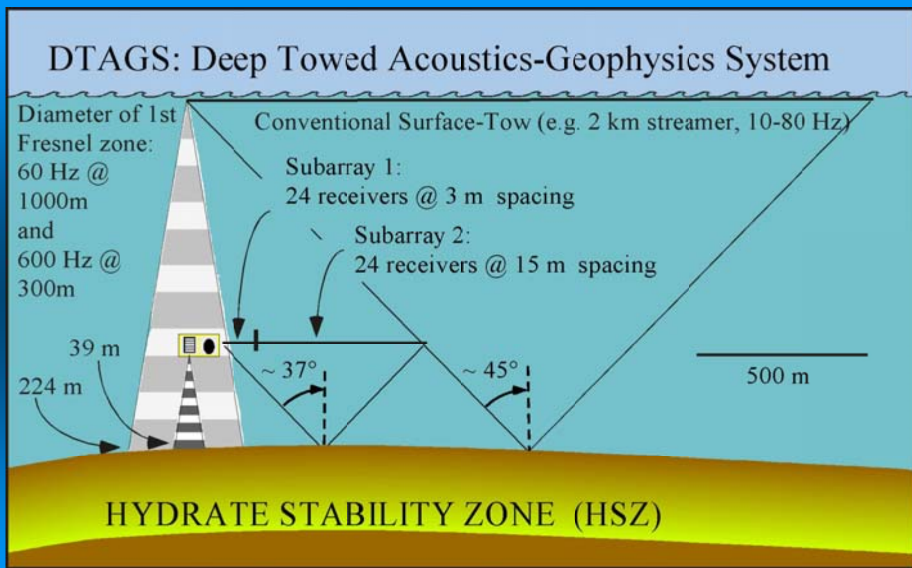
E. Coaxial tow cable

F. Navigation Transponder

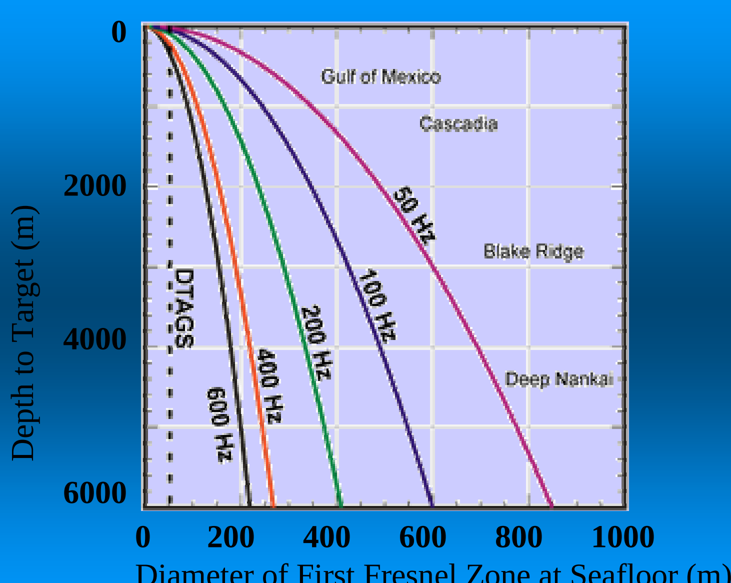




Deep-Tow and Surface-Tow

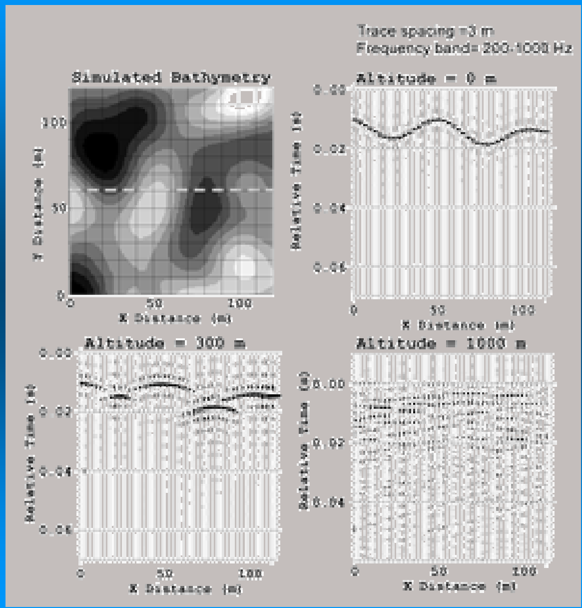


Lateral Resolution

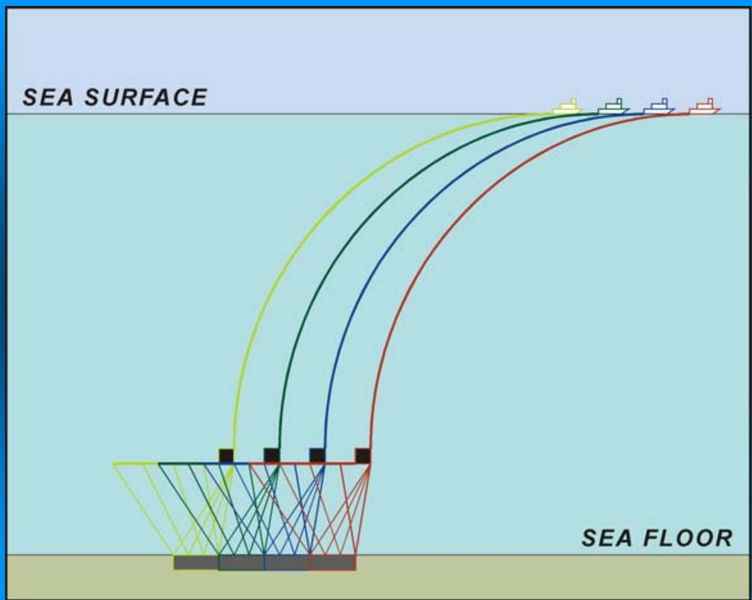


Deep-Tow and Surface-Tow

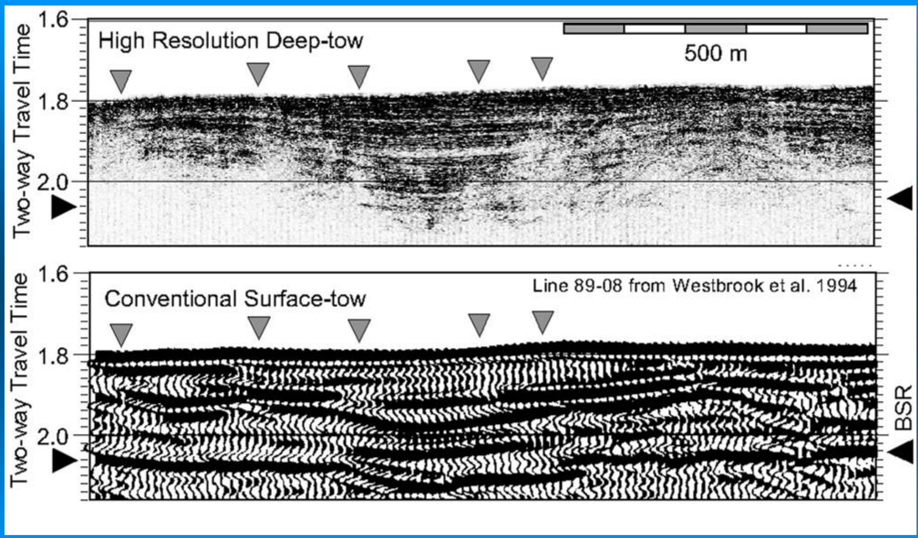
Altitude Sensitivity



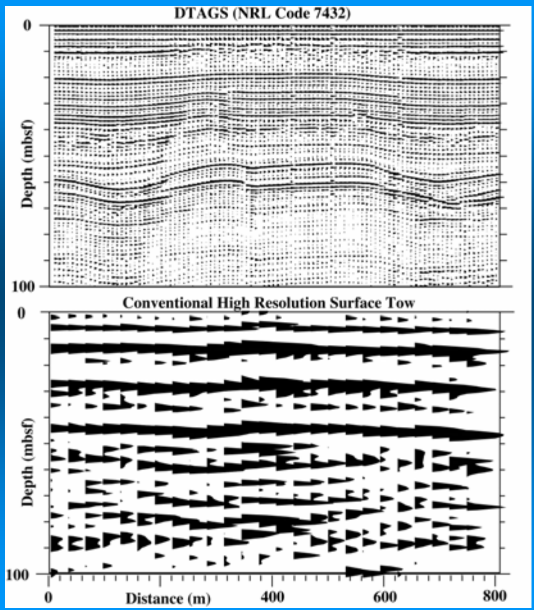
Footprint Processing



DTAGS and Surface Tow



DTAGS & Surface-Tow



High Resolution:
Deep-Tow 220-820 Hz

Distribution of Gas Hydrates:
10s to 100s of meters

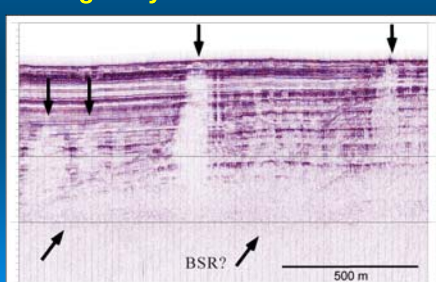
Scientific Background - Seeps

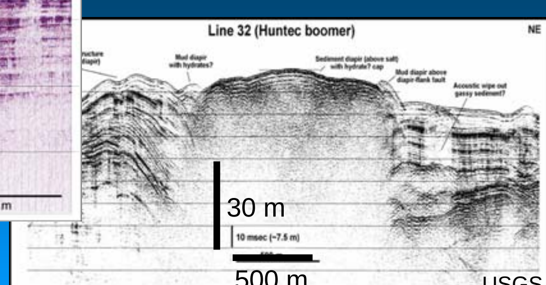
Flux can be many orders of magnitude greater than surrounding sediment

Natural concentration mechanisms for minerals and gas hydrates.

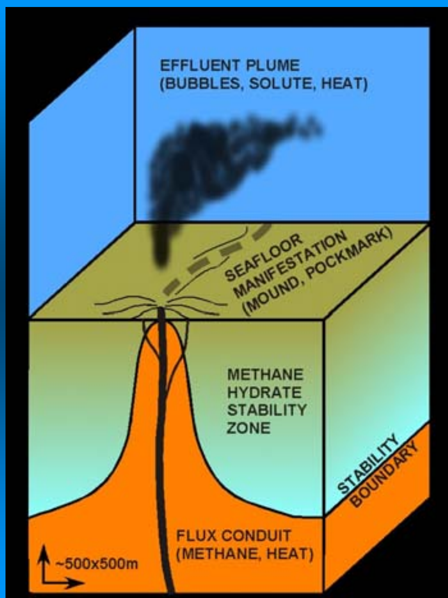
Acoustic anomalies contribute to clutter in littoral approaches.

Global flux of methane may take place predominantly through seeps.





Gas Hydrate Habitat - Seeps



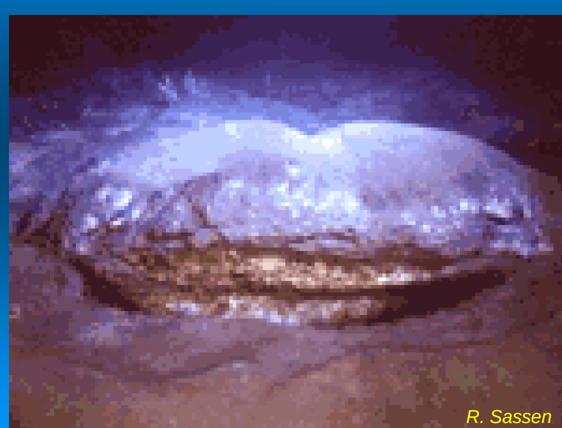
- Overpressured pore fluids
- Heat and methane, other hydrocarbons
- Manifestations: pockmarks, mounds, oil slicks

Specific Issues

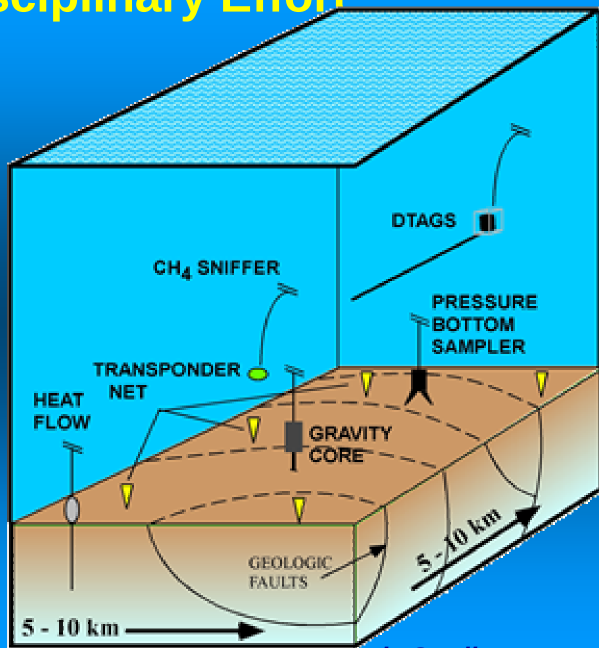
1) Concentration fall off away from seep

2) Correlation of faults flux and gas hydrates

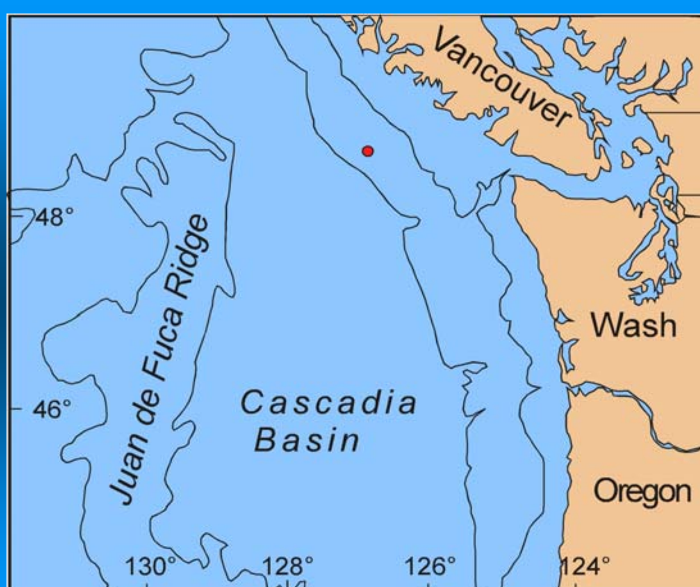
3) For Gas Hydrates; trade off between heat and methane flux



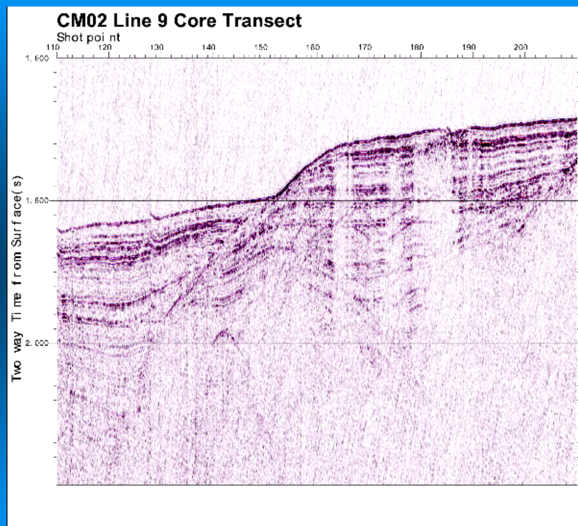
Multidisciplinary Effort



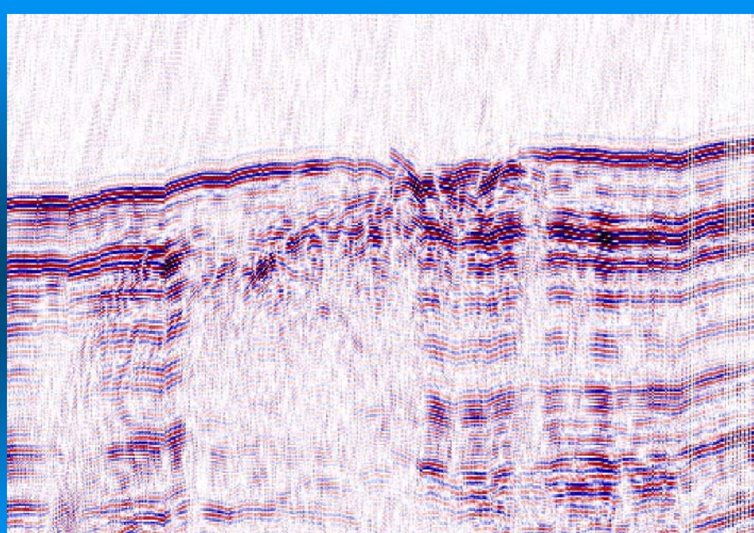
Cascadia Margin

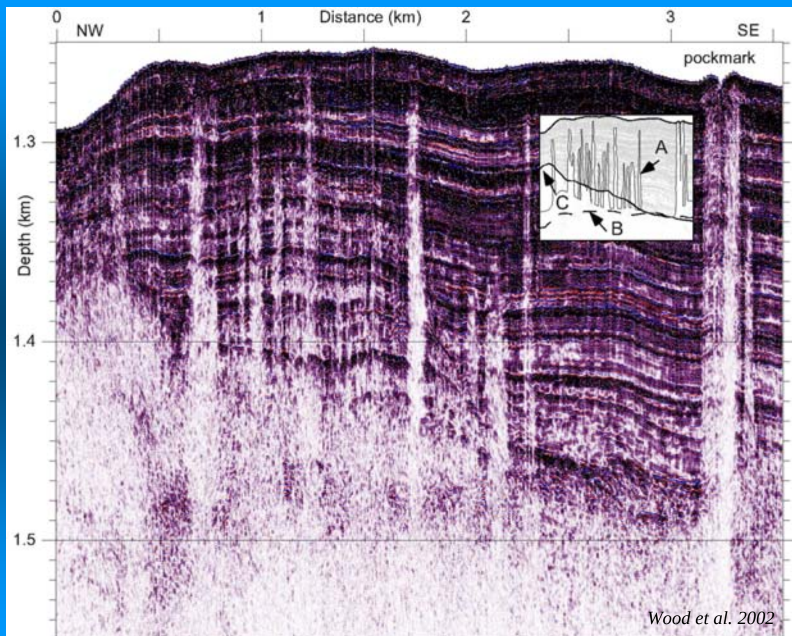


Bullseye Vent Core Transect



Bullseye Blowup

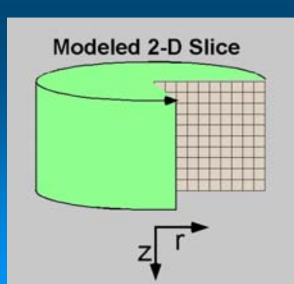


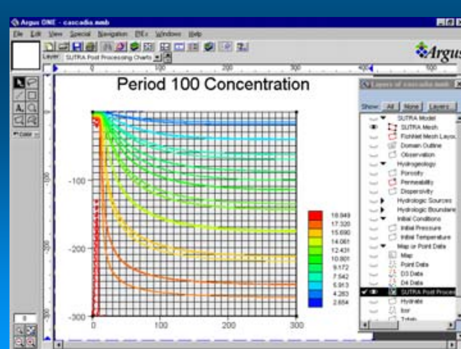


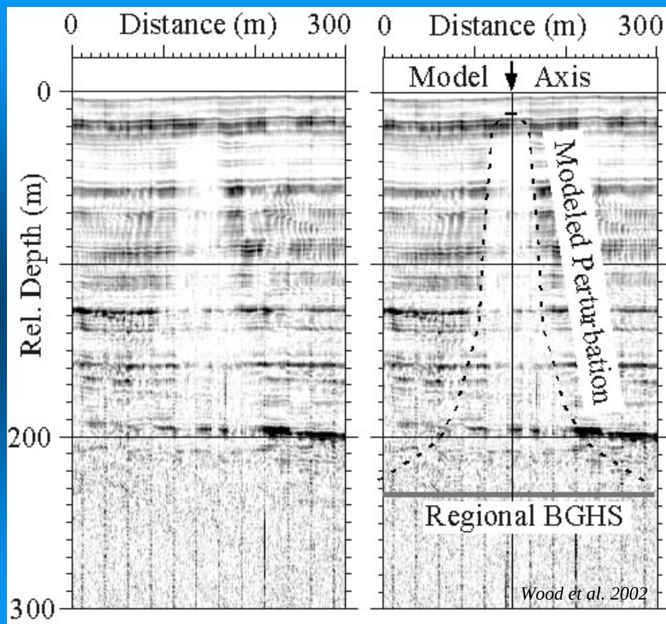
Computer Simulation

Finite Element – SUTRA (Lead: Wood 7400)

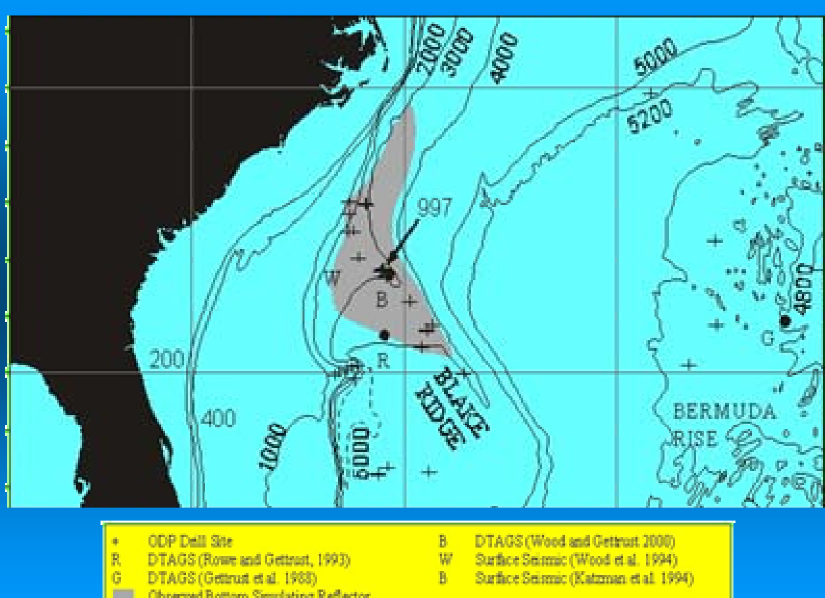
- **Advantages:** well established industry standard, relatively easy to use
- **Disadvantages:** Single non-reactive constituent only; each quantity (e.g. heat, methane, etc.) must be modeled separately

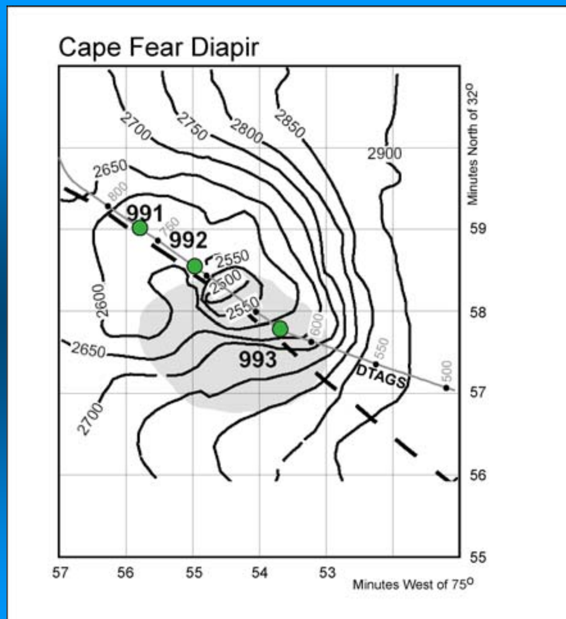




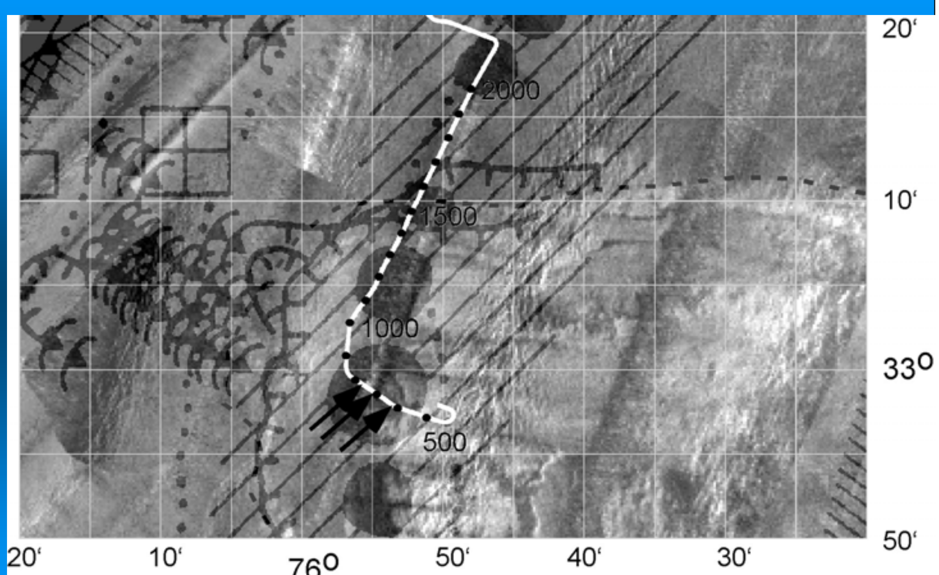

0
Distance (m)
300
0
Distance (m)
300
Model
Axis
0
Rel. Depth (m)
200
300
Modeled Perturbation
Regional BGHS
Wood et al. 2002

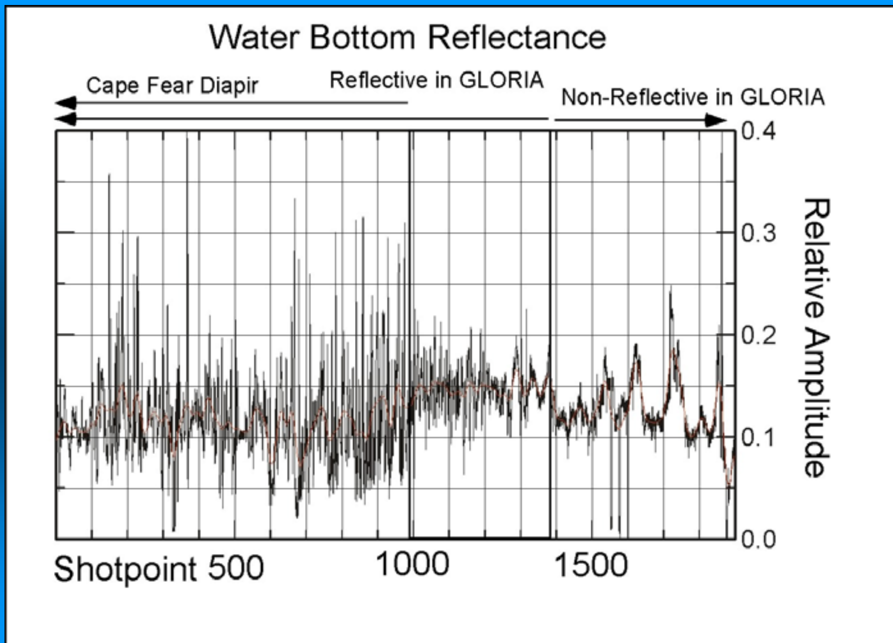
Blake Ridge

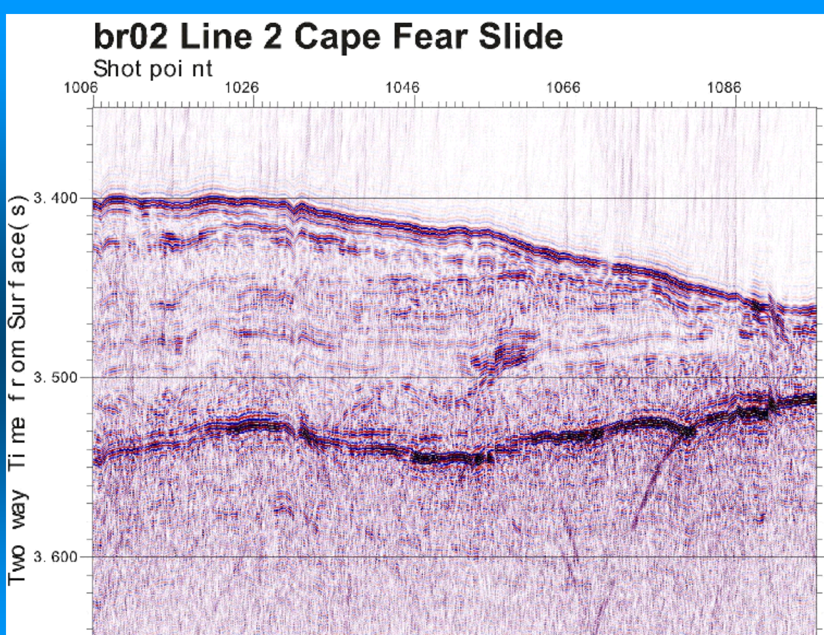

2000
3000
4000
5000
5200
997
W
B
R
G
200
400
1000
5000
4800
BLAKE RIDGE
BERMUDA RISE
ODP Drill Site
R DTAGS (Rowe and Gettrust, 1993)
G DTAGS (Gettrust et al. 1988)
Observed Bottom Simulating Reflector
B DTAGS (Wood and Gettrust 2000)
W Surface Seismic (Wood et al. 1994)
B Surface Seismic (Katzman et al. 1994)

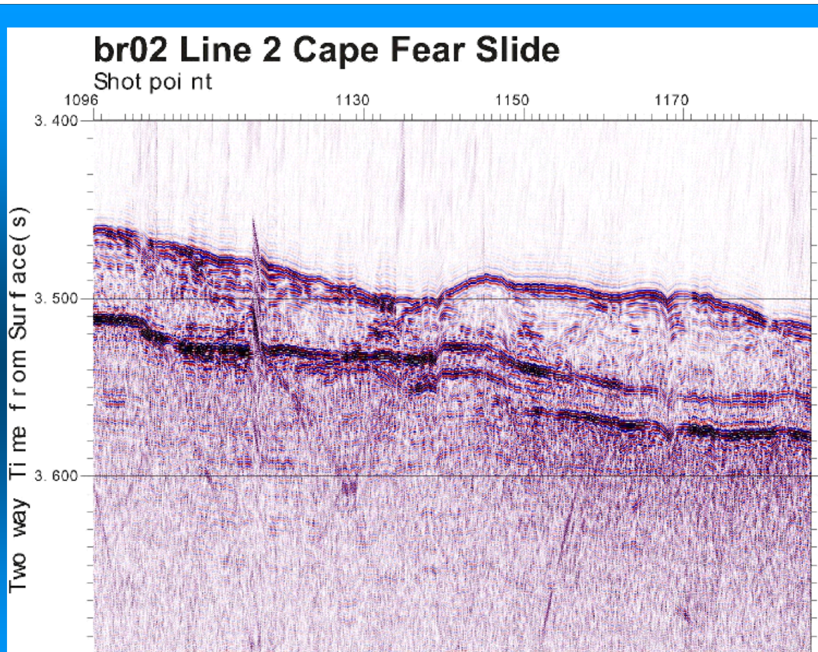


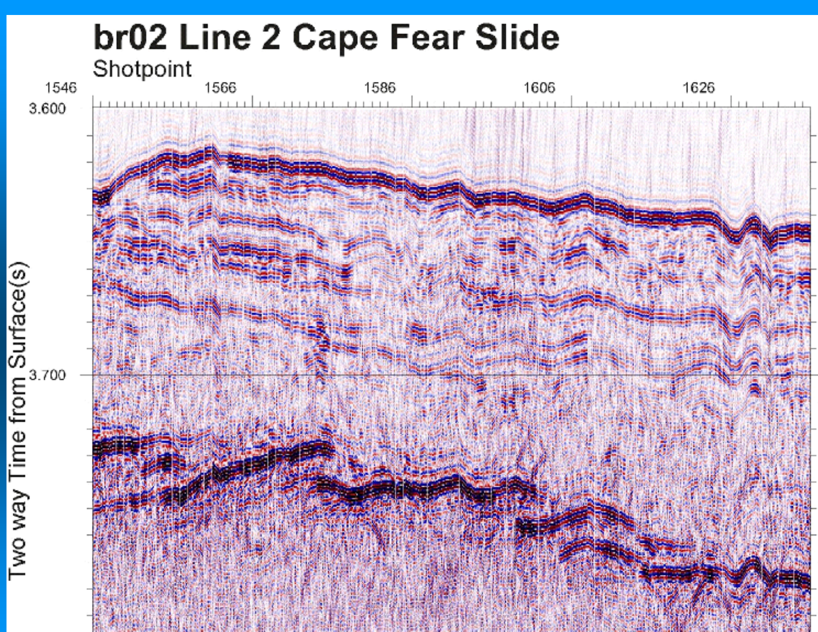
Cape Fear Slide




Water Bottom Reflectance
Cape Fear Diapir
Reflective in GLORIA
Non-Reflective in GLORIA
0.4
0.3
0.2
0.1
0.0
Relative Amplitude
Shotpoint 500
1000
1500


br02 Line 2 Cape Fear Slide
Shot poi nt
1006
1026
1046
1066
1086
3. 400
3. 500
3. 600
Two way Ti me f r om Sur f ace(s)


br02 Line 2 Cape Fear Slide
Shot poi nt
1096
1130
1150
1170
3. 400
3. 500
3. 600
Two way Ti me f r om Sur f ace(s)


br02 Line 2 Cape Fear Slide
Shotpoint
1546
1566
1586
1606
1626
3.600
3.700
Two way Time from Surface(s)

METHANE HYDRATE PRODUCTION FROM ALASKA PERMAFROST

FIELD IMPLEMENTATION PLAN FOR 2003

Thomas E. Williams

Maurer Technology Inc.

ABSTRACT

Phase I of the project in being conducted and completed this year. The project team has analyzed existing geological and geophysical data and obtained new field data required to predict hydrate occurrences; tested methods and tools for drilling and recovering hydrates; developed equipment and procedures for on-site analysis; conducted a modeling study to determine core recovery; designed the completion and production testing program; and obtained permits to safely and economically drill and test gas from hydrates in Alaska in 2003.

Phase II (field implementation) encompasses drilling and coring one or more hydrate wells during the drilling season of 2003. The operation will utilize a small continuous coring mining type rig on a new Arctic Platform design and owned by Anadarko, which will extend the drilling season and be less intrusive on the environment than current exploration methods. The well will then be thoroughly logged and tested. Core will be analyzed on-site using an innovative mobile laboratory. Shallow seismic (VSP) will be shot. A production test will be performed for 10-14 days, and the well will then be monitored for and extended time. Noble Engineering and Development has developed a system that will monitor and relay live data from the drilling operation to Houston.

Alaska Hydrate Project Overview

Methane Hydrate Production from Alaska Permafrost

NETL/DOE DE-PS26-01NT41331
Anadarko Petroleum Corporation
Maurer Technology Inc.
Noble Drilling Corporation

Gas Hydrate Conference
Washington, D.C.
August 28, 2002

Phase I Goals

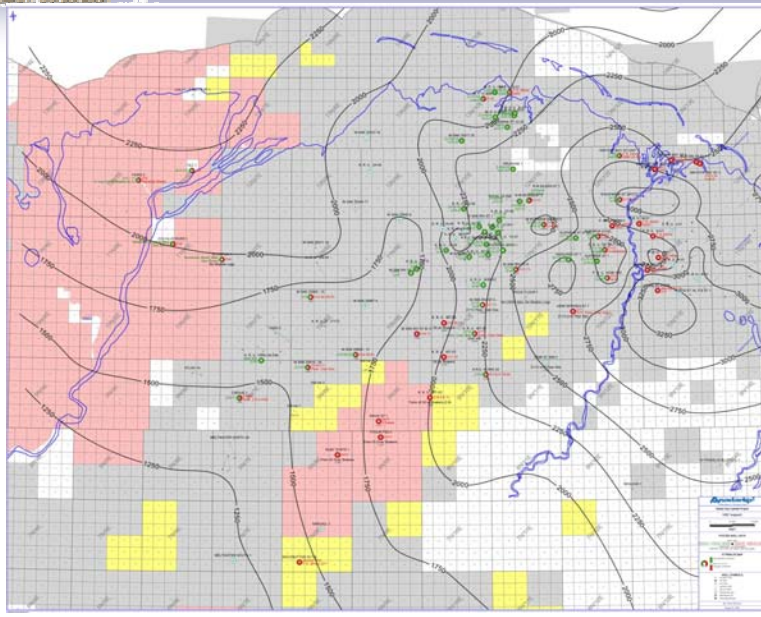
- **Identify best area for potential hydrate accumulation**
  - Performed regional geological and geophysical assessment to determine best opportunity for hydrates on 100% APC acreage
  - Reviewed all available well logs and data
- **Develop refined scope of work for Phase II**
  - Logistical/Well Planning
  - Developed comprehensive budget

Phase I On-going Activities

- Permitting
- Design and engineering of completion and production
- Mobile Lab construction and testing -- will continue through end of year
- Test on-site equipment -- shake-out in January 2003
- Phase II logistics – ongoing activity throughout 2002 into early 2003

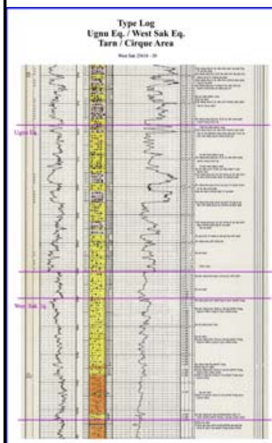
Scope and Modifications

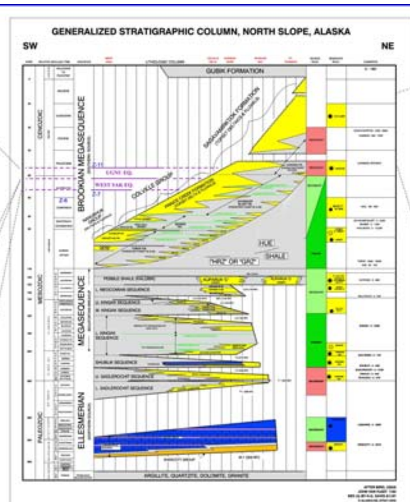
- **Drill, core, log and test one well (HOT ICE #1) to be drilled, completed and tested in 2003**
  - Stand-alone well, will not be drilled near Anadarko exploration well
- **Perform core analysis of hydrates on site**
- **Drilling and completion operations planned to be carried out without use of ice pads or roads**
  - Utilize Anadarko Arctic platform
- **Pending logistics and budget, monitor pressure and temperature throughout summer months**

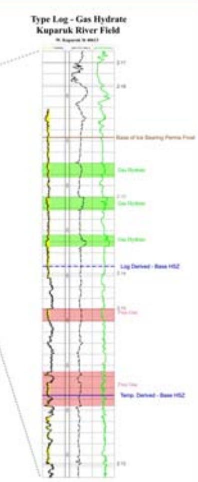


Map of Hydrate Stability Zone Thickness

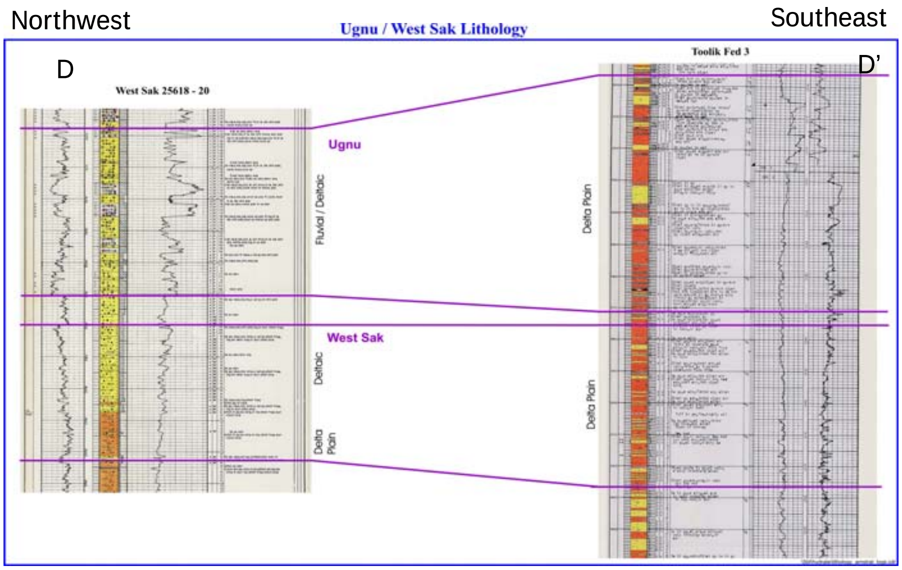
Stratigraphic Column with Type Logs



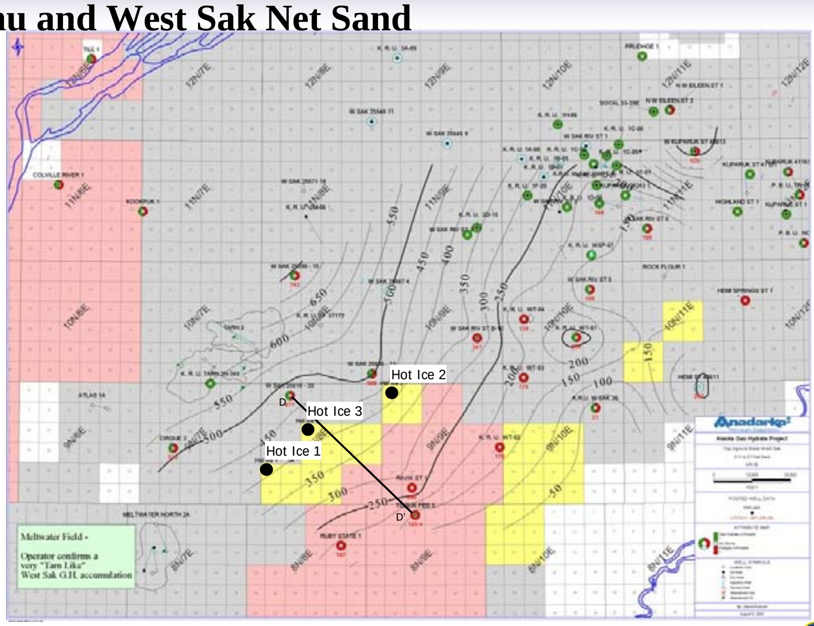




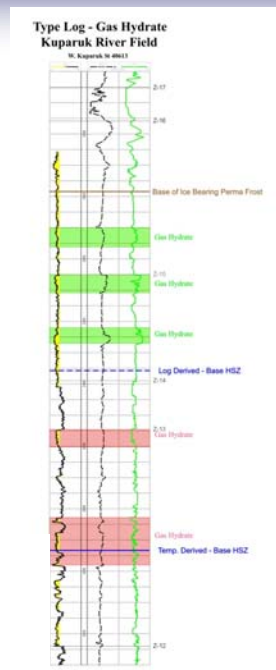
Ugnu / West Sak Lithology



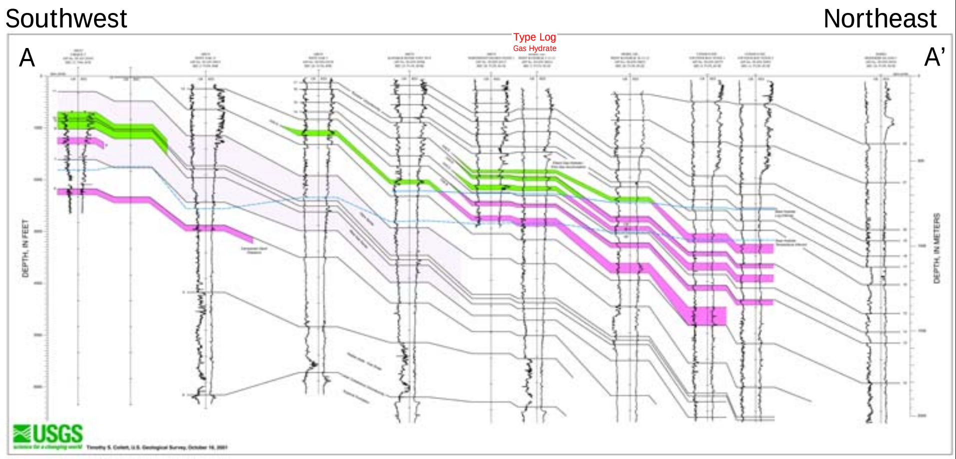
Ugnu and West Sak Net Sand



Gas Hydrate Type Log

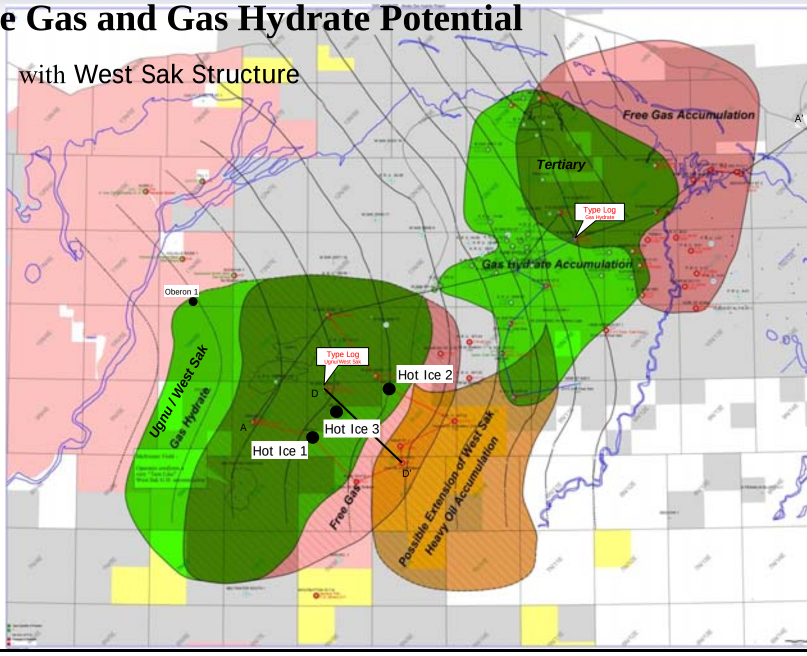


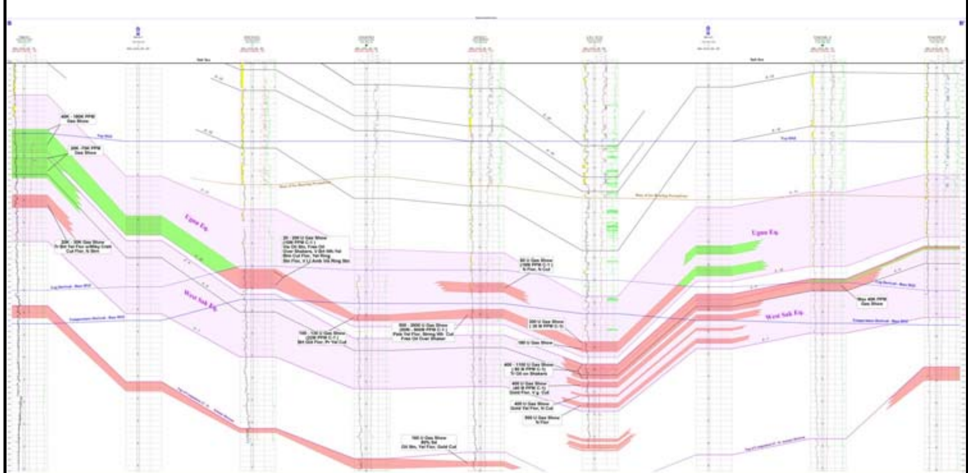
Generalized Cross Section



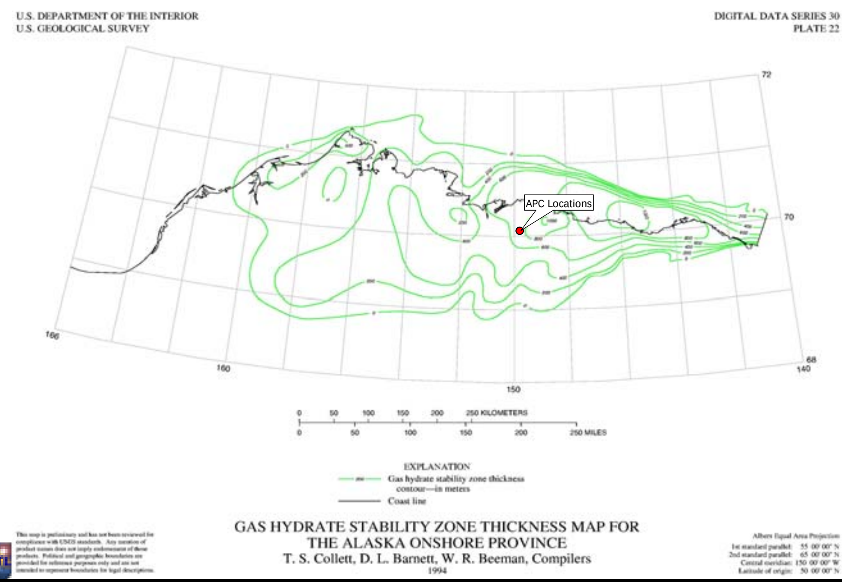
Free Gas and Gas Hydrate Potential

with West Sak Structure

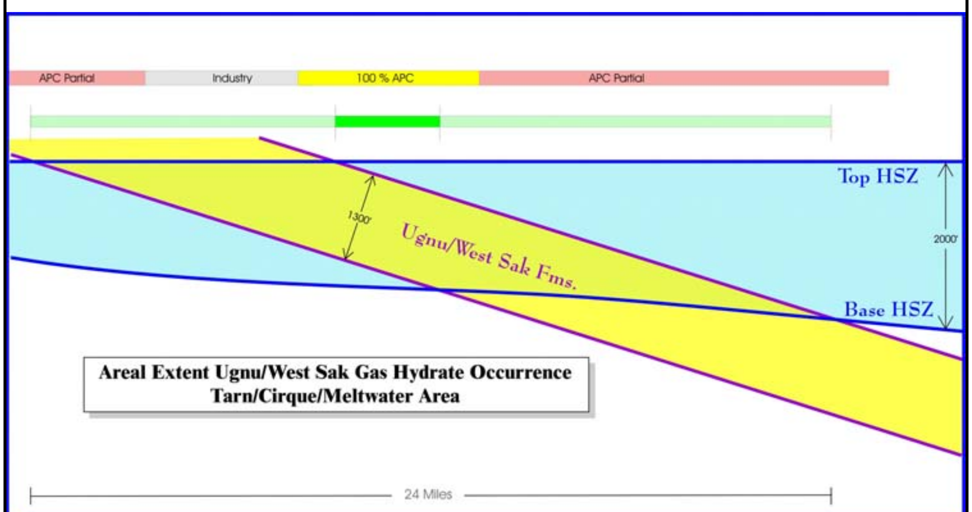




Gas Hydrate Stability Zone Thickness



Areal Extent of Gas Hydrate



Operational Overview

Operational Plan

- **Drill one well**
  - Use Dynatec 1500 mining rig
  - Obtain continuous 3.345" diameter core
  - Ream to accommodate conventional logging suite
  - Will monitor the drilling effort via a live data feed
- **Petrophysical analysis**
  - On-site core analysis
  - VSP's run prior to completing well

Drilling Research Center Core Testing

Prototype Apparatus for Preparing and Testing Frozen Core

Dynatec's UDR 1500 Rig

Drilling Options

- **Drilling well off of Arctic Exploration Platform**
  - Flexibility for extended well test
  - Second well could be drilled quicker and cheaper
  - Extends testing period

Tundra Platform Configuration

Arctic Platform Overview

- **Pilot test the Arctic Platform on the Methane Hydrate project**:
  - Two platforms
    - Operations platform 100' X 100'
    - Camp platform 50' X 50'
  - Purpose is to demonstrate the APC technology to regulatory agencies and the industry partners
  - Provides opportunity to extend drilling season
  - Could significantly drive down costs of exploration
  - Minimize environmental impact

Drilling Preparation

- **Safety is critical**
- **Training requirements**
  - Must ensure all participants have proper training
  - Arctic survival
  - Bear awareness
  - CPR/first aid
  - NSTS
  - H_2S
- **Equipment mobilization**
  - Rig
  - Camp
  - Consumables
  - Core Lab
  - Support equipment

G&G Analysis

Well Logging

Array Induction

Dipole Sonic

Density

Neutron Porosity

Spectral Gamma

CMR

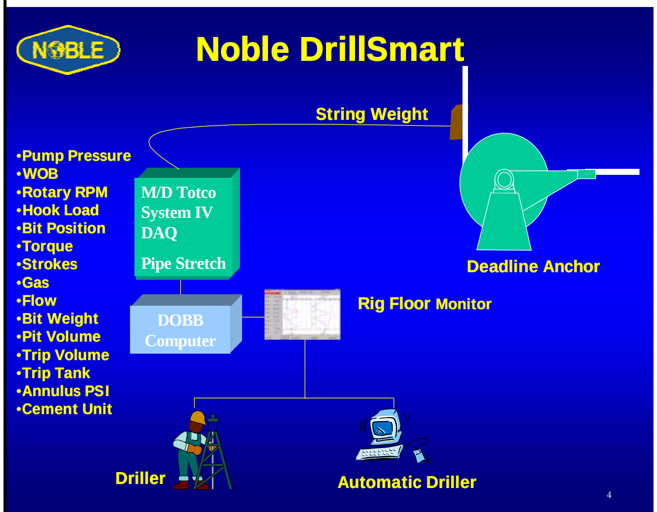
Geophysical Analysis/VSP

Contractor has not been chosen

Post Drilling Core Analysis

Not yet determined

NED Live Data – "DrillSmart Lite" and "DrillGraph"



- DrillSmart, DrillGraph and Live Images are transmitted with one-second replication to NED servers
  - Client can access this data via internet
- Live data to allow office based personnel to concurrently view
  - What is going on down-hole
  - View the operation
  - Improve Drilling Performance
  - Provide technical support as problems arise

Mobile Core Lab Status

- To be Completed, Tested, and Personal Trained by end of 2002
- Currently
- Modules Fabricated
- Equipment ordered, some delivered
  - Equipment testing with USGS hydrate core in November
- Modules Fabricated
- Internal outfitting ongoing
  - Additional equipment is under consideration *(space)*
- Operating Company Chosen

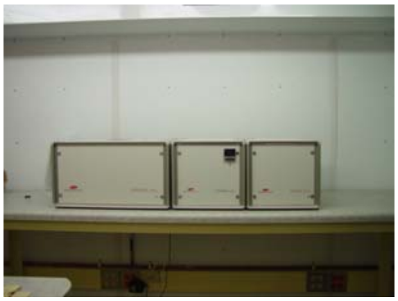
Mobile Core Lab Construction Update

Work Table

View Through Lab

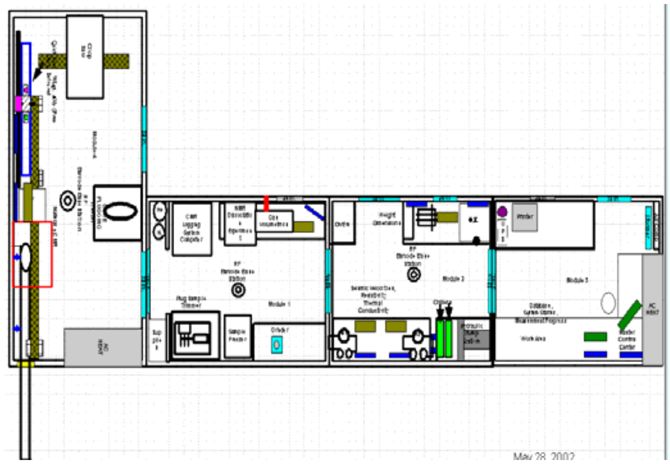
Mobile Core Lab Construction Update

Vacuum Pump



NMR Equipment

Mobile Core Lab Schematic



Hydrate Specific Measurements

Thermal Conductivity

Dissociation Tests

- Controlled Confining Stress, Temperature, and gas Pressure
- Staged NMR Measurements (Free gas and liquid water)
- Gas collected and Analyzed

Standard Measurements

- Grain Density
- Porosity
- Permeability
- Shear and Compressional Velocity
- Resistivity
- Mineralogy
- Grain Size Distribution
- Hg Capillary Pressure

Modeling Activity

- **Lawrence Berkley National Lab, TOUGH2 EOSHYDR2**
- **Modeled core recovery potential**
  - Pressure, temperature, recovery time impacts
  - Determined core recovery potential
- **Confirmed larger OD core 2.5” to 3.5“**
- **Keep mud chilled to 0 degrees C, limit salt and methanol**
- **Phase II – Quantify model / data**

Modeling Activity

Current Activities and Needs

- Numerical Study for completion/testing planning
  - Data requirements
  - Optimum well configuration
  - Stimulation methods
  - Volume estimations

Future Needs

- Conduct simulation studies for recovery potential
  - Specific scope of work and budget being developed

Completion Plan

Well Completion

- Well completed with permanent pressure gauges
- Incorporate heat trace for freeze protection
- No artificial lift installed

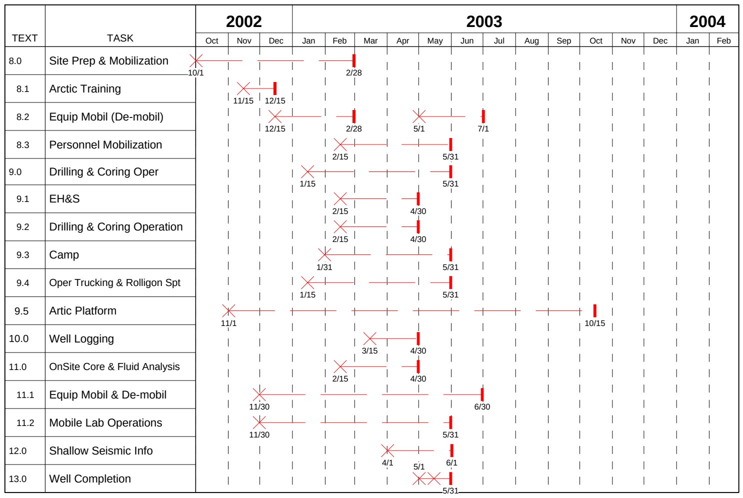
Well Test

- Plan on a 10 - 14 day well test
- Swab and/or flow well
- Plug can be set in profile to minimize wellbore storage
- Set-up to allow pressure monitoring during break-up
- Planned for longer monitoring of well depending on logistics and budget – (Possible Phase III)

Phase II Project Timeline

Methane Hydrate Production from Alaskan Permafrost
PHASE II

10/25/02

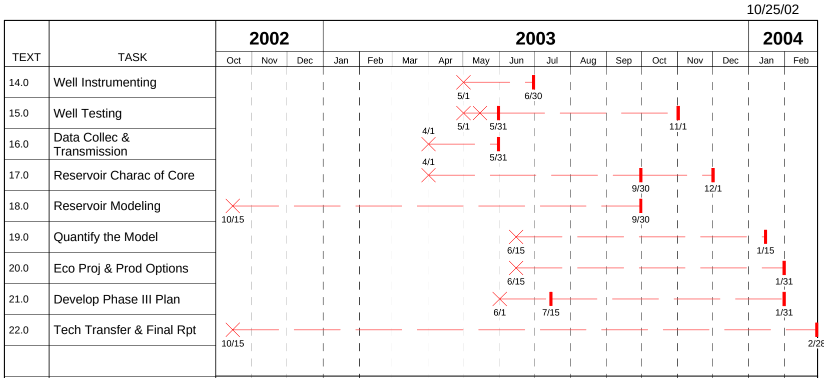


(http://www.maurertechnology.com/index-hydrates.html)

Phase II Project Timeline - Continued

Methane Hydrate Production from Alaskan Permafrost
PHASE II

10/25/02



Questions?

Seafloor Morphology and Seismic Perspective of the Central Western Continental Margin of India in relation Gas Hydrate Occurrences

*M. Veerayya**

Ex-Scientist, National Institute of Oceanography, Dona Paula, Goa 403 004, India
[Presently Principal Investigator, DST (Govt. of India) Project]
veerayya@darya.nio.org

ABSTRACT

Methane trapped as solids within the hydrates and as free gas below the bottom simulating reflector (BSR), may provide a major unconventional energy resource. The continental margins of India – new frontier for hydrocarbon resources, characterized by favorable geological, geophysical and oceanographic conditions, appear to be a potential area for the formation of gas hydrates. Since the first report on the occurrence of gas hydrates in Andaman offshore by the ONGC (Chopra, 1985) and along the western continental margin of India by NIO (Veerayya et al., 1993; 1998), seismic evidence of gas hydrates has been inferred in several offshore areas of the continental margins of India by Indian national Oil & Gas Corporations and Research institutes (ONGC, DGH,GAIL, OIL, NGRI and NIO). However, ground truth data on detailed site-specific geological, geophysical and geochemical characteristics of the sediments and their pore fluids, and oceanographic regime are scarce in Indian offshore areas.

This paper evaluates the geological, geochemical and geophysical aspects of a typical offshore site, which lies in the Konkan- Kerala basin along the central western continental margin of India. Its eastern boundary lies on the middle slope off western India, while westward the study area extends into the Arabian Sea abyssal plain. The study would help in understanding the characteristics of the prospective site (s) and the relationship between geological environment and gas hydrate potential.

The data set comprising of discrete bathymetry, seismic profiles from published reports, seafloor sediment texture and some geochemical parameters have been utilized to draw inferences.

The bathymetry is characterized by distinct topographic variations and can be demarcated into 3 zones: eastern (1000- 2000 m), central (2000 m) and western (>2000 – 3500 m) zones. The eastern zone is marked by steeply dipping seafloor, the western zone is characterized by a gently sloping seafloor towards the W and NW, while the central zone is dominated by uneven to rough seafloor at many places, which in turn reflect the prevailing sedimentation pattern.

Seismic reflection data revealed 4 lithological units, the lowermost unit being underlain by an acoustic basement in a large part of the area. The uppermost seismic unit (Unit I0 comprising of 150-200 ms (twt) of sediments is characterized by chaotic reflections and probably represents (Pliocene – Recent ?) fine-grained clastic facies. The second and the fourth seismic are atypical in that they are characterized by faint reflections and are often acoustically transparent indicating apparent blanking, whereas the third unit sandwiched in between is marked by very strong reflections. Generally, Units II and IV, consisting of blanking zone are about 400-600 ms (twt) thick, while the unit III is about 150-200 ms thick. Most of the

sediments in Units II and IV show horizontal and concordant bedding throughout the area indicating relatively quiet (?) conditions during deposition. Commonly, the BSRs are confined to these units. The indentified lithological units are broadly correlatable with those encountered in the uppermost sedimentary column recovered at DSDP Site 219 (water depth –1764 m) on the Laccadive Ridge, which is in the vicinity of the study area. The data also enabled to delineate the areal extent of macro-to micro-scale morphological and structural features either exposed or buried below the seafloor, which in turn are helpful in understanding the seismic stratigraphy of the area.

The seismic reflection profiles show seismic evidence of gas hydrate occurrences in the form of BSRs in the study area. In general, the inferred BSRs occur at about 260-300 to 500 ms (twt) below the seafloor at 2.0 to 3.5 s (twt) water depth. About 200-300 ms thick, somewhat acoustically transparent strata over lie the BSRs, while partial blanking of the order of 150-200 ms and even up to 400-500 ms of blanking of seismic records is seen above the acoustic basement, mainly west of 2000 m isobath. The BSRs are mostly confined to the area north and west Laccadive Ridge Complex. The BSRs also occur in and around topographic highs. At one location, a double BSR is discernible. The data also reveal reversal in polarity. Seismic study of ONGC further suggests that the Konkan- Kerala offshore as well as the Laccadive Ridge area are characterized by BSRs, wherein the BSRs lie at 260- 375 ms (twt) below the seafloor at 2.2 to 2.65 s (twt) water depth (Kuldeep Chandra et al., 1998). The apparent blanking of seismic records above the inferred BSRs may, perhaps, be due to gas hydrate-bearing strata, while that below the BSRs , characterized by lack of almost any internal reflections, may reflect fluid/gas saturated sediments or fine-grained sedimentary facies, such as shale(?), which need confirmation by ground truth data.

The surficial sediments are characterized by organically- rich (Corg= 0.98 to 1.45%), fine-grained silty clays, besides the presence of hydrocarbons ranging from methane (120 ppm) to Butane (6 ppm).

Rapid sedimentation and organic-carbon rich sediments coupled with optimal lithostatic and hydrostatic pressures favour the formation of gas hydrates along the margin. Further, seafloor doming, faulting and contorted sedimentary layers above the BSRs seem to suggest the existence of probable pathways for upward migration of fluid/gas from the deep.

Concerted efforts aimed at understanding geological, geophysical, bio-geochemical, physical oceanographic aspects and in situ measurements for gas hydrate exploration are underway, which would help in identifying and quantifying the potential gas hydrate resources along the continental margins of India in general, and in the study area in particular.

……………………..

SESSION II

Biological Influence on Hydrate Formation, Stability, Content and Lattice Saturation

Chairman: Prof. Rudy Rogers
Chemical Engineering Department
Mississippi State University, Mississippi

Rapporteur: Dr. Kenneth Grabowski
Naval Research Laboratory, Washington, DC

Molecular Diversity and Activity of Microbial Communities Associated with Gas Hydrates in the Gulf of Mexico

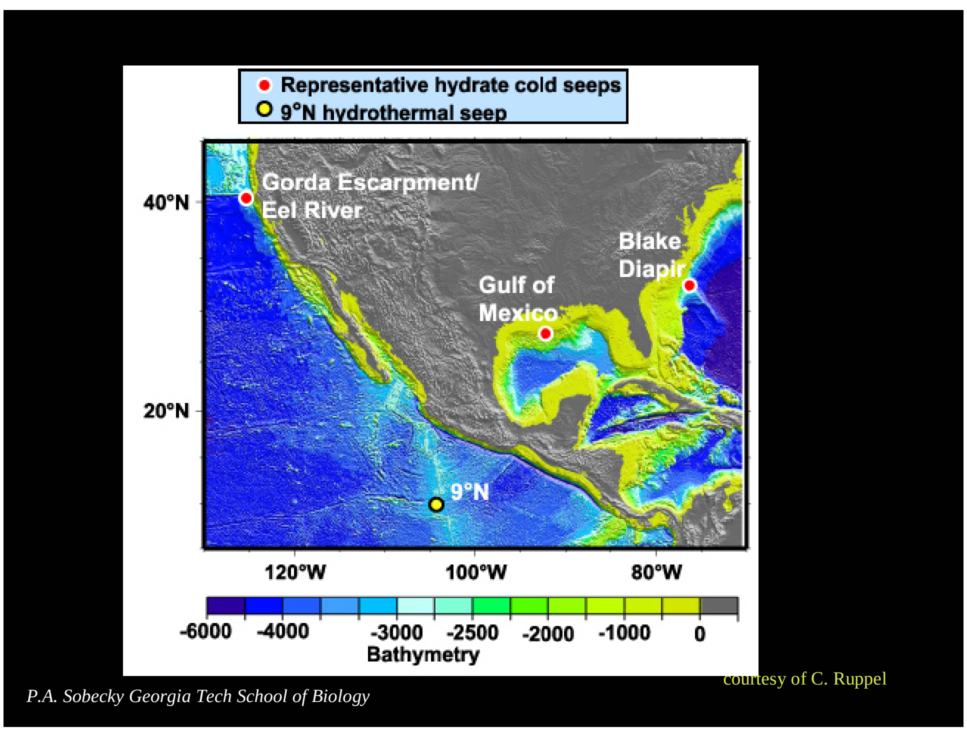
Patricia Sobecky, (patricia.sobecky@biology.gatech.edu; 404-894-5819)

School of Biology, 310 Ferst Drive, Georgia Institute of Technology
Atlanta, GA 30332-0230

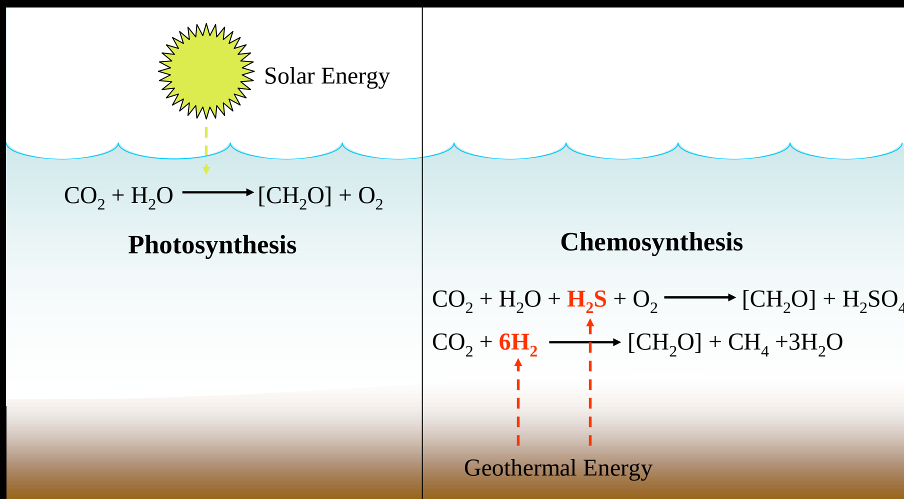
ABSTRACT

The sediments in the northern Gulf of Mexico contain considerable reservoirs of liquid and gaseous hydrocarbons. The geologically active nature of the region is evidenced by the presence of sea-floor gas vents and seeps, subsurface and sediment surface-breaching gas hydrate as well as brine pools and mud volcanoes. Oil, gas and brine seepage, and the co-migration of these fluids, creates distinct and extreme environmental niches promoting the growth of thriving communities of macro- and microorganisms. Dense mats of bacteria, vestimentiferan tubeworms, methanotrophic mussels, bivalves and methane-hydrate-dwelling worms colonize the Gulf of Mexico hydrocarbon seep and methane hydrate habitats. Chemoautrophs living in hydrocarbon seep habitats rely on reduced carbon in the form of methane gas and crude oil present in migrating seep fluids. The macro- and microorganismal communities thrive in environments that would be highly toxic to most known organisms functioning through chemosynthetic processes and unique interactions that we are only beginning to identify and understand. What is the significance of these communities with respect to hydrates? What is their role in fixing or dissolving effluents and gases? The ability to address such questions requires long-term as well as interdisciplinary research efforts. As part of our multi-disciplinary NSF-sponsored Life in Extreme Environments (LExEn) project, we have undertaken studies to characterize the genetic diversity of the microbial communities at these extreme habitats. We have constructed *Archaeal* and *Bacterial* 16S rRNA clone libraries from DNA extracted from sediments associated with gas hydrates. Bacterial clone libraries were dominated by delta- and epsilon-*Proteobacteria* while archaeal clone libraries were dominated by ANME-1 and ANME-2. Rarefaction analysis indicated low archaeal diversity relative to bacterial diversity. The frequency of extrachromosomal plasmid elements in culturable (bacterial) isolates ranged from 10-15%. Lastly, microbial activity, as determined by characterizing ectoenzyme activity, varied considerably with lowest measurements observed in 'pure' gas hydrate samples. These results and other data from other cold seep environments will be presented in this talk.


NSF LExEn: Molecular Microbial Ecology and Biogeochemistry of Methane Hydrates and Brine Pools
Co-Investigators:
Joseph P. Montoya
Georgia Institute of Technology
Samantha B. Joye
University of Georgia
Ian R. MacDonald
Texas A&M University
NSF
NETL
NOAA
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE
P.A. Sobecky Georgia Tech School of Biology


Representative hydrate cold seeps
9°N hydrothermal seep
Gorda Escarpment/
Eel River
Blake
Diapir
Gulf of
Mexico
9°N
40°N
20°N
120°W
100°W
80°W
-6000
-4000
-3000
-2500
-2000
-1000
0
Bathymetry
courtesy of C. Ruppel
P.A. Sobecky Georgia Tech School of Biology

Photosynthesis vs. Chemosynthesis



adapted from C.L Van Dover (2000)

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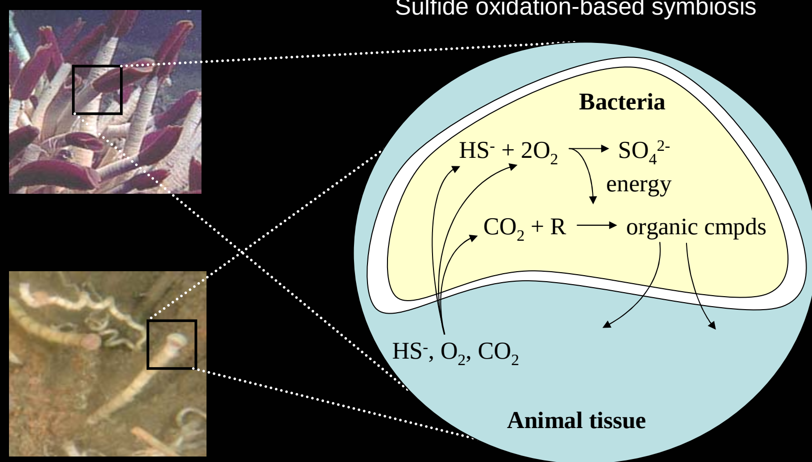
Not to scale!

P.A. Sobecky Georgia Tech School of Biology

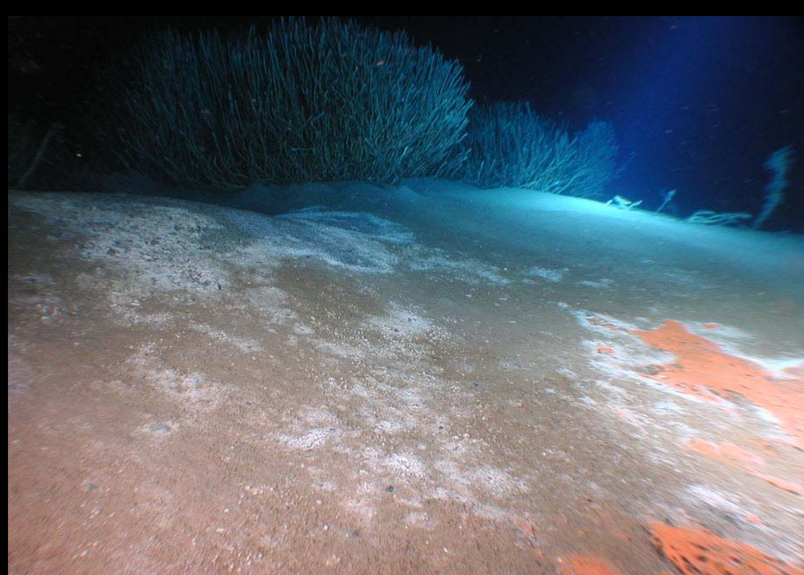
Invertebrate-Microbe Associations: Endosymbiosis

Sulfide oxidation-based symbiosis



Other; methanotrophy-based symbiosis: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

Riftia image from http://www.discovery.com/stories/science/seavents/zooms/tubeworm.html



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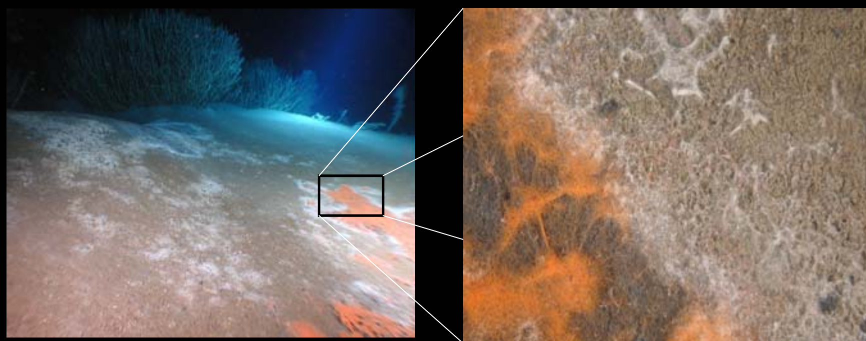
Microbial Mats



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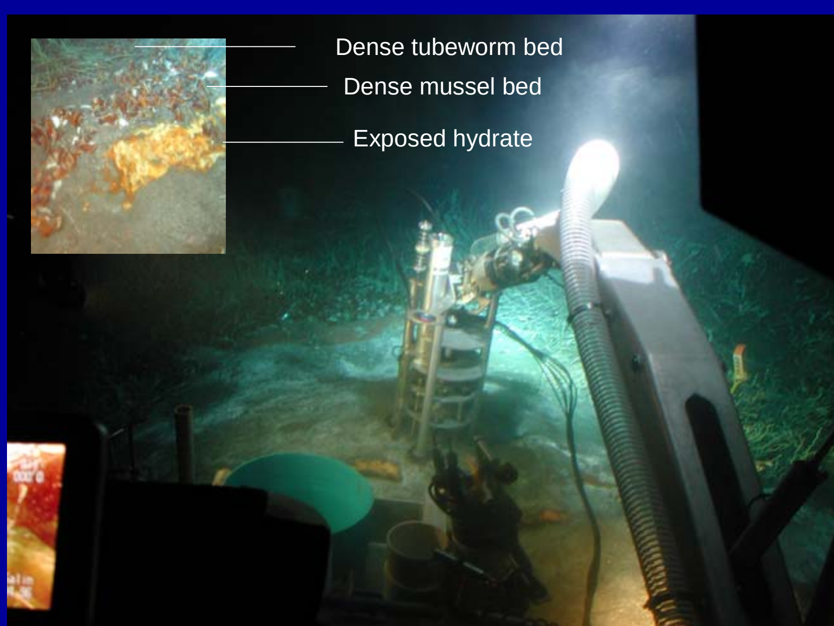
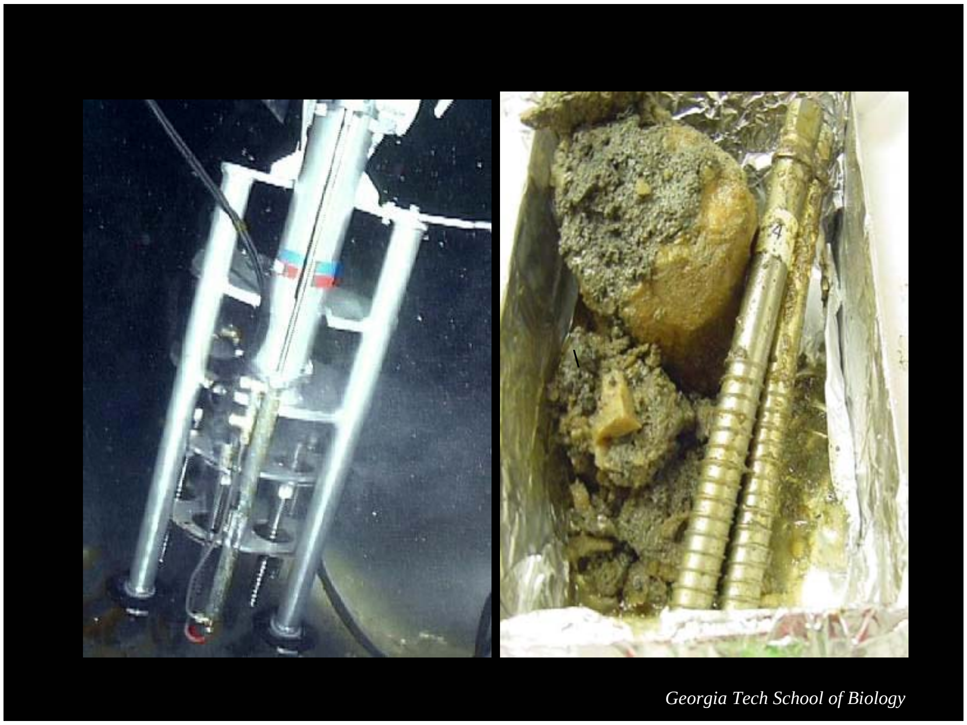
“Ice Worms” (Hesiocaeca methanicola)

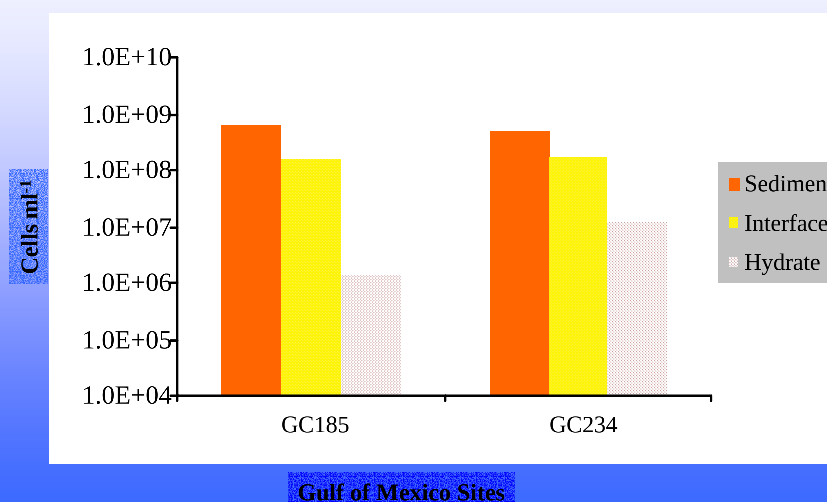
Discovered in GoM 1997 (Fisher & Santos)
~2-4 cm polychaete; note high densities

Epi- and/or Endosymbionts??

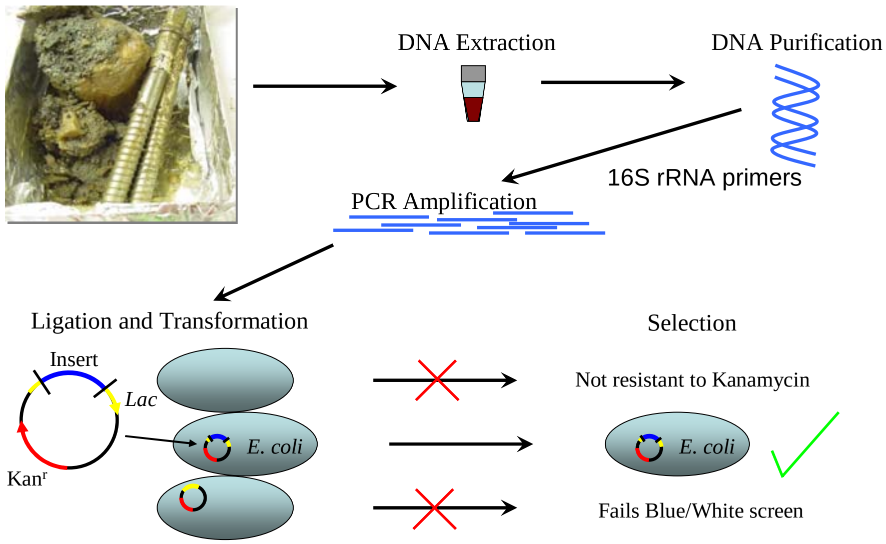




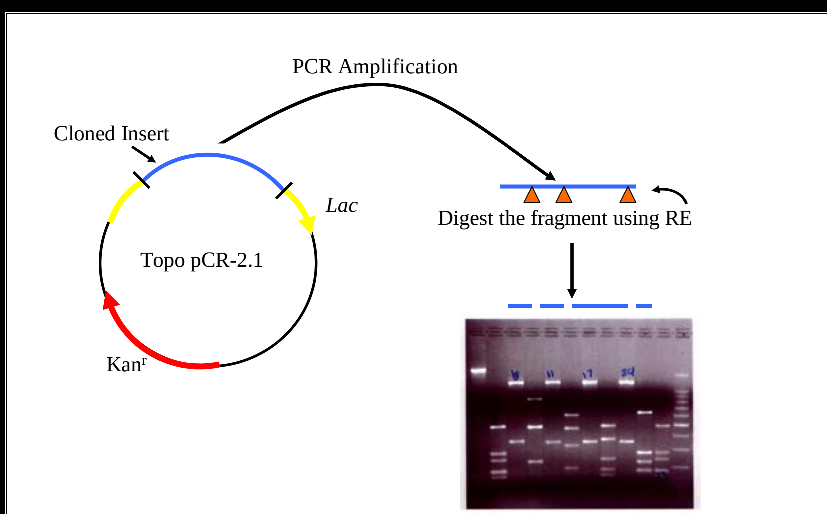
Direct microbial cell counts from 'pure' hydrate and associated sediments



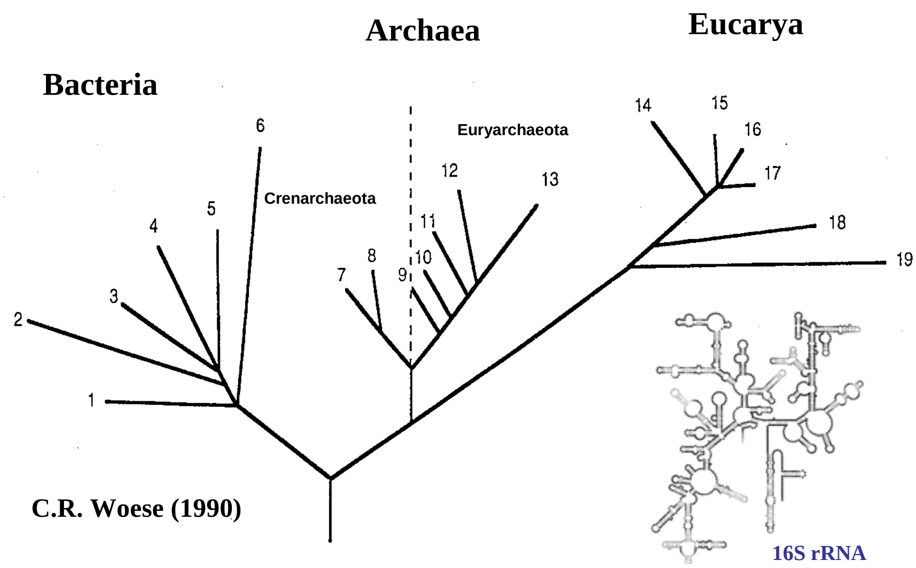
Construction of 16S rDNA Clone Libraries



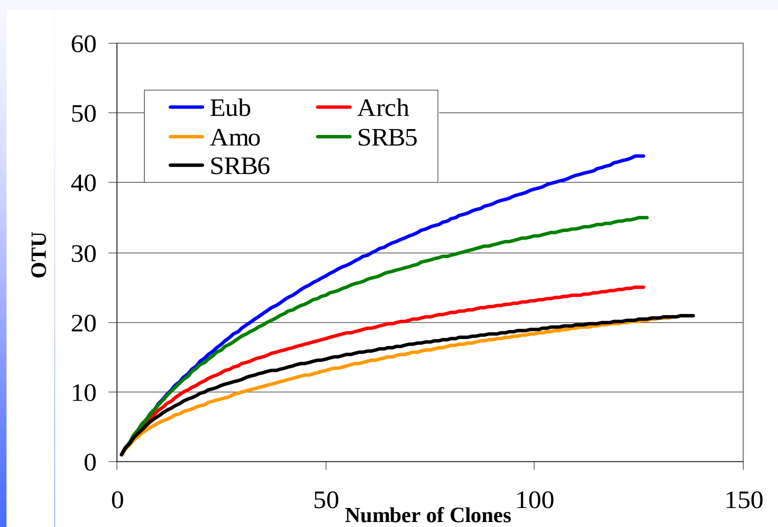
Screen for unique clones by restriction digest(s)



The Three Domains of Life



Rarefaction analysis of 16S rRNA clone libraries



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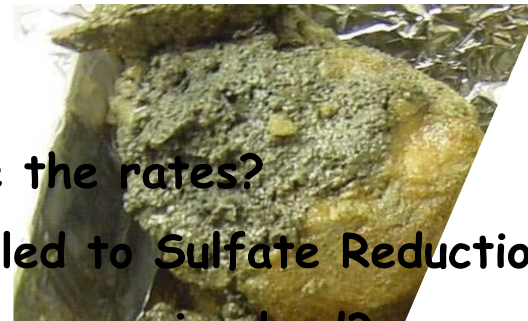
Anaerobic methane oxidation:

$$CH_4 + SO_4 \rightarrow HCO_3^- + HS^- + H_2O$$

(Hoehler et al. 1994)



How fast are the rates?

Is AMO coupled to Sulfate Reduction?

Which microbes are involved?

Acknowledgements

Post-doctoral Fellow: Sandra Story

Graduate Students: Heath Mills, Rob Martinez

Technician: Cassie Hodges

Undergraduate Student: Kristen Wilson

Captains & Crew:
R/V Seward Johnson I
R/V Seward Johnson II (formerly the Link)

Crew of the Johnson Sea Link

Surface and Subsurface Manifestations of Gas Movement Through a North-South Transect of the Northern Gulf of Mexico

Jean Whelan and Lorraine Eglinton[1], [2]*Larry Cathles and Michael Wizevitch,* [3]*Harry Roberts*

[1]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MS 02543; [2]Department of Geological Sciences, Snee Hall, Cornell University, Ithaca, N.Y. 14853; [3]Coastal Studies Institute, Louisiana State University, Baton Rouge, LA 70703

ABSTRACT

Large volumes of gas appear to have vented through a north-south transect of the offshore northern Gulf of Mexico. Even though very large quantities of gas appear to be involved, the specific sites of venting are generally highly localized at faults and fractures in the seafloor and may also be episodic making the actual hydrocarbon fluxes involved difficult to estimate. This venting gas causes significant changes in compositions of reservoired oils, both in the past and at the present time. This upward gas movement produces a number of interesting effects at the seafloor, including support of a prolific and diverse biological community, formation of seafloor gas hydrates, and sometimes massive disruption of the subsurface and surface sediments including ejection of fossils from older deeper sediments to the modern seafloor. In some cases, methane bubbles issuing from the seafloor appear visually to be venting directly into the atmosphere, possibly providing a deep sea source of the greenhouse gas, methane. Venting is accompanied by natural oil slicks at the sea surface and can be followed for miles. An overview and initial evaluation of surface and subsurface manifestations of this gas will be presented including a summary of potential influences on subsurface oil and gas accumulations.

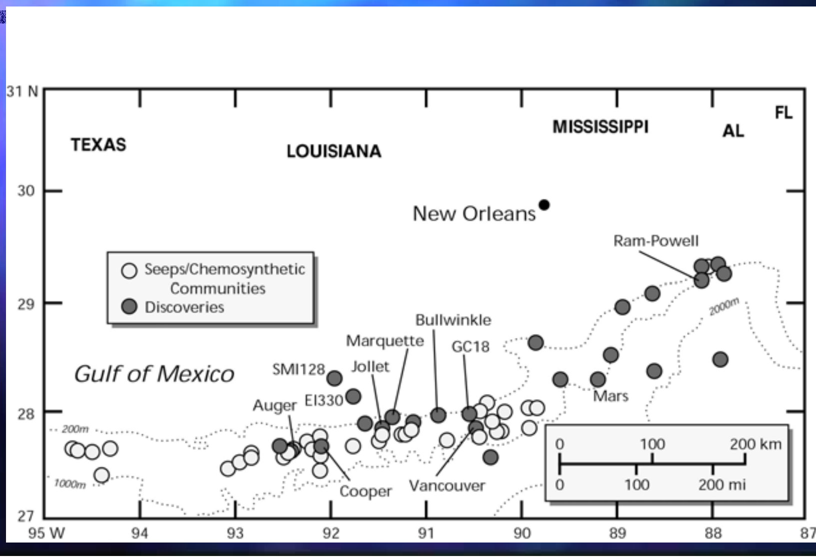
Surface & subsurface manifestations of gas movement through a north-south transect of the northern Gulf of Mexico

Jean Whelan & Lorraine Eglinton
Woods Hole Oceanographic Institution
Larry Cathles, M. Wizevich & S. Losh
Cornell University
Harry Roberts
Louisiana State University

Support gratefully acknowledged from:

- Department of Energy
- Woods Hole Oceanographic Institution

Gulf of Mexico - natural gas seeps and producing wells (modified from Sassen et al)



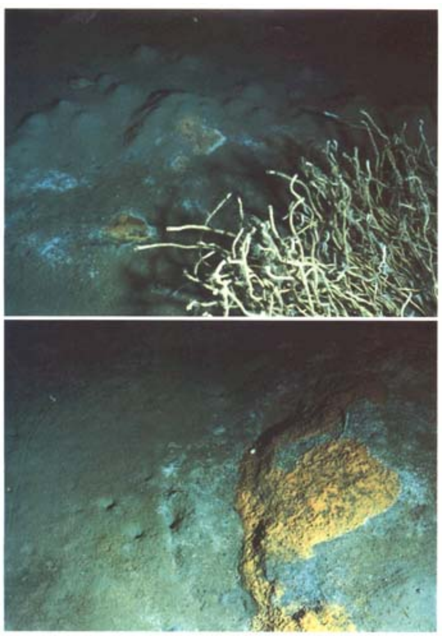
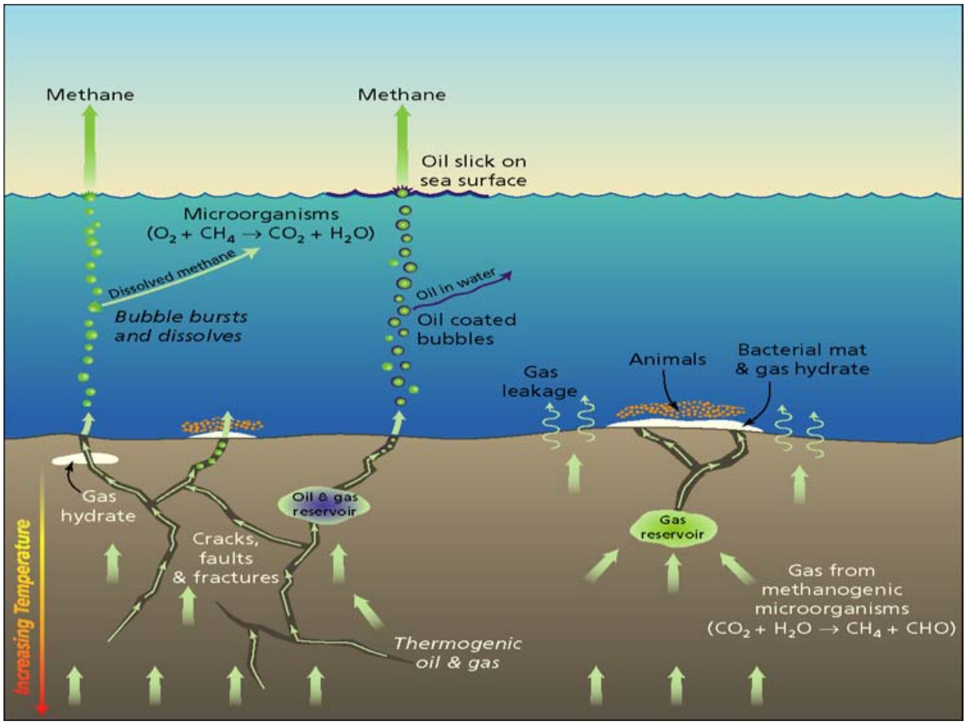


Fig. 2. Photographs of *Beggiatoa* mats at cold hydrocarbon seeps in Green Canyon. At top, scattered white and pigmented *Beggiatoa* mats can be seen on the sediment surface behind a colony of tube worms. At bottom, a large pigmented *Beggiatoa* mat is seen that drapes one edge of a buried gas hydrate mass. Two small laser dots near the center of the images are 10 cm apart, and provide scale.

Gulf of Mexico,
Green Canyon 184
(from Sassen et al., 1993)



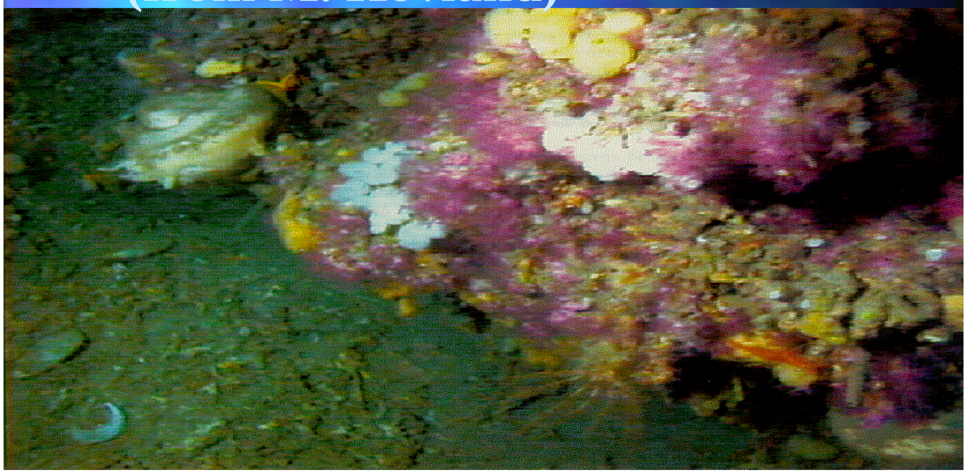
Carbon Reservoir	Amount (g)	Rate (g/yr)	Reference
Reduced insoluble carbon in Sedimentary rocks	1.1xE22		Hunt 1996, pp 19-21
World ocean DOC	1.70 x E18		Druffel et al. 1992
Marine primary production		5 x E16	Martin et al., 1987
Ocean DOC turnover		*1 x E14*	*Williams Druffel, 1987*
Gas Reservoirs			
Annual global methane flux to atmosphere		*5.4 x E14*	*Cicerone & Oremland, 1988*
Total Methane flux to atmosphere		5.1xE14	Khalil & Rasmussen, 1995
Hydrates (marine only)	*2-8 xE18*	*2 to 8 xE14*	*Whitaker, 1994*
Methane hydrates (oceans only)	1.3xE22		DoE , 1999
	>1xE19		Kvenvolden, 1993
Ocean margins, normal compaction		2.5 x E10	Elderfield et al., 1990
Methane venting, Dive site 2894, Gulf of Mexico, Aug 1999 (Through fracture in 1m2 area)		*>0.9xE8*	*Whelan et al. 2000*

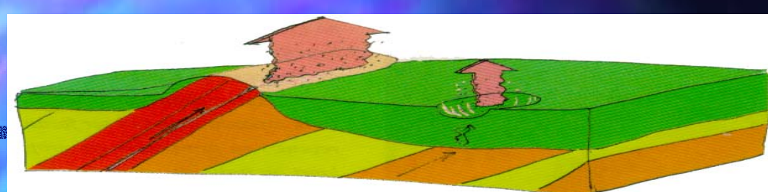
Not confined to Gulf of Mexico - important in many geographic areas, particularly in river deltas and continental margins. Only a few areas studied at all to date. Examples:

- North Sea
- Black Sea
- Eastern Mediterranean
- Persian Gulf
- Timor Sea (off Australia)
- Caspian Sea
- Japan sea & and continental margin
- Niger Delta
- Amazon Delta
- Penobscot Bay, Maine
- Continental Margins - eastern & western N. America

Gas & water continuously rise from one of numerous mud volcanoes in Azerbaijan. Submerged mud volcanos are also common in Caspian Sea. (from M. Hovland, Satoil)

North Sea - a violet coral and various sponges living on Haltenpipe reefs (from M. Hovland)





Gas seeps up along dipping sedimentary rocks through seafloor in the Haltenbanken area of the North Sea. Seepage on left occurs through ridge; seepage on right through a layer of clay causing seafloor pockmarks (from M. Hovland, Statoil)

Algerian Sahara - fossilized coral reefs previously buried in sand. When living, they existed at estimated depth of about 400m, similar to depths of Norwegian coral reefs. (Wendt et al. 1997)

Fossil methane seepage from the ocean bottom may be influencing global climate:

- Methane is a greenhouse gas
- Estimated that:
  - 50 Tg/yr vented to ocean bottom (Results seep workshop , Kvenvolden & Lorenson, June 2001, EOS, 2001)
  - Up to 30 Tg/yr may be vented directly via bubbles to the atmosphere
  - 10-30 Tg/yr would have significant effect on global climate

Gas hydrates

- One of largest carbon reservoirs on earth
- Future natural gas source??
- Commonly associated with upward gas flow - Calthles - model calculations Gulf of Mexico, GC184: 10% of gas trapped in hydrate; 90% vented upward

- **Seafloor gas hydrates are associated with significant gas flow which is often many times larger than the volume of hydrate**
- **At Green Canyon, the gas is primarily from thermogenic sources.**
- **In most other areas worldwide, methane appears to come mainly from biogenic (rather than petroleum) sources**

Effects of upward migrating gas:

- In surface sediments:
  - Complex interaction between upward methane migration, oxidation, and interaction with microbial sulfate reduction
- Subsurface reservoirs:
  - anaerobic oil biodegradation - microorganisms maintained by moving fluids and gas (methane & nutrients)
  - Quality ($/barrel) of reservoired oil dependent on relative timing of reservoir filling, in situ biodegradation, and effects of gas washing

Upward gas flow from global mass balance point of view:

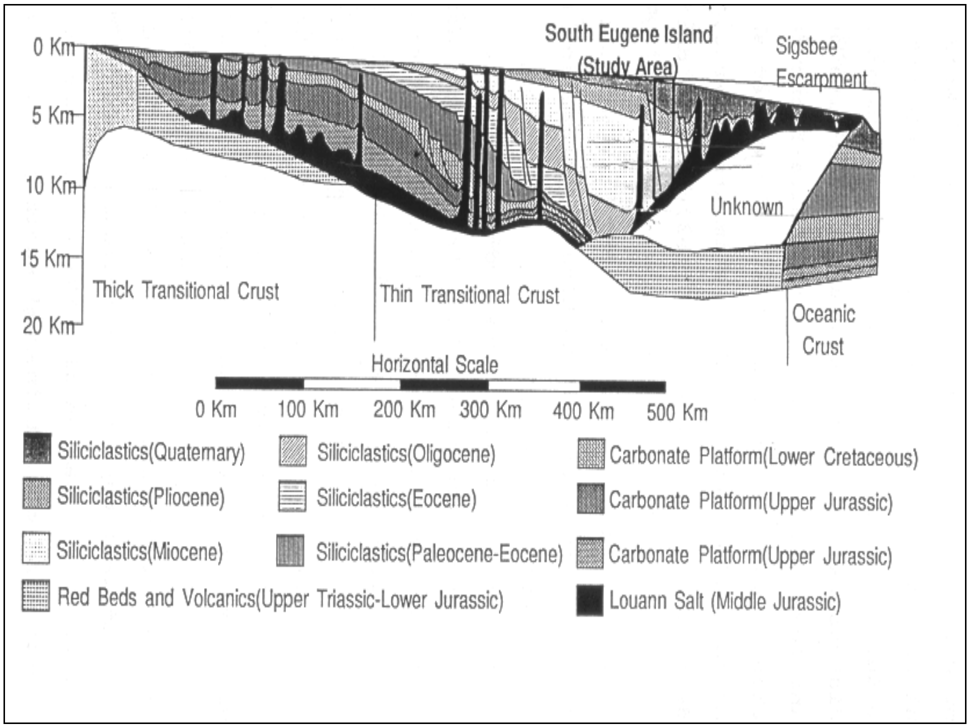
- Thermogenic gas generation from cracking of residual oil left in source and reservoir rocks which continue to subside:
- 2% of generated gas and oil trapped in producible reservoirs
- Of remainder, 54% is discharged at sediment surface into overlying ocean.

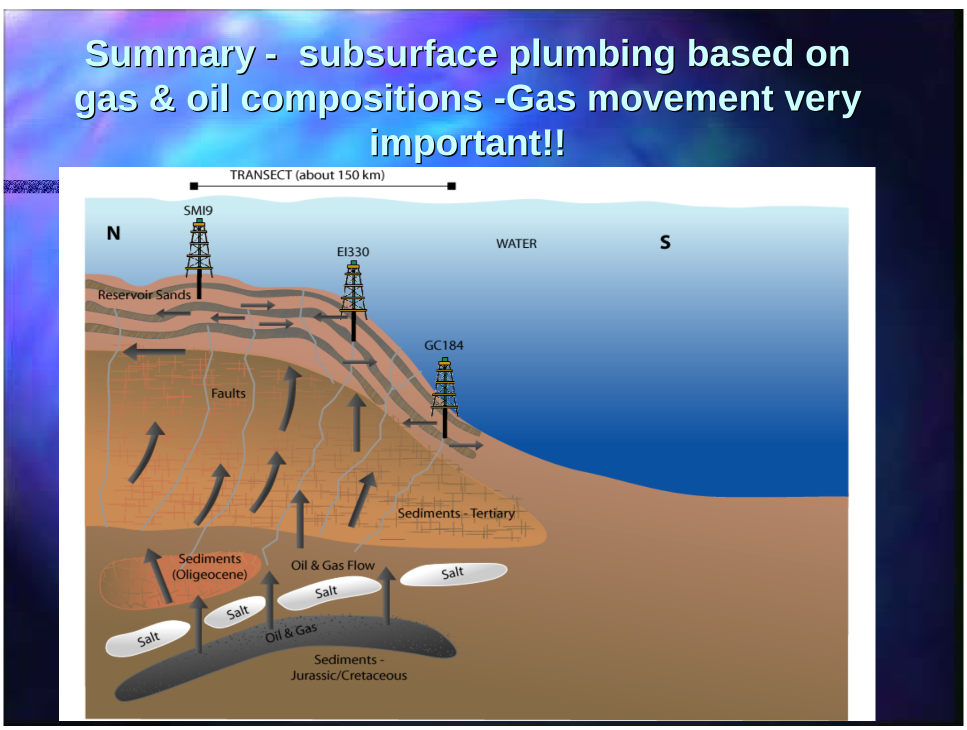
Questions about upward gas seepage through reservoirs and seafloor:

- How widespread?
- Volumes of gas and oil involved?
- Discharge rates?
- How to monitor very heterogeneous system over time?

The subsurface part of the problem

Examining fluid flow through a N-S cross section of the northern Gulf of Mexico:


South Eugene Island
(Study Area)
Sigsbee
Escarpment
0 Km
5 Km
10 Km
15 Km
20 Km
Unknown
Thick Transitional Crust
Thin Transitional Crust
Oceanic
Crust
Horizontal Scale
0 Km
100 Km
200 Km
300 Km
400 Km
500 Km
Siliciclastics(Quaternary)
Siliciclastics(Oligocene)
Carbonate Platform(Lower Cretaceous)
Siliciclastics(Pliocene)
Siliciclastics(Eocene)
Carbonate Platform(Upper Jurassic)
Siliciclastics(Miocene)
Siliciclastics(Paleocene-Eocene)
Carbonate Platform(Upper Jurassic)
Red Beds and Volcanics(Upper Triassic-Lower Jurassic)
Louann Salt (Middle Jurassic)


Summary - subsurface plumbing based on gas & oil compositions -Gas movement very important!!
TRANSECT (about 150 km)
SMI9
N
EI330
WATER
S
GC184
Reservoir Sands
Faults
Sediments - Tertiary
Sediments
(Oligeocene)
Oil & Gas Flow
Salt
Salt
Salt
Salt
Oil & Gas
Sediments -
Jurassic/Cretaceous

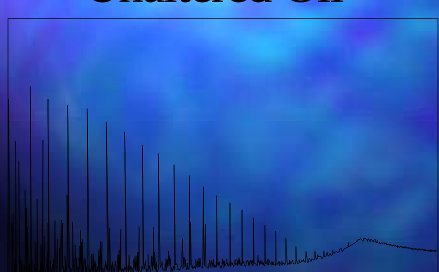
How fast is upward gas flow?

- Subsurface reservoirs - increases in biodegradable oil components occur over short time periods (<10 years). (EI330)
- Rates oil biodegradation at in situ reservoir conditions: a few months to a few years (probably not 100s to 1000s of years)
- If rate charging = rate biodegradation, then rate of gas charging must be much higher than we normally consider

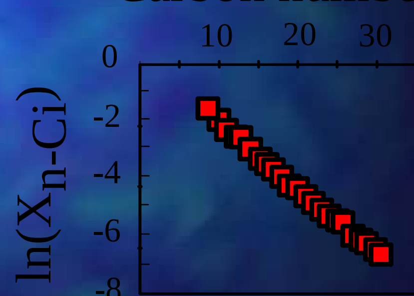
"Gas washing" - Gas flows upward through petroleum reservoirs and fractionates oils in a predictable way (Meulbroek & Losh):

Unaltered oil gives a straight line on a log plot of n-alkane abundance vs carbon number:

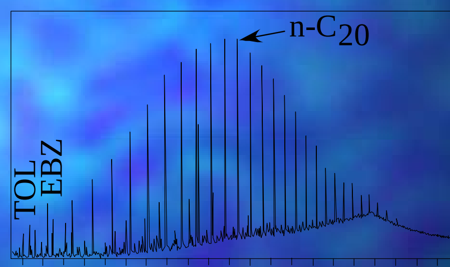
Unaltered Oil



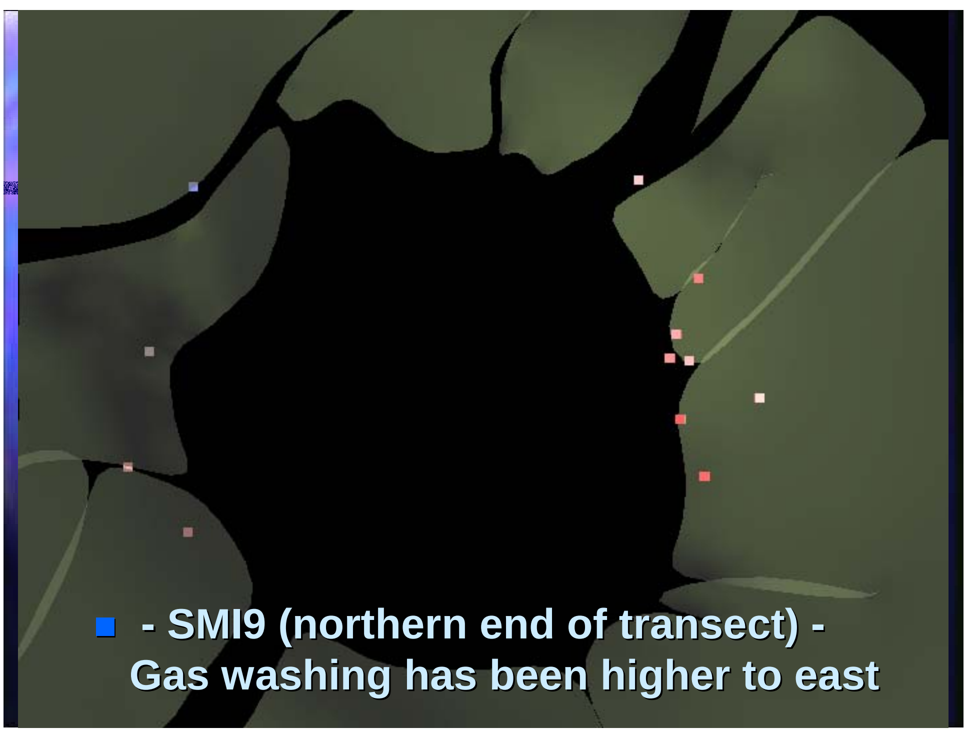
Carbon number

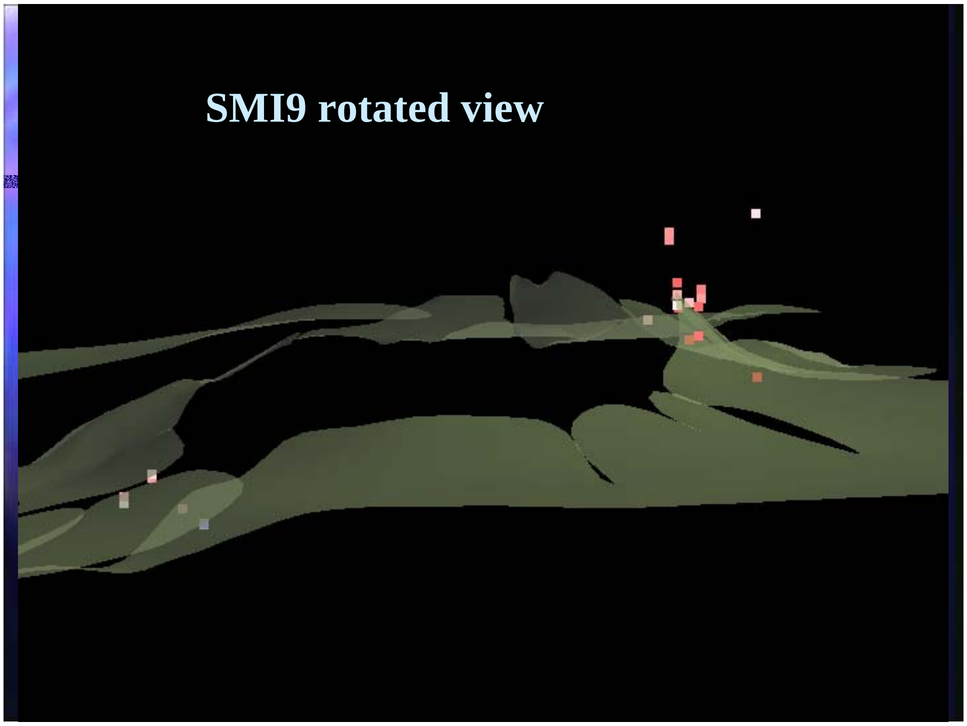


Gas Washing Produces Diagnostic Fingerprint



- Depletion of all light ends while preserving heavier n-alkanes (not biodegradation)
- Preservation of light aromatic compounds (not water washing)





Summary - fluid flow -SMI9 to north:

- Many volumes of gas washing have altered oils in the past
- **Oil charging from deeper more mature more marine sources to East**
- **More gas washing to east**
- **Data consistent with: trapping of oils at greater depth for longer to east (more gas formation- more gas washing)**
- **No present day surface gas seeps at SMI9**

Contrast: GC184 to south

- Reservoirs : Little or no gas washing
  - (but if oil biodegraded at same or greater rate than reservoir charging, n-alkanes would be absent and gas washing would not be observable)
- Surface seeps - huge amount on-going gas movement
- Unbiodegraded oil overlies degraded oil in most reservoirs examined to date
- Oil and gas charging probably occurring now

Conclusions - subsurface:

- Gas migration is or has been very dynamic throughout transect
- Past and on-going movement of large volumes of gas throughout transect very important in determining subsurface oil compositions in reservoirs
- Similar processes probably important in many areas worldwide

Biogeochemistry of Hydrate Sediments and Development of a Pressurized In-situ Pore Water Sampler

L. L. Lapham[1], J. P. Chanton[2], C.S. Martens[3], D.B. Albert[4]

[1]University of North Carolina, Chapel Hill, USA, llapham@email.unc.edu; [2]Florida State University, Tallahassee, USA, jchanton@mailer.fsu.edu; [3]University of North Carolina, Chapel Hill, USA, cmartens@email.unc.edu; [4]University of North Carolina, Chapel Hill, USA, dan_albert@unc.edu

ABSTRACT

The FSU/UNC geochemistry group has three primary objectives: 1. To develop long term in situ porewater sampling devices for deployment at a Gulf of Mexico gas hydrate monitoring station; 2. To determine spatial variability in geochemical processes and chemical distributions at potential monitoring sites for eventual comparison with temporal variability; and 3. To serve as the ground truth for geophysical characterizations. To achieve these goals, we developed an in situ pressurized porewater sampler which was deployed and successfully tested on the Johnson Sea Link this summer. This sampler is capable of collecting a 10 port depth profile of interstitial water and delivering samples to the surface without degassing. Results from this summer's cruise have yielded the highest dissolved hydrocarbon concentrations reported. We are presently evaluating the isotopic composition of dissolved gases to determine the relative importance of petroleum and dissolved methane in supporting microbial respiration at these sites. Microbial respiration was evaluated by measuring rates of sulfate reduction.

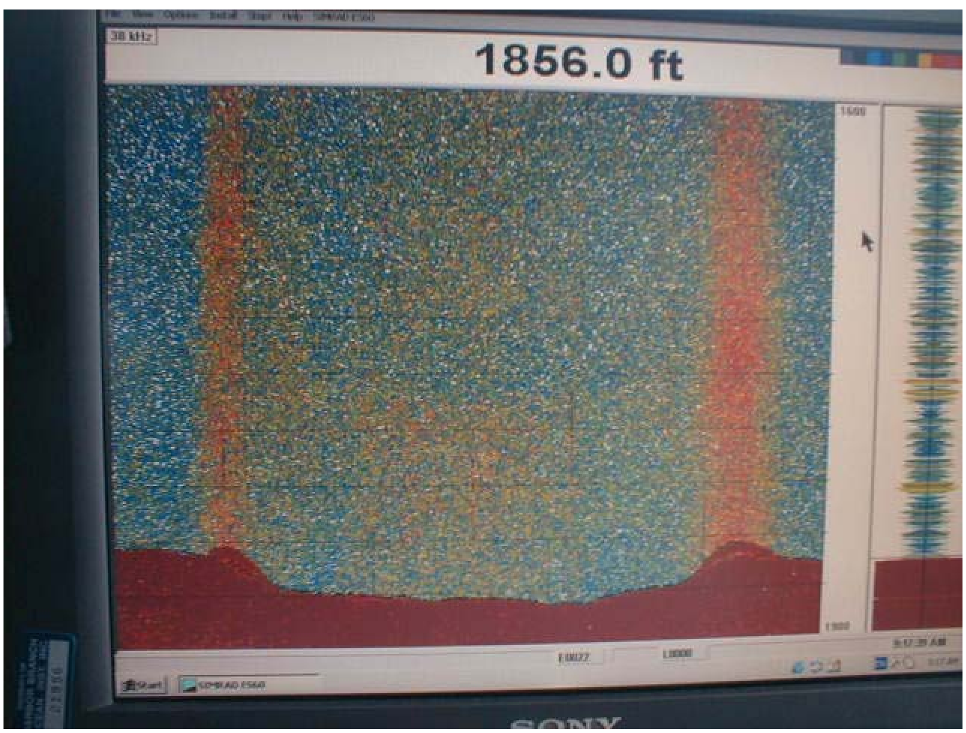
Biogeochemistry of Hydrate Sediments

and

Development of a Pressurized In-situ Pore Water Sampler.

GOM Hydrates Research Consortium

Laura Lapham, Jeff Chanton and Chris Martens
University of North Carolina at Chapel Hill
and Florida State University at Tallahassee



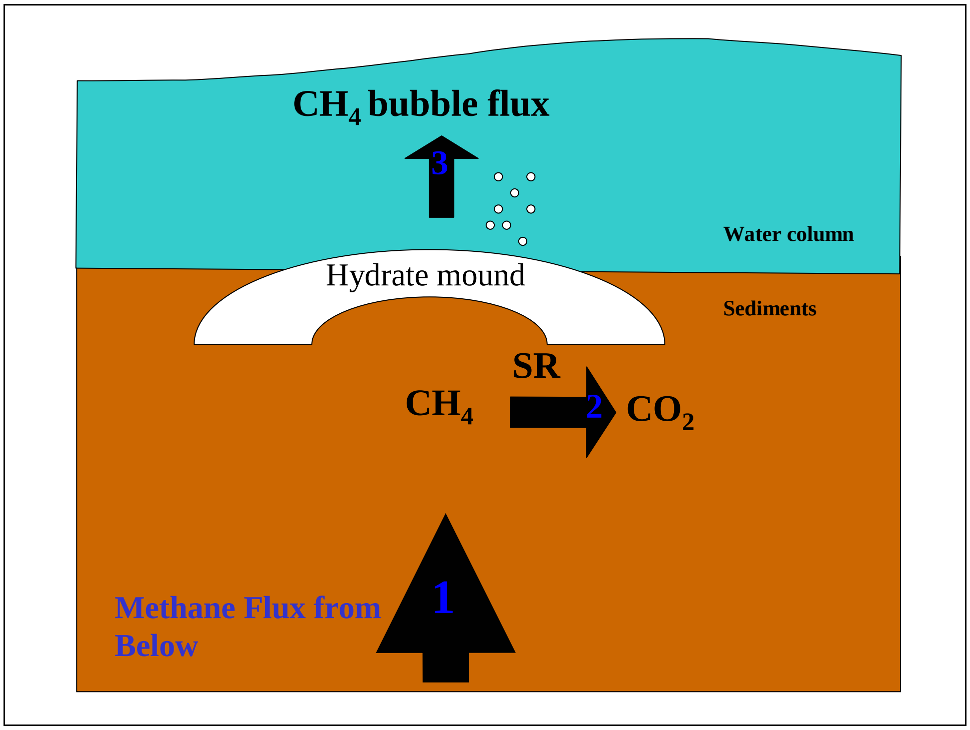
3 Primary Objectives

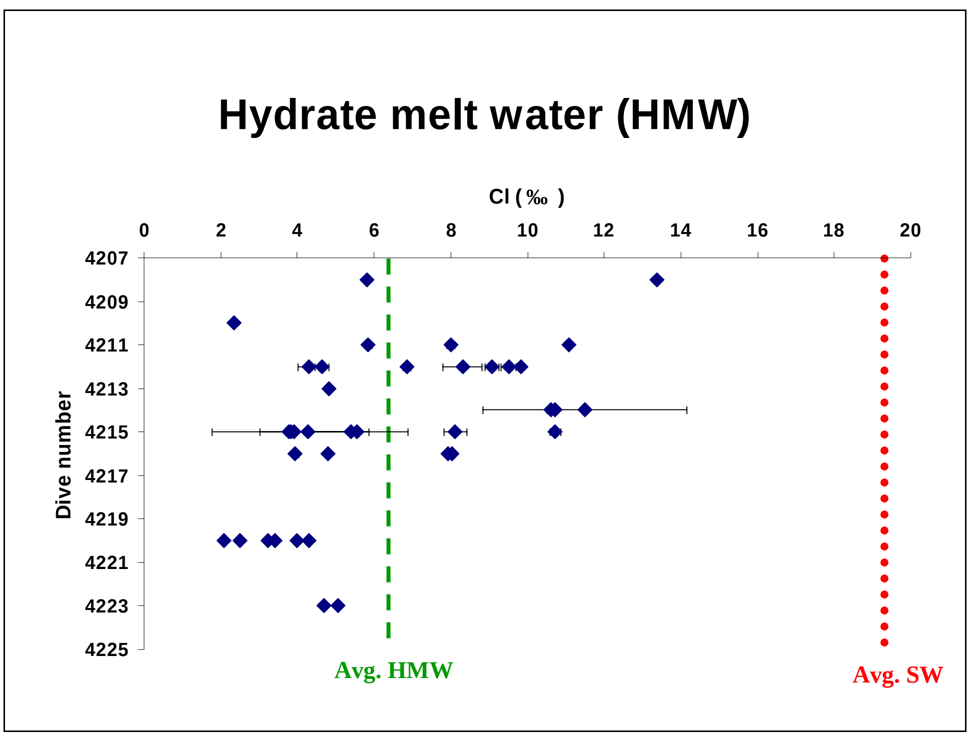
UNC/FSU part of the GOM Hydrates Research Consortium

- to develop long term in situ porewater sampling devices for deployment at a Gulf of Mexico gas hydrate monitoring station
- to determine spatial variability in geochemical processes and chemical distributions at potential monitoring sites for eventual comparison with temporal variability
- to serve as the ground truth for geophysical characterizations

Project Questions

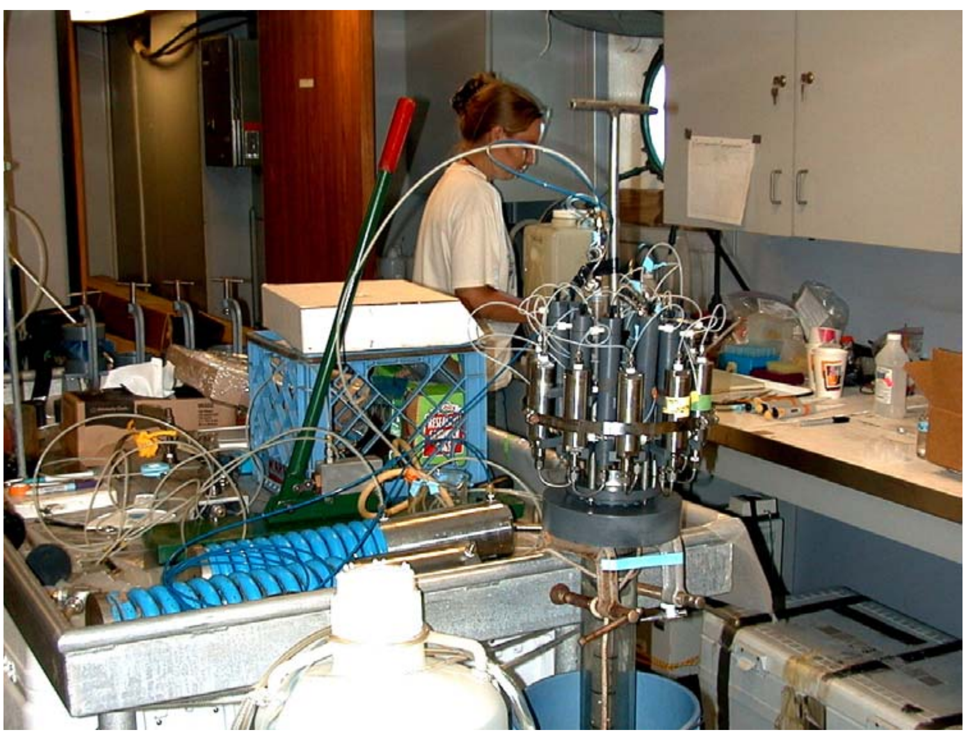
1. What is the source of gas to GOM hydrates?
2. Are GOM hydrates currently forming or decomposing?
3. How do hydrates affect surrounding sedimentary bacterial processes?
4. To what extent does methane consumption drive bacterial processes?

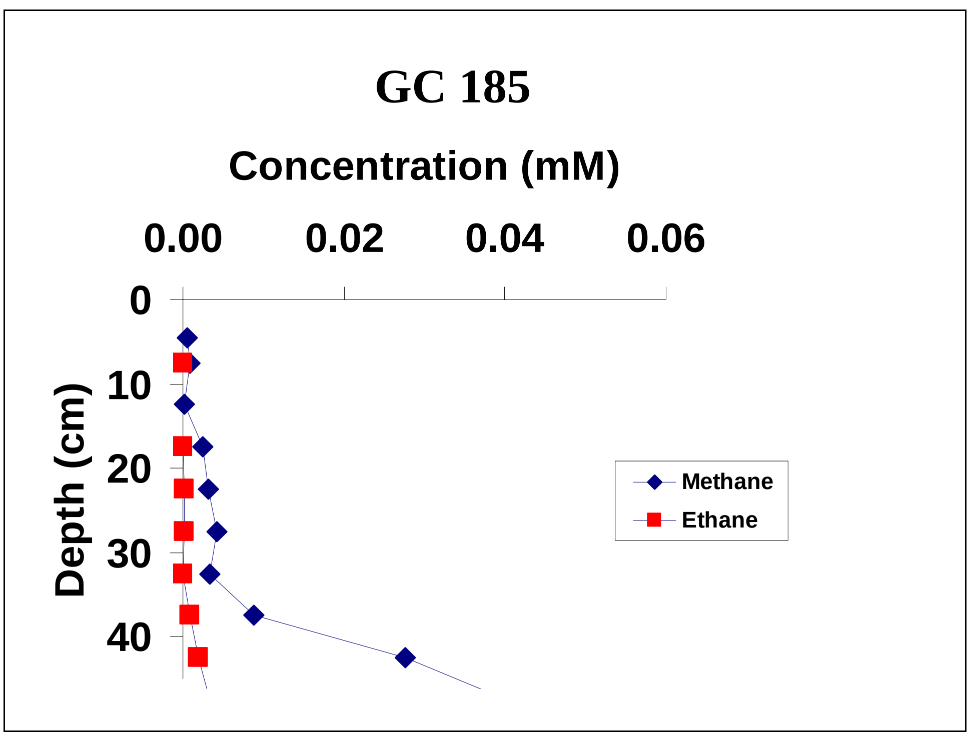

CH4 bubble flux
3
Water column
Hydrate mound
Sediments
SR
CH4
2
CO2
Methane Flux from Below
1

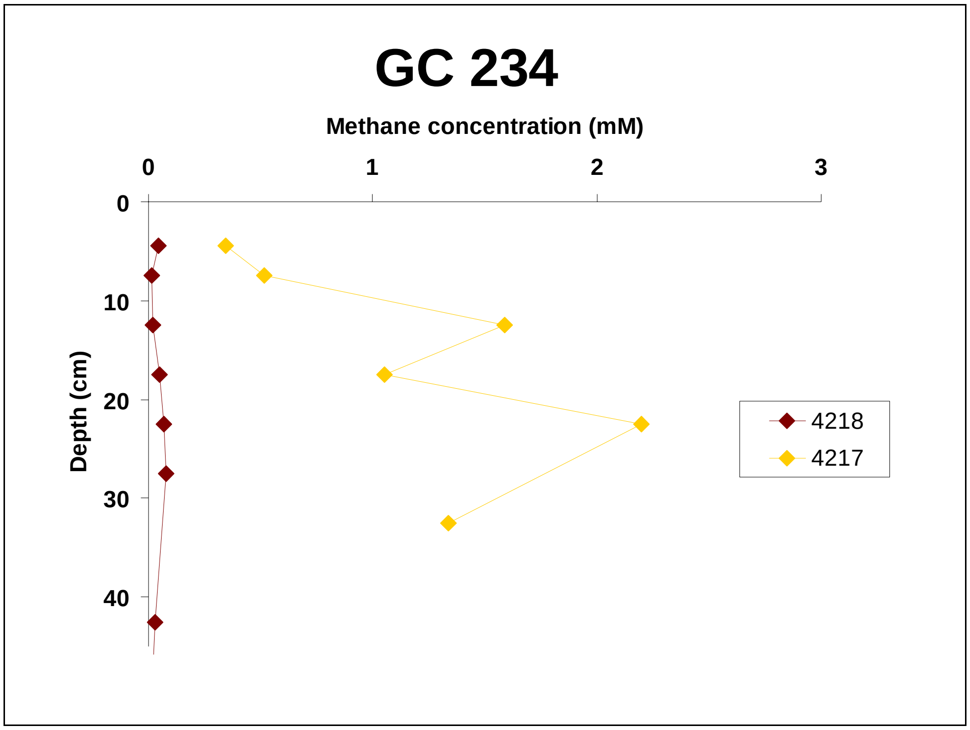

Hydrate melt water (HMW)
Cl (‰)
0
2
4
6
8
10
12
14
16
18
20
Dive number
4207
4209
4211
4213
4215
4217
4219
4221
4223
4225
Avg. HMW
Avg. SW

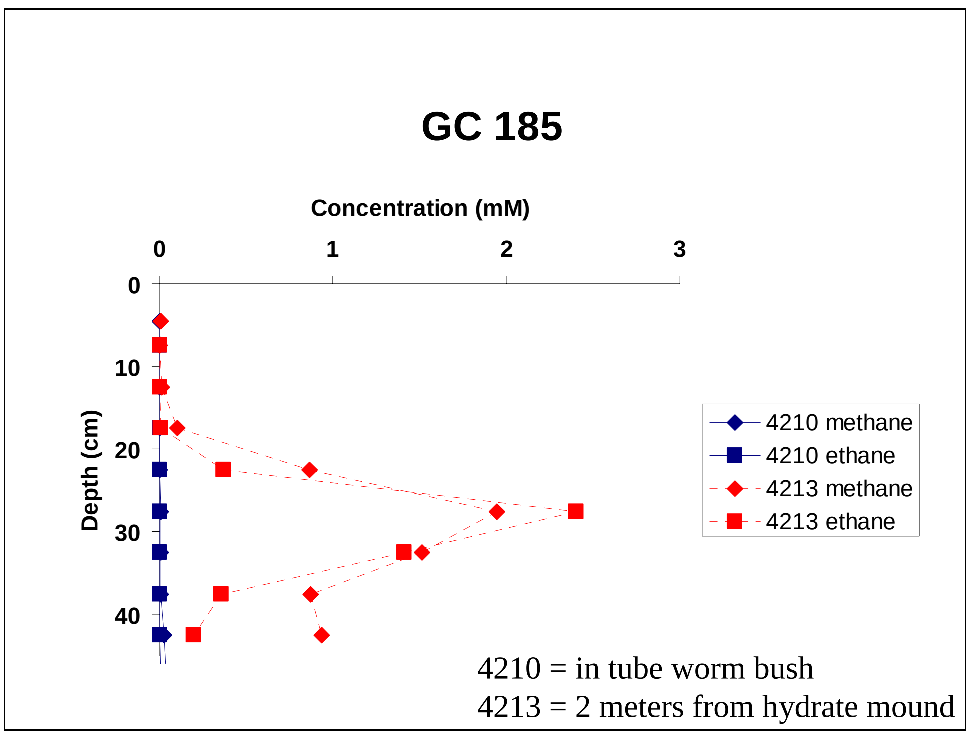
Developing an In-situ pore water sampler

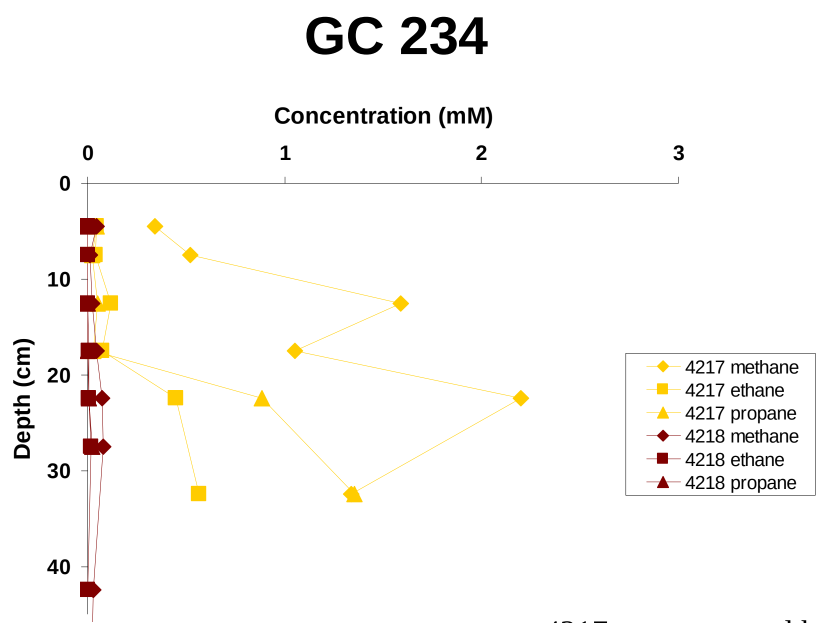
- Should be capable of extracting pore waters from sediments and bringing them to the surface without depressurization and degassing
- Should be able to collect a depth sequence over differing intervals




GC 185
Concentration (mM)
0.00
0.02
0.04
0.06
Depth (cm)
0
10
20
30
40
Methane
Ethane

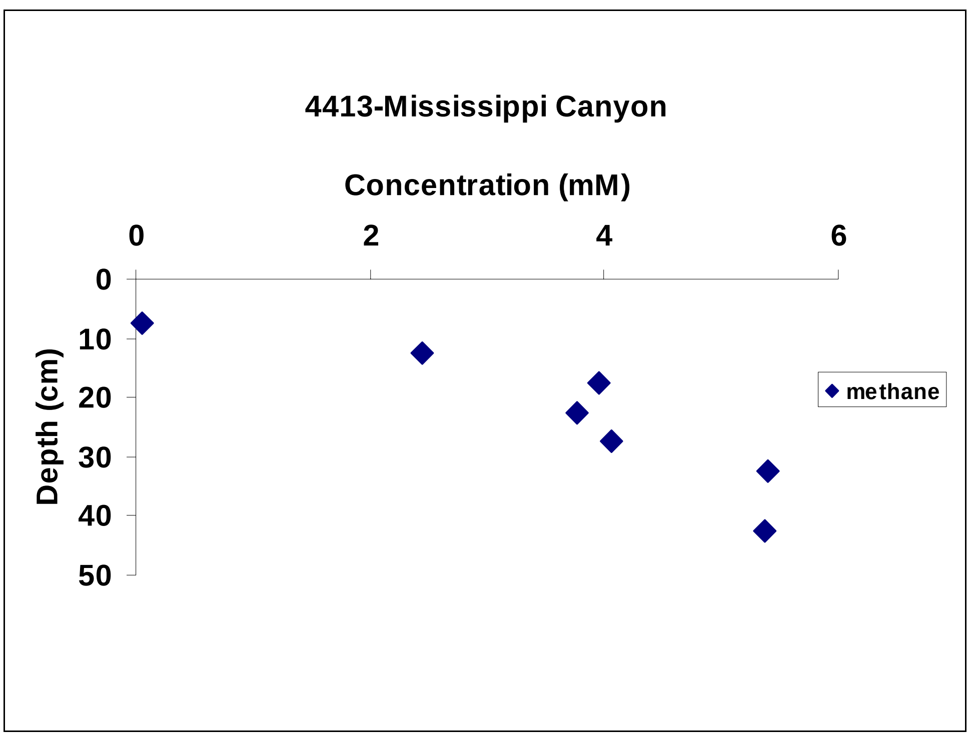

GC 234
Methane concentration (mM)
0
1
2
3
0
10
20
30
40
Depth (cm)
4218
4217


GC 185
Concentration (mM)
0
1
2
3
0
10
20
30
40
Depth (cm)
4210 methane
4210 ethane
4213 methane
4213 ethane
4210 = in tube worm bush
4213 = 2 meters from hydrate mound

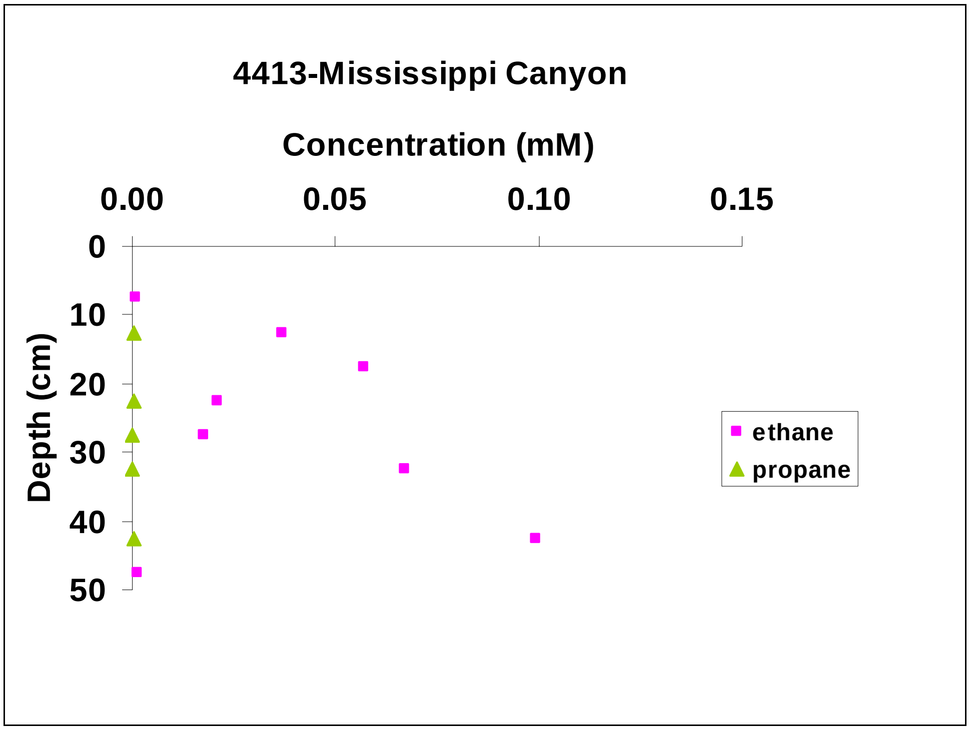


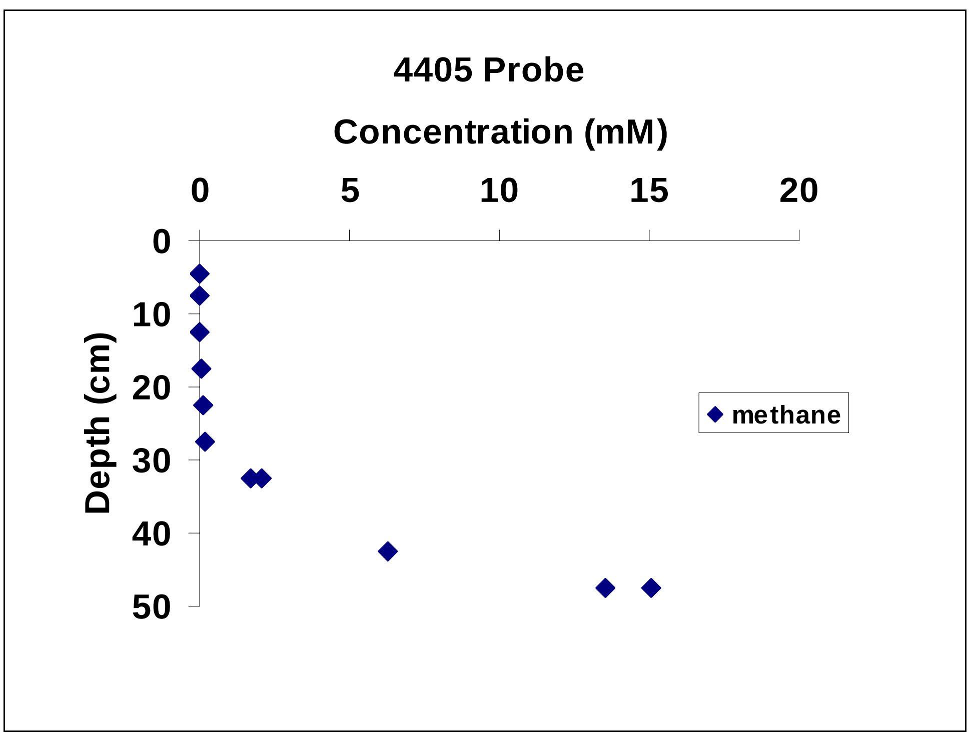
4217 = near mussel bed
4218 = ?

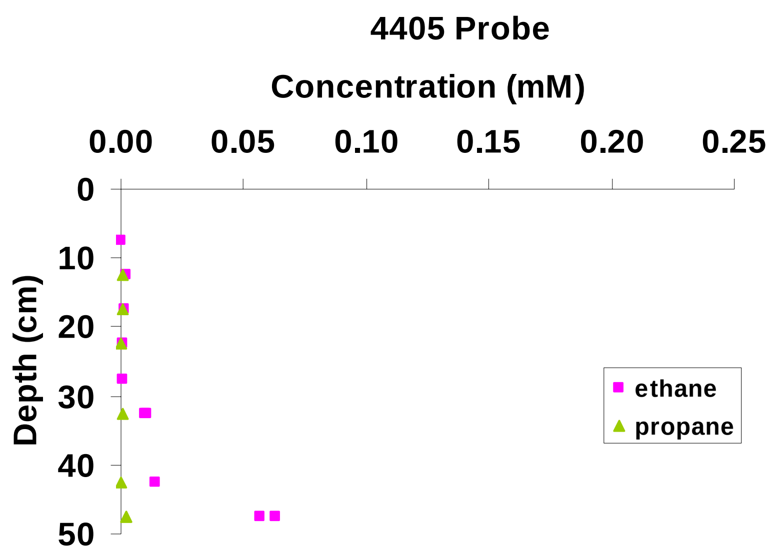
A pressurized probe results in greater concentrations



4413-Mississippi Canyon
Concentration (mM)
0
2
4
6
0
10
20
30
40
50
Depth (cm)
methane


4413-Mississippi Canyon
Concentration (mM)
0.00
0.05
0.10
0.15
0
10
20
30
40
50
Depth (cm)
ethane
propane


4405 Probe
Concentration (mM)
0
5
10
15
20
0
10
20
30
40
50
Depth (cm)
methane

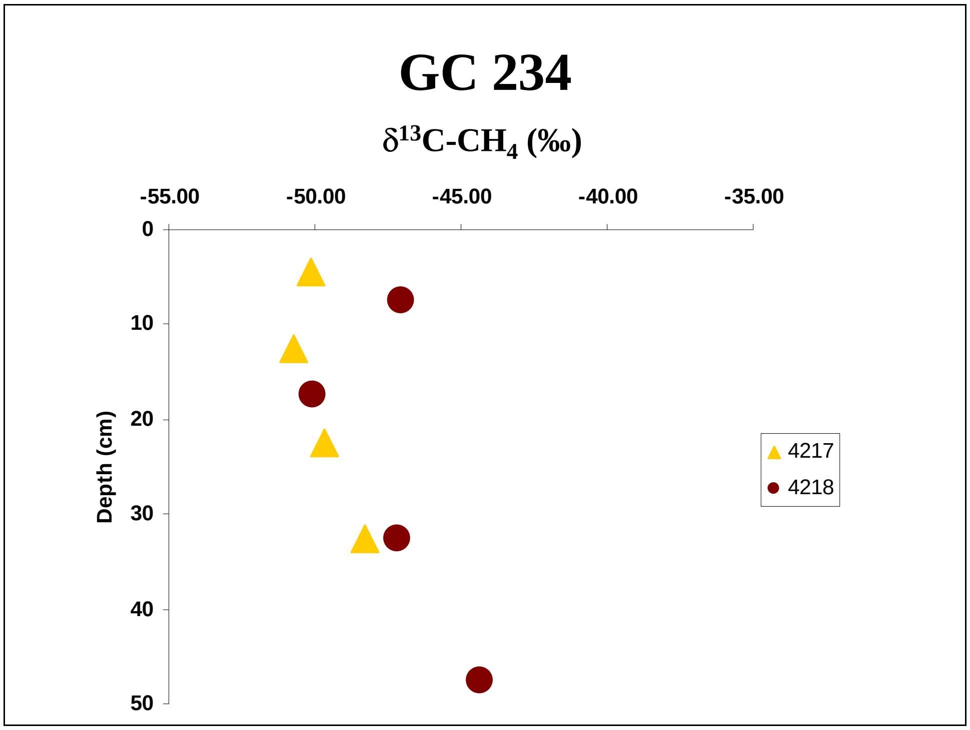


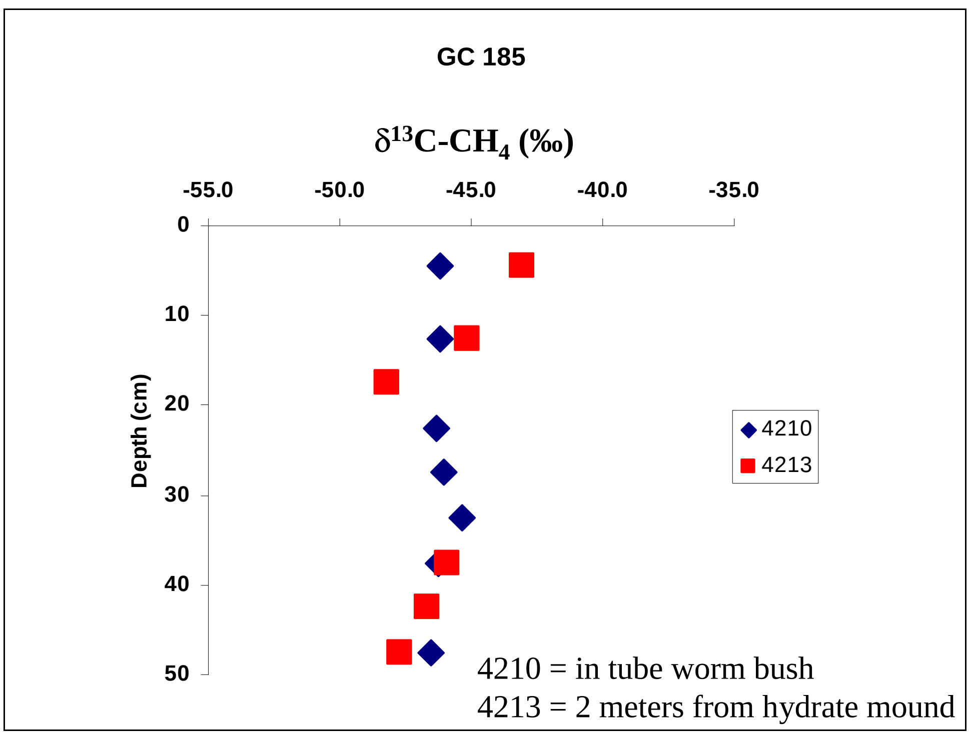
Carbon Isotopes

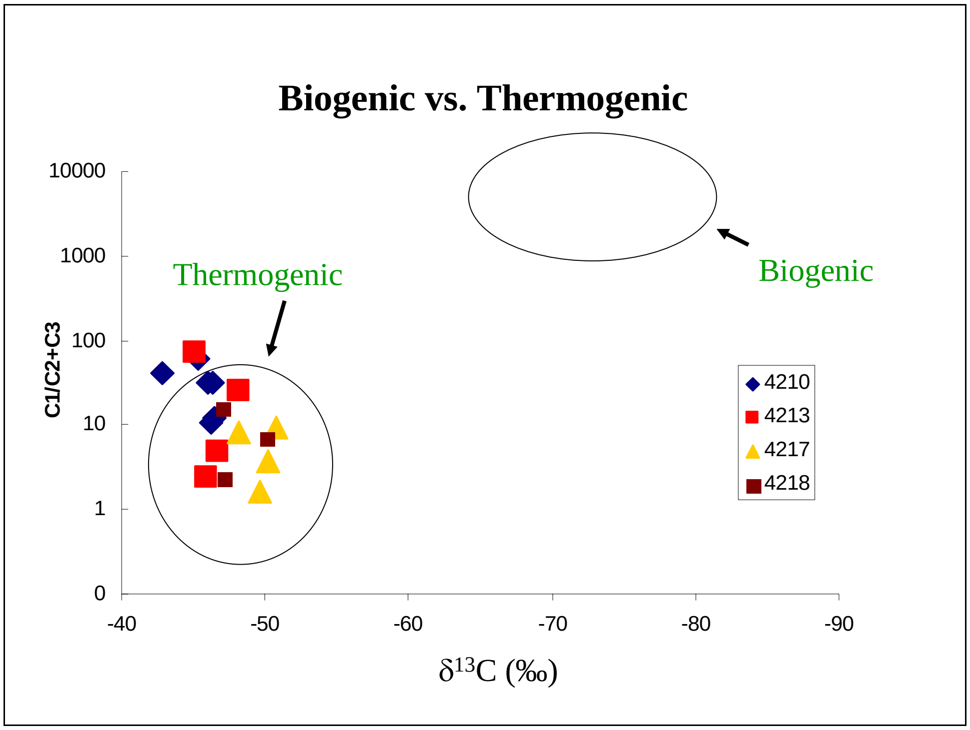
$$\delta^{13}C(‰) = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right] x1000$$

Standard = Peedee Belemnite (PDB)

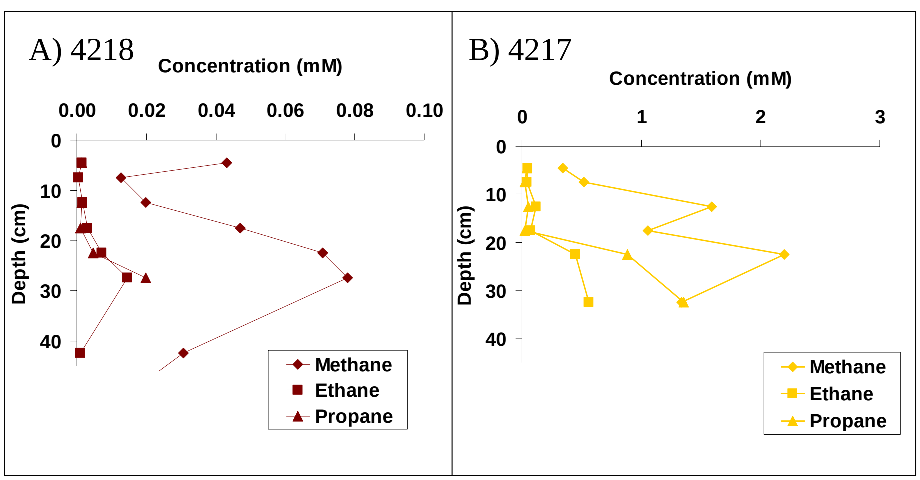
- Reactant becomes enriched in heavy isotope- “heavy”
- Product becomes depleted in heavy isotope- “light”

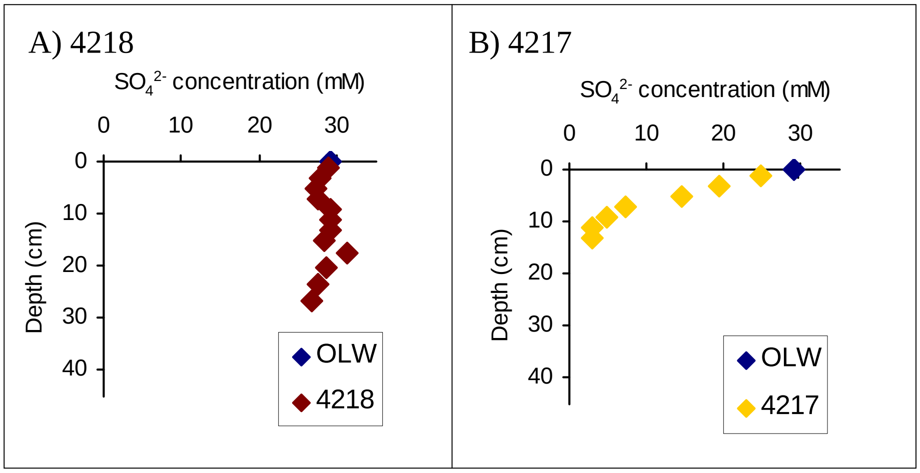

GC 234
δ13C-CH4 (‰)
-55.00
-50.00
-45.00
-40.00
-35.00
Depth (cm)
0
10
20
30
40
50
4217
4218

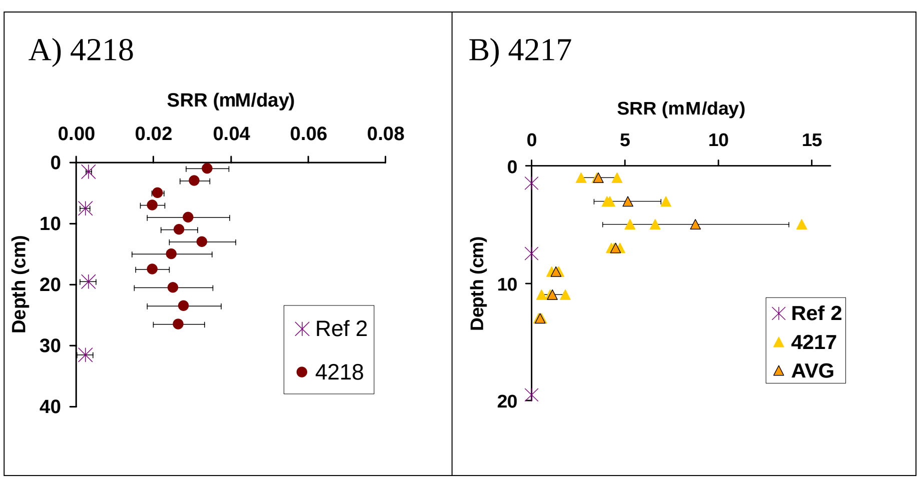

GC 185
δ13C-CH4 (‰)
-55.0
-50.0
-45.0
-40.0
-35.0
Depth (cm)
0
10
20
30
40
50
4210
4213
4210 = in tube worm bush
4213 = 2 meters from hydrate mound

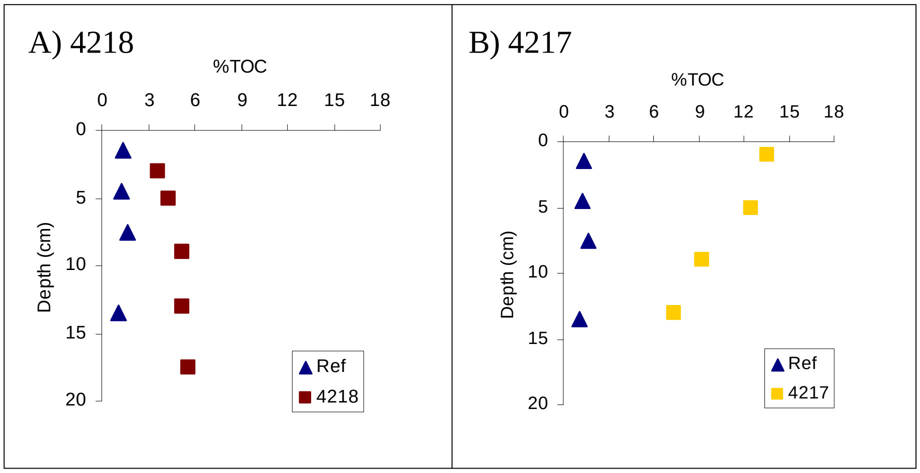


Determining spatial variability

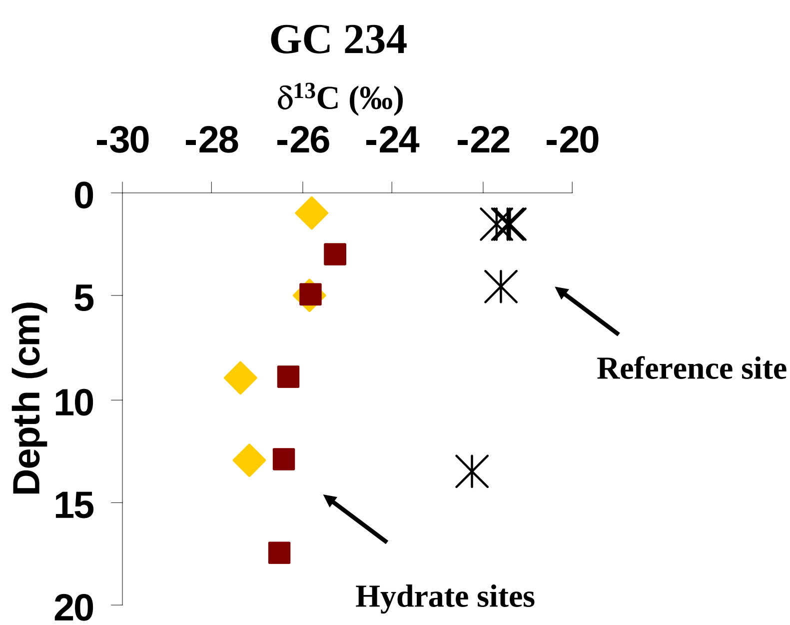


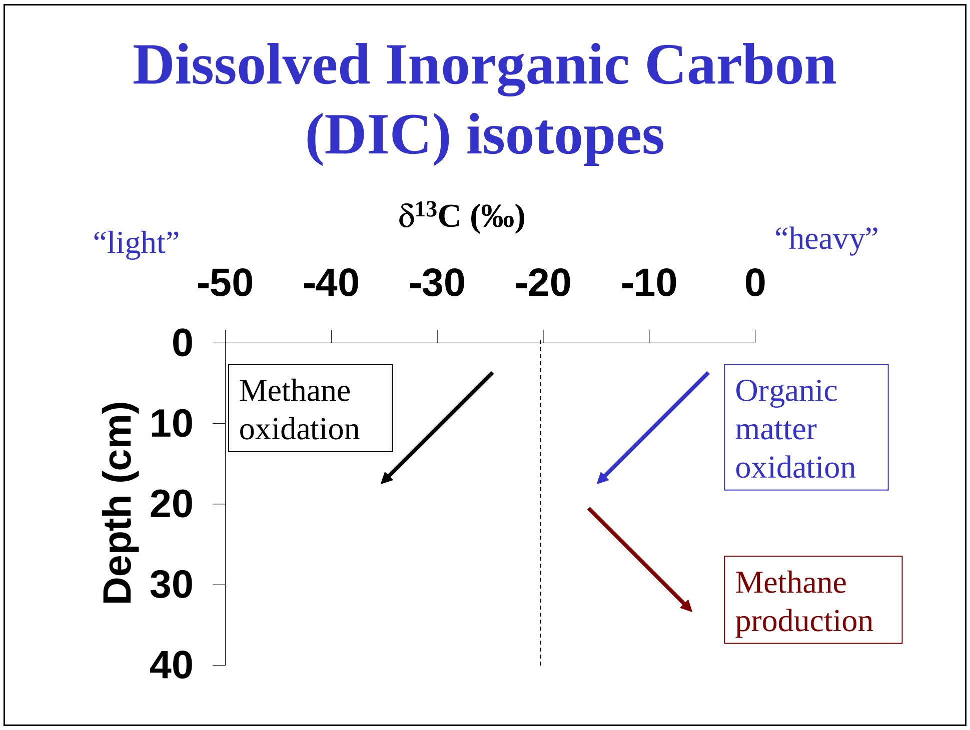

A) 4218
SO$_4^{2-}$ concentration (mM)
0
10
20
30
Depth (cm)
0
10
20
30
40
OLW
4218
B) 4217
SO$_4^{2-}$ concentration (mM)
0
10
20
30
Depth (cm)
0
10
20
30
40
OLW
4217

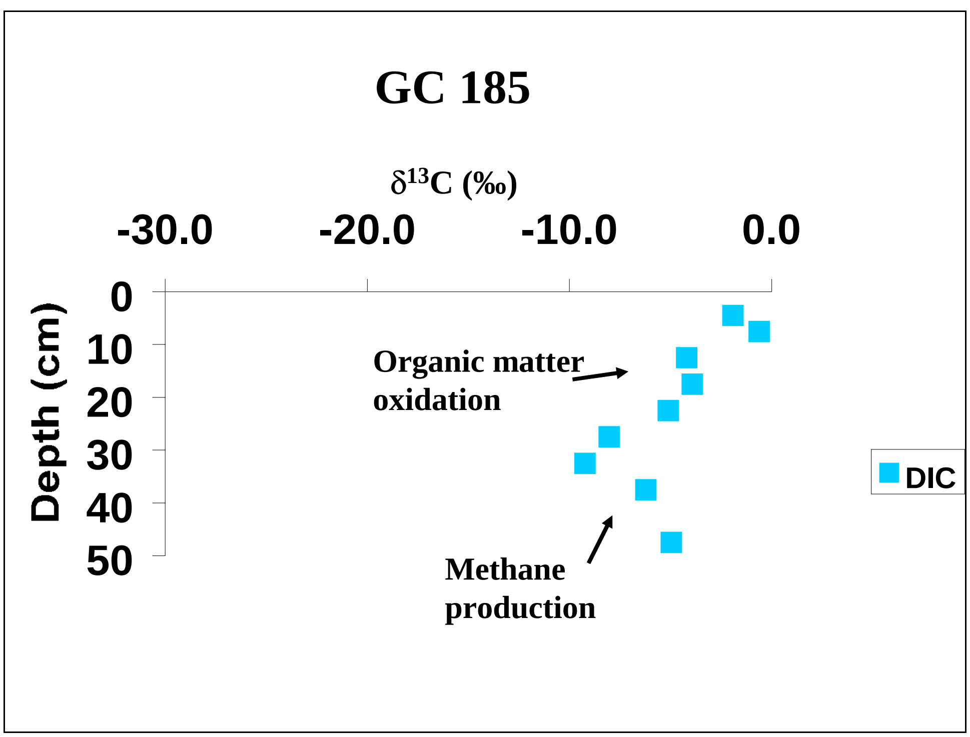

A) 4218
SRR (mM/day)
0.00
0.02
0.04
0.06
0.08
Depth (cm)
0
10
20
30
40
Ref 2
4218
B) 4217
SRR (mM/day)
0
5
10
15
Depth (cm)
0
10
20
Ref 2
4217
AVG

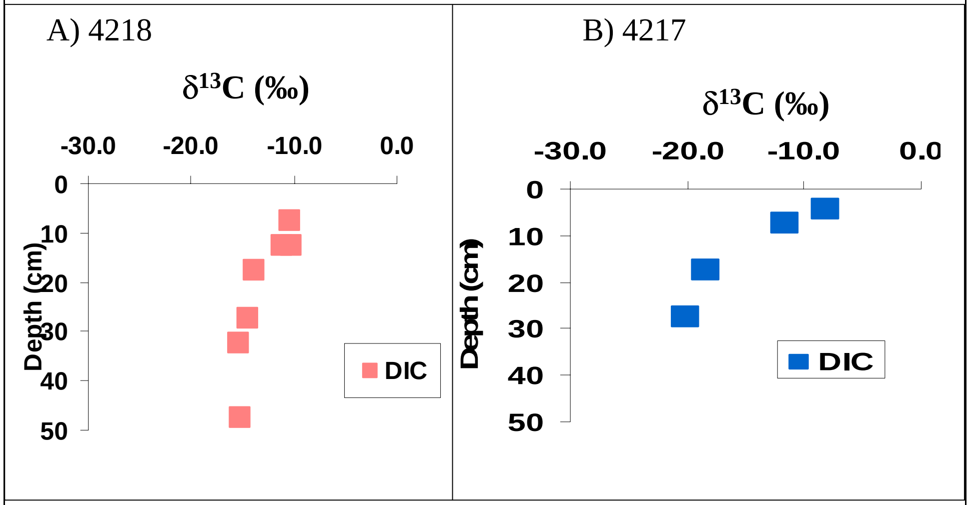


- 40-60% of organic carbon preserved in sediments is "old" carbon (Wang et al., 2001)

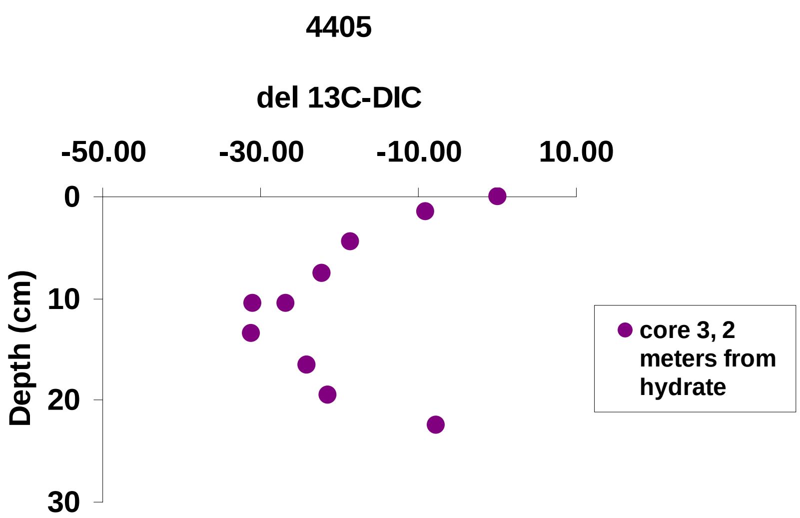


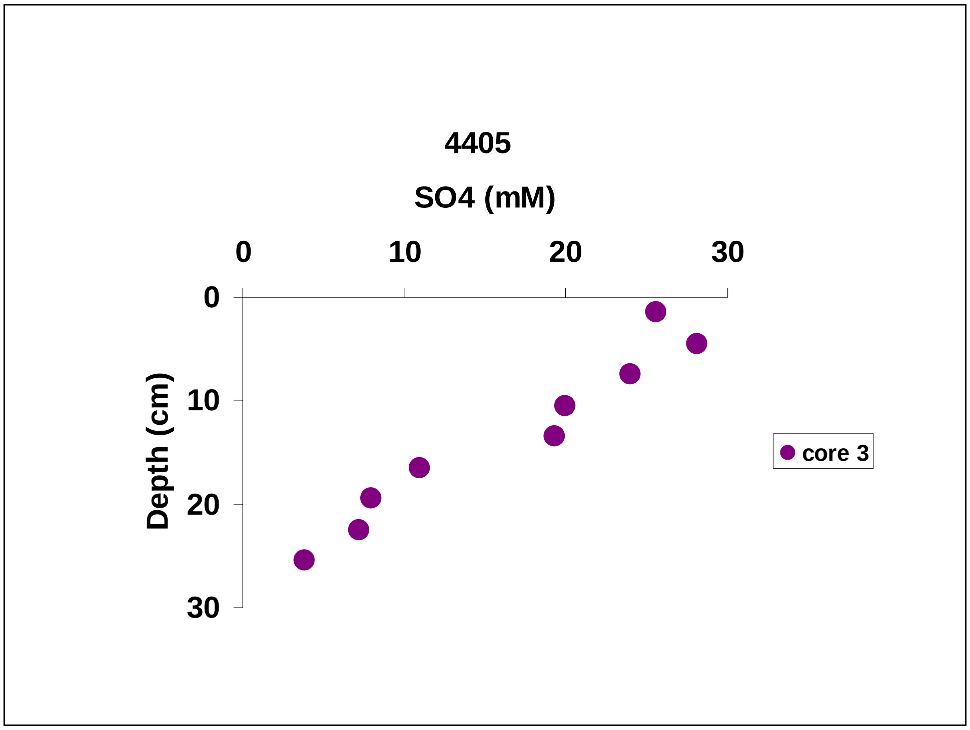

Dissolved Inorganic Carbon (DIC) isotopes
δ13C (‰)
"light"
"heavy"
-50
-40
-30
-20
-10
0
Depth (cm)
0
10
20
30
40
Methane oxidation
Organic matter oxidation
Methane production

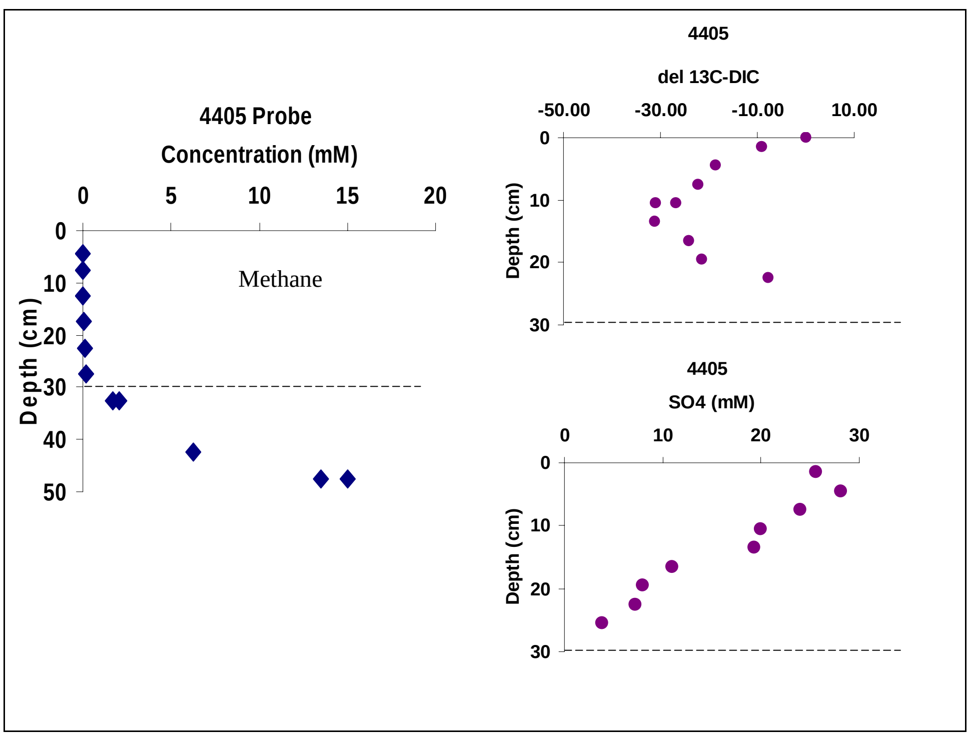

GC 185
δ13C (‰)
-30.0
-20.0
-10.0
0.0
Depth (cm)
0
10
20
30
40
50
Organic matter oxidation
Methane production
DIC

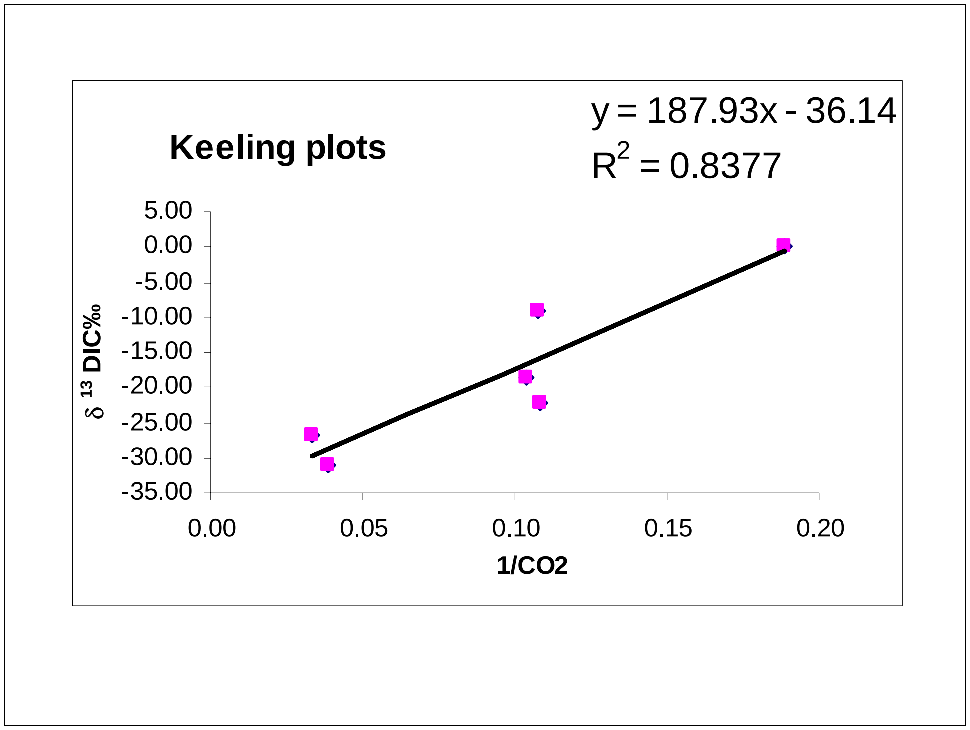


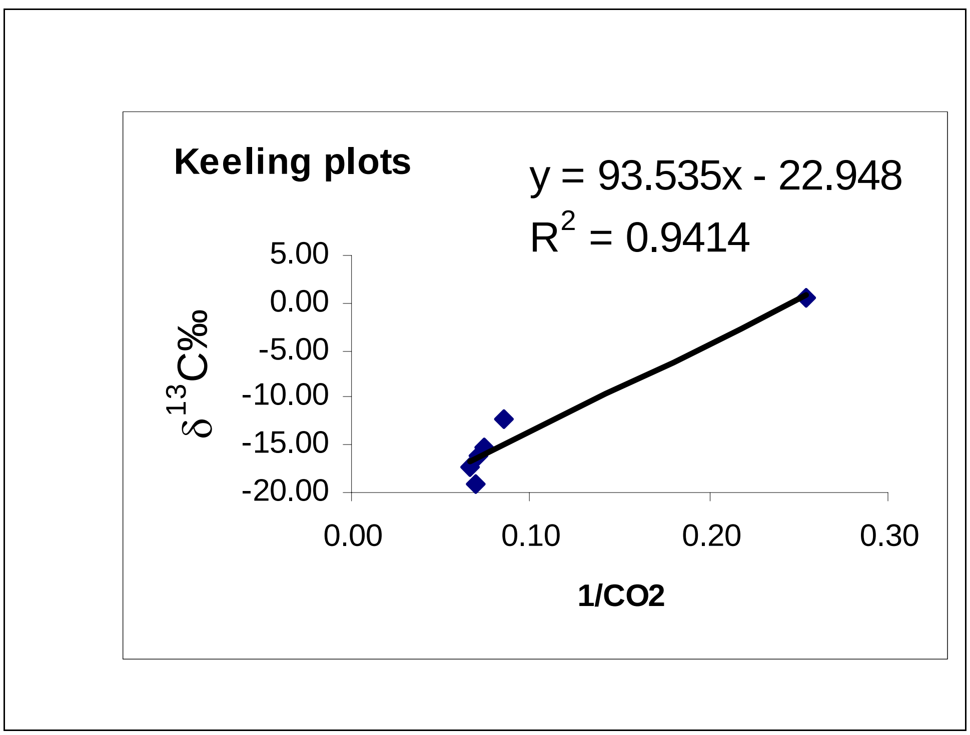
Organic matter or methane oxidation?




4405
SO4 (mM)
0
10
20
30
Depth (cm)
core 3


4405 Probe
Concentration (mM)
0
5
10
15
20
Depth (cm)
10
20
30
40
50
Methane
4405
del 13C-DIC
-50.00
-30.00
-10.00
10.00
Depth (cm)
4405
SO4 (mM)
0
10
20
30
Depth (cm)

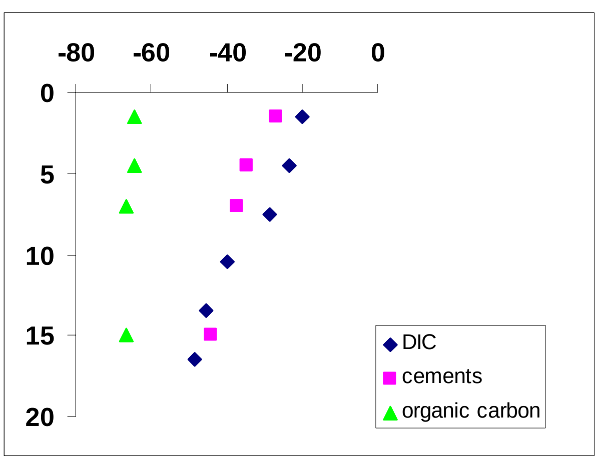

Keeling plots
y = 187.93x - 36.14
R2 = 0.8377
δ 13 DIC‰
5.00
0.00
-5.00
-10.00
-15.00
-20.00
-25.00
-30.00
-35.00
0.00
0.05
0.10
0.15
0.20
1/CO2


Keeling plots
y = 93.535x - 22.948
R2 = 0.9414
δ13C‰
5.00
0.00
-5.00
-10.00
-15.00
-20.00
0.00
0.10
0.20
0.30
1/CO2

Cement $CaCO_3$ **$\delta^{13}C$ ‰**

Sample ID	**δ 13C**
Bucket 3, 709, Miss. Canyon, 4413	-23.8
4405, 5/30/02, Rock	-20.5
4401, 5/29/02, Carbonate	-22.0
4413, Core 6 Rocks from 6-9 cm 6/3/02	-26.8
4403, #6, 27 cm carbonate, 5/29/02	-18.0
GC 232, 4403, core #4, carbonate at 21 cm	-14.6
4401, Core #2, 5/29/02, carbonate	-18.0
4405, 5/30/02	-22.0
4408, 6/1/02 Offshore 65-1	-49.7
4413, 118 Miss. Canyon 6/3/02	-28.6
Gc 234, 4407, 5/31/02 smaller of 2 rocks	-20.4
4413, Miss Canyon, Block 3/6/02, 709, Bucket 9	-28.2

West Florida Scarp Profiles Considerably More Negative




Clark
(probe)

Methanogens in Hydrate-Bearing Sediments: Who's There and How Active Are They?

F. S. Colwell, D. Reed, M. Delwiche, S. Boyd

Idaho National Engineering and Environmental Laboratory, Biotechnology Department

ABSTRACT

Studies of sediments that contain hydrates often reveal the presence of microorganisms by either direct detection or by the chemistry of the gases. Knowledge of the types of microbes present in these sediments as well as their in situ activities is essential for predicting hydrate distribution and the rates at which methane is made in these sediments. Models that seek to describe the rate of hydrate formation or the amount of methane supply in the sediments frequently account for the activity of methanogens. However, there are no reliable values for the actual rate of methane production in the sediments leaving the models unconstrained by this variable. Our microbiological studies of hydrate bearing sediments focus on: 1) molecular characterization of the cells present and 2) their in situ activities. We have found that the deep sediments of the Nankai Trough contain diverse archaea and bacteria at various depths above, within, and below the hydrate stability zone. Many of these sequences (all of the archaea and 90% of the bacteria) are represented by unique groups or clades that are <95% similar to known cultured cells. These data are distinct from results of similar studies of hydrate-associated sediments from the Gulf of Mexico and the Cascadia Margin in which many of the sequences were quite similar to cultured organisms. In those studies about 75% of the bacterial sequences from the Gulf of Mexico and >85% of the bacterial clones from Cascadia Margin were >97% and >95% similar to known cells, respectively. That microbial cells can be detected and will produce methane when grown in the lab indicates that they survive in these sediments. Furthermore, the presence of biogenic methane in the sediments suggests that some low level of in situ activity adds methane to the hydrates. Typically, laboratory derived microbial metabolic rates are far higher than actual values that occur under in situ conditions. Thus, the mean rates of methanogenesis in deep sediments must be exceedingly low; perhaps as much as six orders of magnitude lower than values obtained in the lab. Our current work focuses on deriving realistic methane production rates for these communities by determining the numbers of methanogens in the sediments at specific depths and the lowest rate of methanogenesis possible when these cells are starved. These results will lead to estimates of the "biological volumetric productivity" of the sediments where the hydrates occur.

Idaho National Engineering and Environmental Laboratory

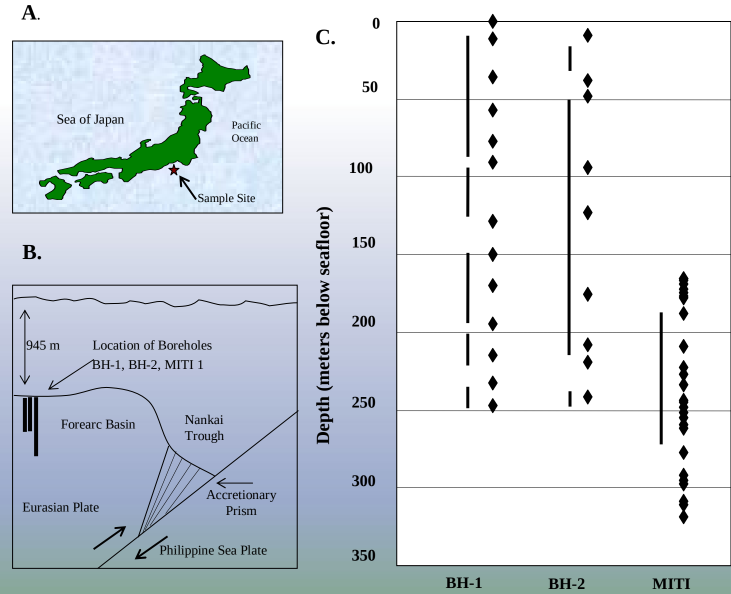
Methanogens in Hydrate-Bearing Sediments: Who's There and How Active Are They?

F.S. Colwell, D. Reed, M. Delwiche, S. Boyd
Idaho National Engineering and Environmental Laboratory

Acknowledgements: Japanese Petroleum Exploration Co., INEEL Laboratory Directed Research and Development, U.S. Department of Energy, Office of Fossil Energy

Methanogenesis and hydrates

- ***Biogenic methane is important (how important?)***
- ***Microbial communities present in and around hydrated sediments***
- ***Methane source locations are unknown but may be:***
  - ***In situ, proximal to hydrates***
  - ***At some distance from the hydrates***
- ***Objective: Evaluate*** **potential** ***methane production by methanogens from different sediment depths under varied thermal and energy substrate conditions***



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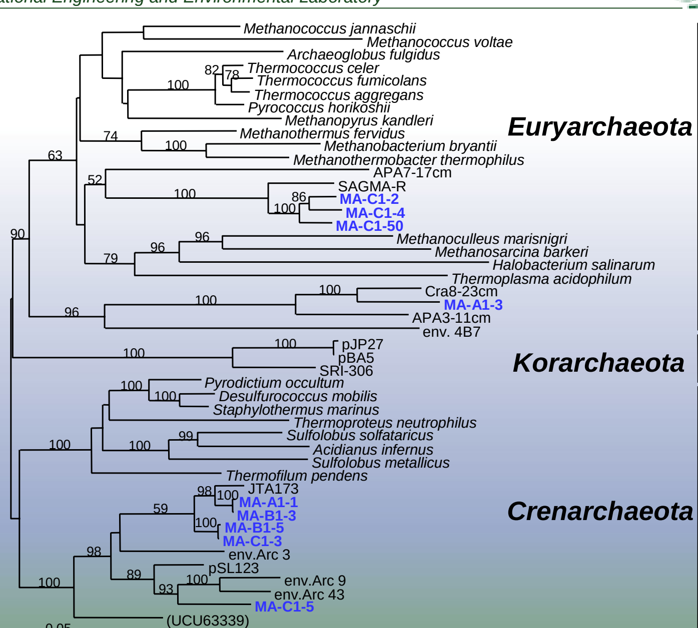

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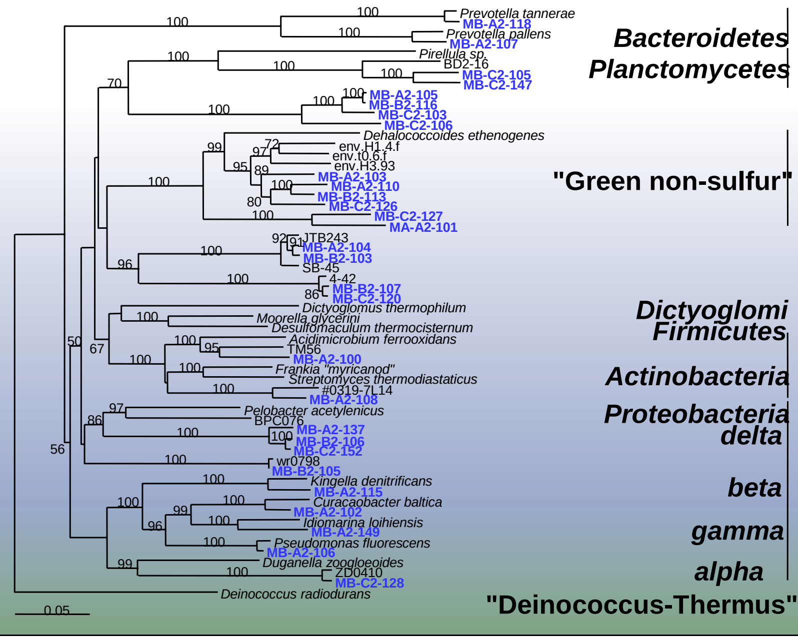

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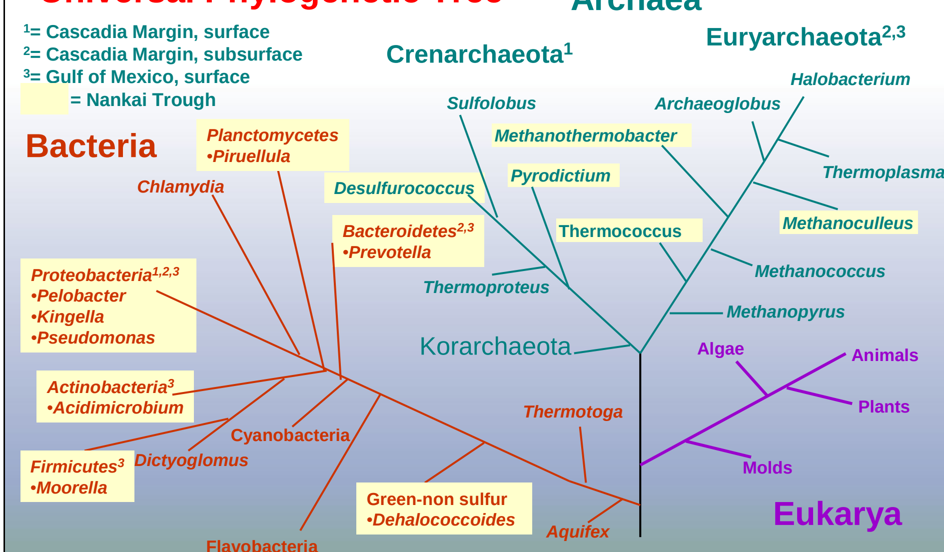
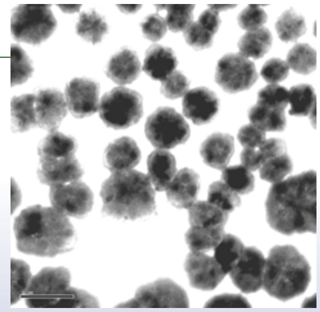
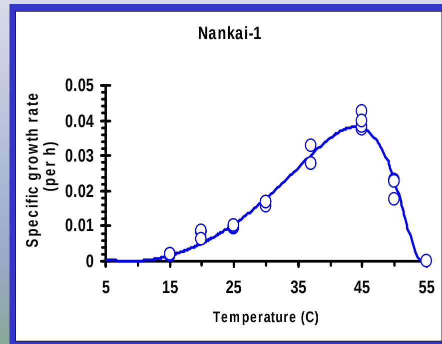
Universal Phylogenetic Tree

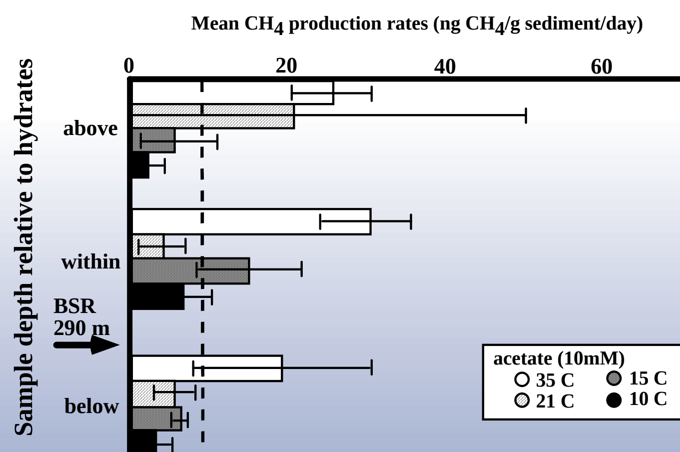


Methanoculleus marisnegri *Nankai-1*



- *Member of Euryarchaeota, Order Methanomicrobiales*
- *99% similar to type strain M. marisnegri JR1 (from Black Sea sediments) by 16S rDNA*
- *From 247 mbsf; ca. 16°C, 120 atm*
- *0.5-2.0 μm in diameter*
- *Grows on H_2/CO_2 or formate; requires acetate*
- *Specific growth rate highest at 45°C, pH 5.5-7.6; halotolerant*





- *Highest mean rates at 35°C incubations but not significantly higher*
- *Higher rates not always associated with higher temperatures*
- *Often 10°C incubations with the lowest rates; always lower than unamended controls*

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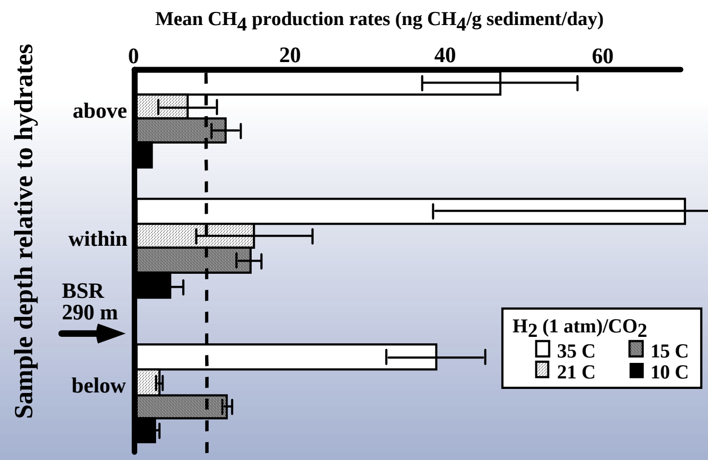

- *Highest mean rates at 35°C incubations; one value of 110 ng/g/day*
- *Higher rates not always associated with higher temperatures*

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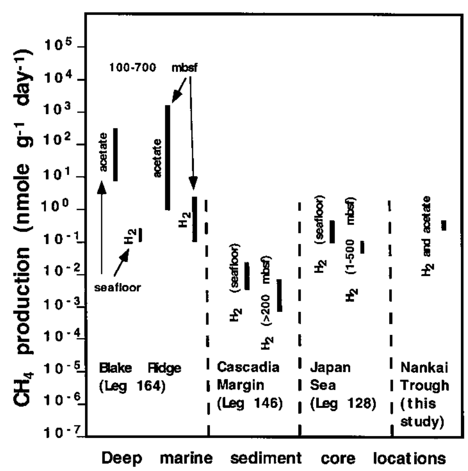
Realistic rates?

At 5 ng CH_4/g/day (10°C) need only 5500 yrs to convert 1% total organic carbon to CH_4

Yet, residual organic carbon exists in these sediments, which are as old as 1.7 million years

In situ methanogenic rates are much lower, unless these cells receive unaccounted sources of energy and carbon



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

Modeling of hydrates needs biological data

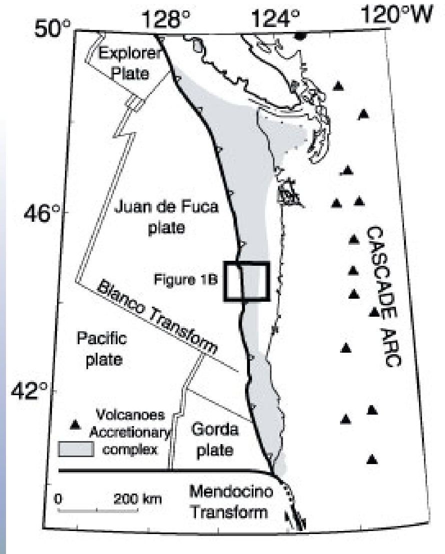
- *Models predicting occurrence, distribution, and quantity of methane hydrates in sediments include a biological component:*
  - *Davie and Buffett 2001: "…key parameters in this model are the rate of sedimentation, the quantity and quality of the organic material, and a rate constant that characterizes the vigor of biological productivity."*
  - *Xu and Ruppel, 1999: Biogenic methane gas production rates contribute to the primary methane supply and can assist estimates of the timescale for hydrate accumulation*
- *Catabolic, geochemical, and thermodynamic rate estimates*

Hypothesis

- *In situ rates of biogenic methane production can be estimated using a combination of methanogenic catabolic rate models and thermodynamic experiments to understand constraints*

Objectives

- *Collect samples from the Mallik 5L-38 and ODP Leg 204 cores for microbiological analysis*
- *Enumerate methanogens in sediments (CoM, real time PCR)*
- *Determine methane output of model methanogens under energy constrained conditions in biomass recycle reactors*
- *Determine methanogenic activity at realistic subsurface pressures and substrate/product concentrations when ΔG_{rxn} is just positive or just negative*

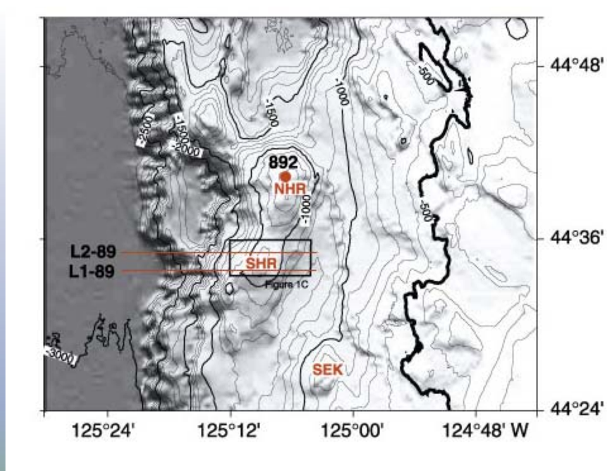


ODP Leg 204 July-September, 2002

Map of Cascadia subduction zone.

Idaho National Engineering and Environmental Laboratory

ODP Leg 204



Bathymetric map of the Cascadia accretionary prism in the vicinity of Hydrate Ridge

NHR: North Hydrate Ridge
SHR: South Hydrate Ridge
L2-89, L1-89: seismic traces
SEK: Southeast Knoll
892: borehole from ODP leg 146 (1992)

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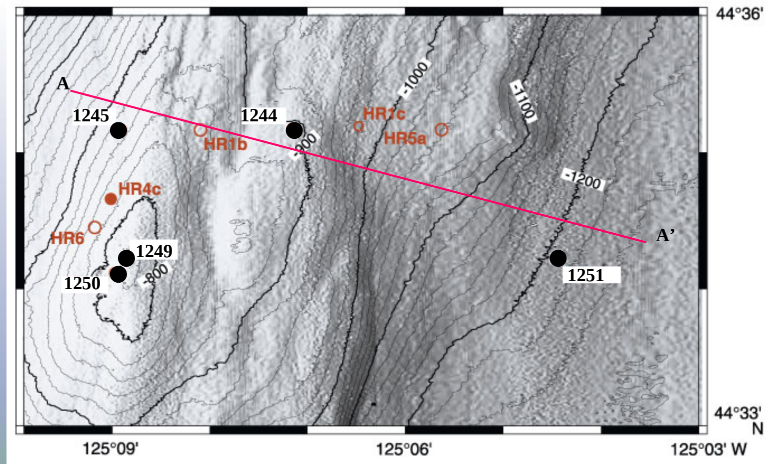
Bathymetric map of Hydrate Ridge coring sites from which samples were taken for microbiology. Section A:A' shown in next slide



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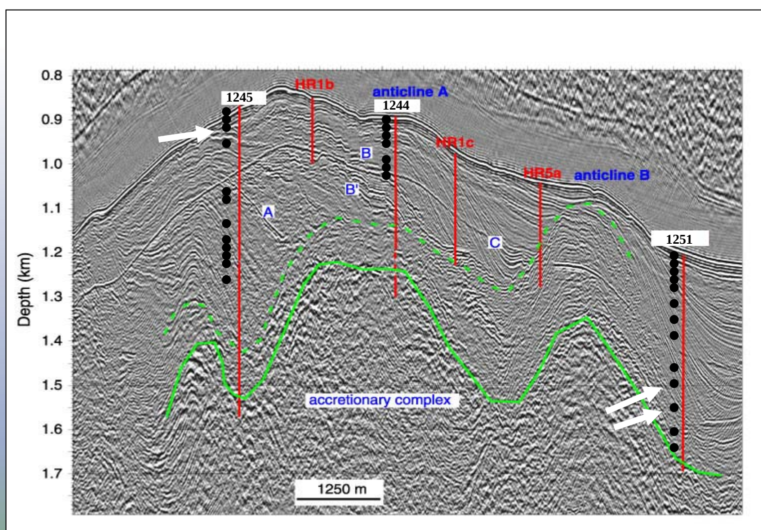
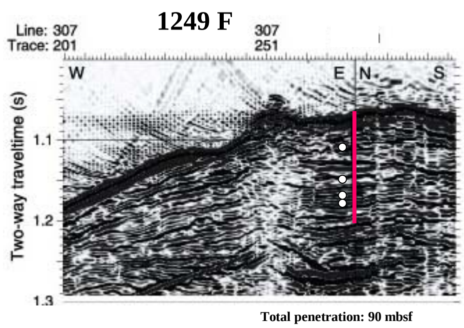
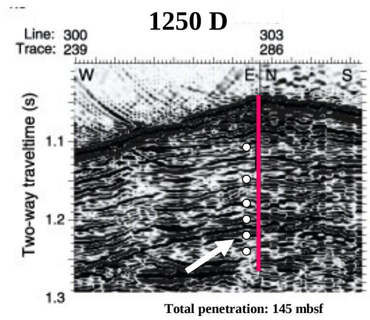
Section A:A' ***Microbiology sample locations shown. Arrows indicate preliminary analyses for methanogens.***



"L" seismic profiles of sites 1249 F and 1250 D near the summit of South Hydrate Ridge. Location of microbiology samples indicated.





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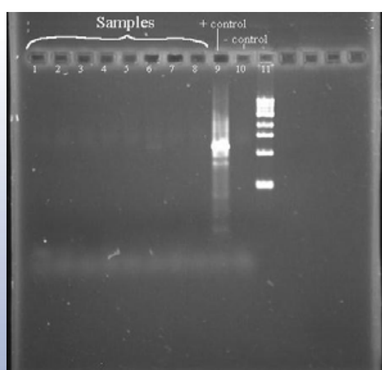
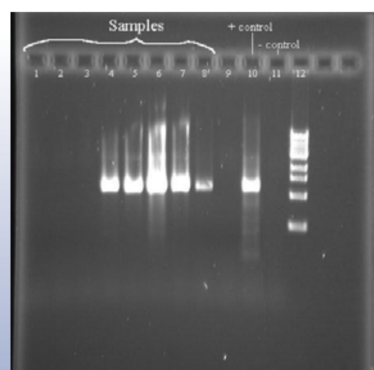
Hydrate Ridge: A Low Methanogen Biomass System?

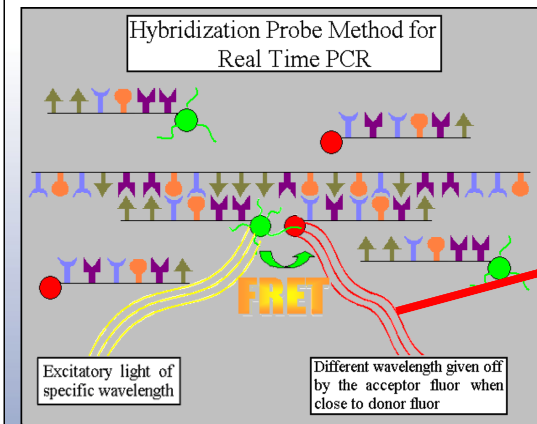


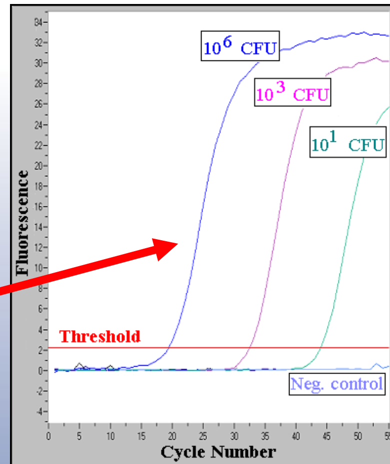
Amplification using methanogen-targeted 16s primers



Amplification using a nested approach (archaeal primers followed by the same 16s primers)

Quantification using RT-PCR





A signal is only given when the 2 primers and 2 probes all align in the right spots

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

Summary

- ***High microbial diversity*** *in/near hydrates*
- *In culture, methane produced at* ***higher temperatures*** *than "capture depth"*
- ***In situ methanogenic rates are likely far lower than laboratory estimates***
- *Future directions include determining how much methane can be made when cells are:*
  - ***1) at maintenance level activities typical of the subsurface (catabolic rate estimates)***

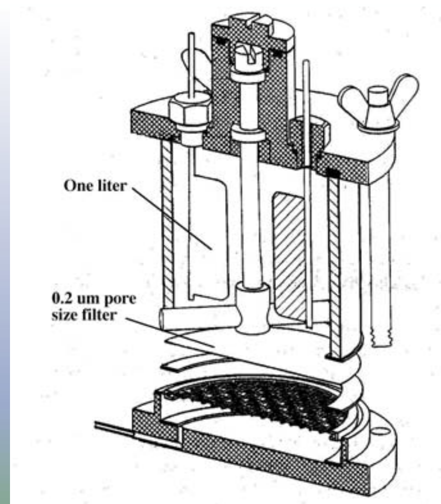
  maintenance energy demand = substrate provision rate ÷ biomass
  - ***2) thermodynamically constrained - at the threshold of their ability to survive***
- ***Expected product: Methanogenic volumetric productivity*** *for researchers seeking realistic biological activity terms needed for* ***hydrate distribution and production models***

Biomass Recycle Reactor

- ***Assumption: Batch reactors and chemostats work poorly for defining behavior of slowly growing microorganisms. Need to study post-exponential phase when cells are chronically starved.***

- ***100% biomass retention, filtrate removed at rate that substrate is provided***
- ***Biomass is constant at low activity levels***
- ***Reactants/products measured in filtrate***

Figure from Tappe et al. 1996



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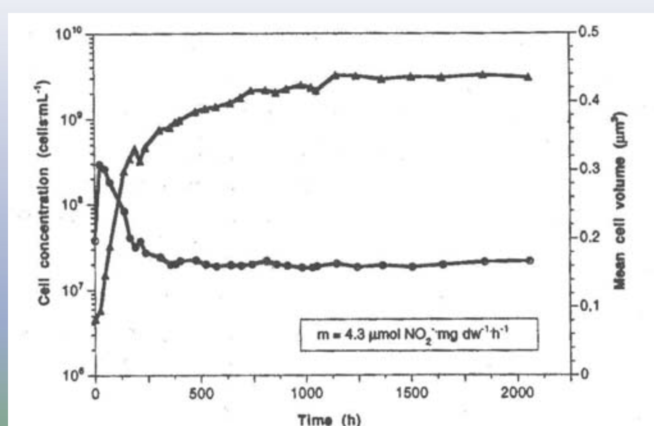
Nitrobacter winogradskyi *batch grown on NO_2^- (14 mM) then switched to BRR mode (1.42 mmol NO_2^- per h)*

Determine catabolic rate when growth no longer occurs ($\mu = 0$)

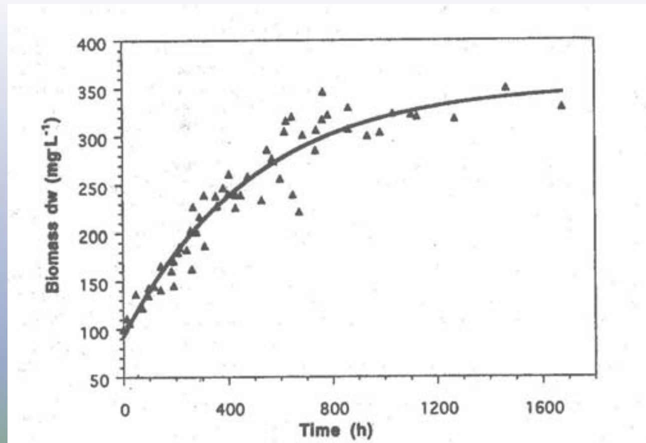
maintenance energy demand = substrate provision rate ÷ biomass

m = 1.42 mmol NO_2^- h^{-1} ÷ 332 mg dry weight L^{-1} = 4.3 µmol NO_2^- mg DW $^{-1}$ h $^{-1}$

can also determine from nonlinear analysis



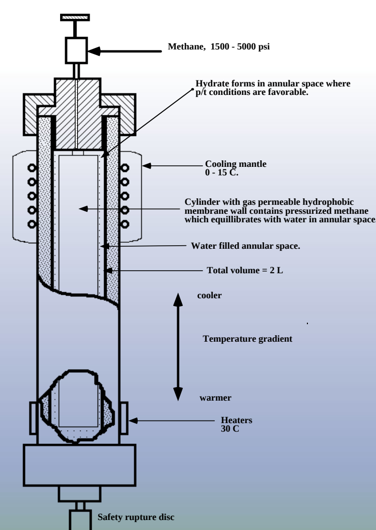
- *At constant substrate supply biomass of* N. winogradskyi *in BRR reached approximately 332 mg dry weight L^{-1} (results of three independent runs)*
- *True steady state or zero growth was approached but not reached*



Thermodynamic studies

- ***Ussler thermodynamics suggest:***
  - ***At high methane and DIC, ΔG_{rxn} is positive; methanogens inhibited; substrates (acetate) pool***
  - ***Methanogenesis resumes when acetate conc increases beyond the threshold required to make ΔG_{rxn} negative***

- ***The calculated thermodynamic constraint can be demonstrated with methanogen cultures and will occur irrespective of the origin of the methanogens***



Biosurfactants: The Link Between Microbes and Gas Hydrates

Rudy Rogers

Mississippi State University

ABSTRACT

In a 1997 grant from DOE to study the feasibility of storing natural gas in gas hydrates for use at electrical power plants at peak loads, it was found that a synthetic surfactant could greatly enhance the process if the surfactant was above its critical micellar concentration (CMC). With surfactant in a non-stirred water/hydrocarbon gas system, hydrate formation rates were increased by a factor of about 700, the hydrates self-packed by adsorbing on a metal surface at the water-gas interface, and most of the interstitial water reacted to completion. The mechanism causing the surfactant enhancement was the following. 1. The hydrophobic tails of the surfactant oriented to form a spherical core of alkyl groups (micelle), and this core solubilized the hydrocarbon gas; the hydrophilic moieties oriented on the periphery of the sphere in association with the surrounding water. 2. The gas-laden micelles then acted as nuclei for the initiation of the hydrate crystal. 3. The hydrate crystals, being less dense than the water medium, were buoyed to the surface. 4. At the water surface, the micelle-developing-hydrate-crystal moved rapidly to be adsorbed on the cold metal surface at the interface. 5. Particles of hydrate packed symmetrically as they grew radially from the cylindrical test cell wall until the vessel was filled with hydrate. 6. The porous packing of hydrate particles on the walls allowed gas to diffuse and react with interstitial water.

In a follow-on grant, the process is currently being scaled up.

This dramatic effect of some synthetic surfactants on gas hydrate formation raised a fundamental question. Could ocean-floor biosurfactants in a related manner be catalyzing gas hydrate formation, since microbes in water of ocean sediments produce biosurfactants to access insoluble organic matter?

To answer the question, biosurfactants from the five basic classifications were tested for their effects on gas hydrate formation. The classifications are the following: 1. hydroxylated and crosslinked fatty acids, 2. polysaccharide lipid complexes, 3. glycolipids, 4. lipoprotein-lipopeptides, 5. phospholipids. Representative biosurfactants from each of the five classifications were obtained from commercial sources.

Tests showed that the CMC in seawater at hydrate-forming conditions for rhamnolipid, a glycolipid from the microorganism *Pseudomonas aeruginosa*, was 12 ppm which is an order-of-magnitude less than the CMC rhamnolipid exhibits at ambient conditions. The CMC was found to be most accurately determined at hydrate conditions by measuring gas hydrate induction time as a function of biosurfactant concentration. This result indicates a very low threshold concentration necessary for a micellar-forming biosurfactant to initiate hydrate formation.

A series of tests were performed to determine effects on gas hydrate induction time of at least one biosurfactant from each basic classification. A sand/bentonite pack saturated with seawater-biosurfactant

and pressurized with natural gas was cooled from ambient to hydrate-forming conditions. The effect was dramatic. For example, Surfactin, a lipopeptide from the microorganism *Bacillus subtilis*, decreased hydrate induction time 71% compared to a control test with no biosurfactant in the seawater.

In the same series of tests, hydrate formation rates were determined for the seawater-biosurfactant saturated sand/bentonite packs. Again, the lipopeptide Surfactin increased the hydrate formation rate, as measured directly after hydrate initiation, by about 400% compared to a control test with no biosurfactant in the seawater.

It is noteworthy that Lanoil, et al., "Bacteria and Archaea Physically Associated with Gulf of Mexico Gas Hydrates," in *Applied and Environmental Microbiolog*y, Nov. 2001, report that *Pseudomonas aeruginosa* and *Bacillus subtilis* were among those microorganisms identified from Gulf of Mexico samples of gas hydrates and of sediments around gas hydrate deposits.

Other important inferences were drawn from the experiments: 1. Rhamnolipid micelles migrated through the sand pack, raising the possibility of microbial action outside the hydrate zone that could create biosurfactants, solubilize hydrocarbon gases, migrate to a hydrate zone, and catalyze gas hydrate formation. 2. Visual observation showed unique surface specificities of the biosurfactants for sand, bentonite or kaolin. 3. Biosurfactants that do not form micelles demonstrate porous-media surface specificities and promote gas hydrates by helping associate the water and hydrocarbon gas through concomitant hydrophobic and hydrophilic groups.

Biosurfactants: The Link Between Microbes and Gas Hydrates

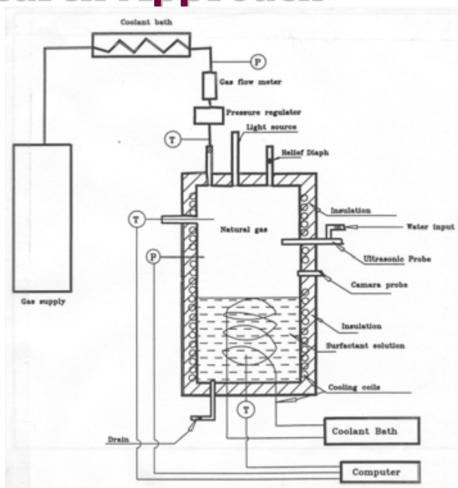
Rudy Rogers, Mississippi State University

ACKNOWLEDGMENTS

Department of Energy
The Mississippi Mineral Resources Institute
Swalm School of ChE Graduate Students: Yu Zhong, May Lee, Chandra Kothapalli

Research Approach

Laboratory Apparatus



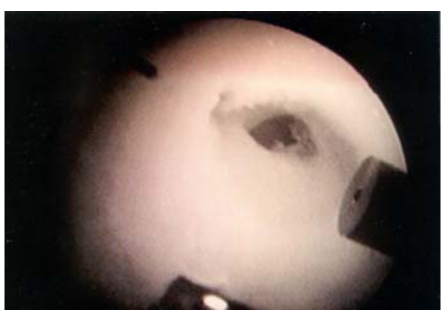
Film Retardation of Hydrate Growth in Quiescent, Pure Water-Gas System

Laboratory Results

- Hydrate symmetry from micellar solutions

Laboratory Results

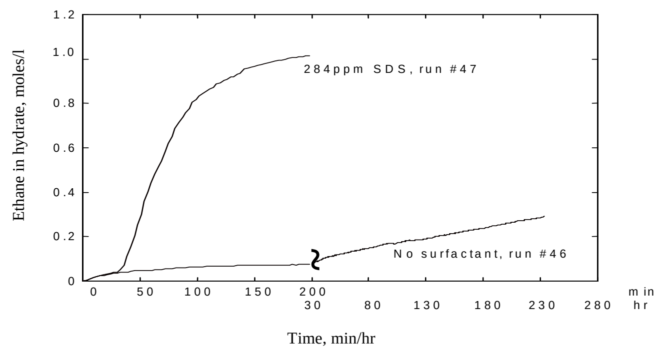
- Hydrate packing continues until test cell filled.



Natural Gas

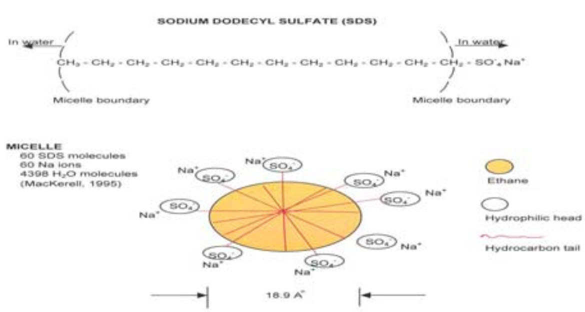
Laboratory Results

- **Micellar solutions increase hydrate rate > 700 times**

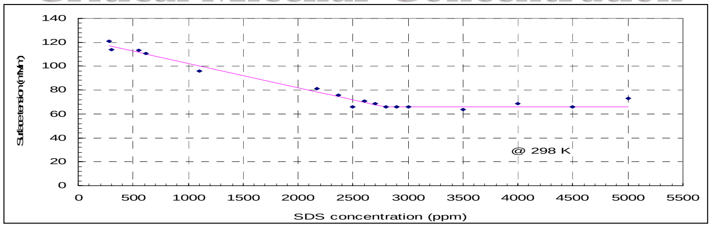


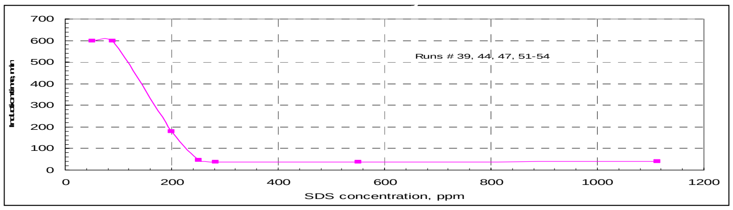
Laboratory Results

- **Theory of micellar effect on hydrate formation**



Critical Micellar Concentration





Objective

Evaluate biosurfactants from microbial activity in ocean sediments:

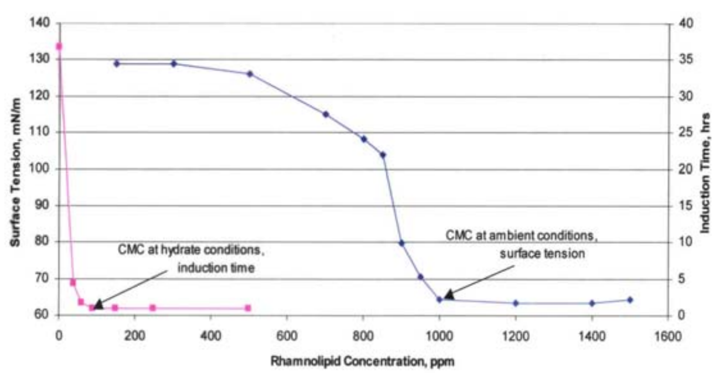
- **Catalysis of gas hydrate formation**
- **Interaction with clay and sand surfaces**
- **Effects on creating dispersed, massive, stratified, nodular gas hydrate forms**
- **Influence on mechanism of gas hydrate formation**

Biosurfactant Classification

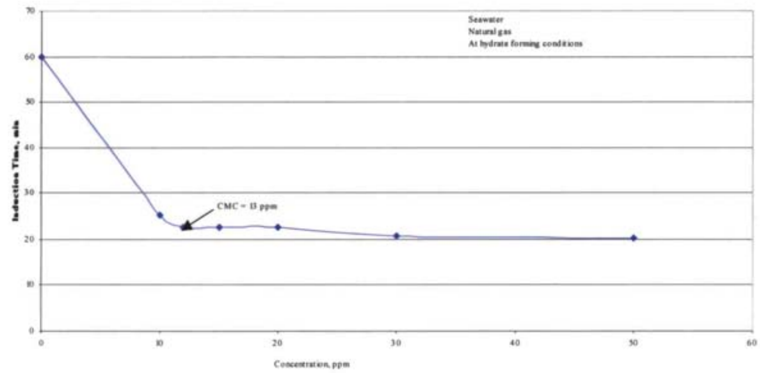
(Kosaric, 1992; Fujii, 1998)

Biosurfactant Classification	Microbe	Biosurfactants Evaluated	Reference
Hydroxylated and Crosslinked Fatty Acids	*Corynebacterium lepus*	DL-A-Hydroxystearic acid*	Rosenberg, 1986
Polysaccharide-lipid-complexes	1. *Pseudomonas syringae* 2. *Acinetobacter calcoaceticus*	1. Snomax 2. Emulsan	Goodnow et al., 1990 Rosenberg, 1993
Glycolipids	*Pseudomonas aeruginosa*	Rhamnose lipid	Fujii, 1998 Kosaric, 1992
Lipoprotein-lipopetides	*Bacillus subtilis*	Surfactin	Rosenberg, 1986 Kosaric, 1992
Phospholipids	1. *Thiobacillus* species 2. *Corynebacterium* species	DMPC * DPPS * POPC *	Fujii, 1998 Genzyme, 2001

CMC Reduction of Rhamnolipids



CMC of Rhamnolipid at G.H. Conditions



Dave C. Swalm School of Chemical Engineering

Hydrate Formation on Clay Surfaces, Emulsan-Seawater Saturated

1000 ppm Emulsan, Natural Gas, Seawater

Note: Exclusive adsorption and hydrate formation on clay surfaces

Dave C. Swalm School of Chemical Engineering

Hydrate Formation on Clay and Sand Surfaces, Surfactin-Seawater Saturated

Note: Hydrate formation on all surfaces
x 3.2 shorter induction time
x 4.0 faster formation rate

Hydrate Formation on Clay Surface Unconsolidated Sands

1000 ppm Rhamnolipid, natural gas, seawater

Note: Contribution to seafloor instability…"flowing sands"

Defining an Induction Time and Rates

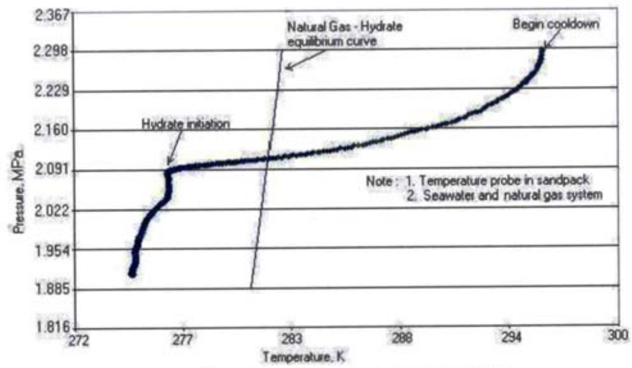
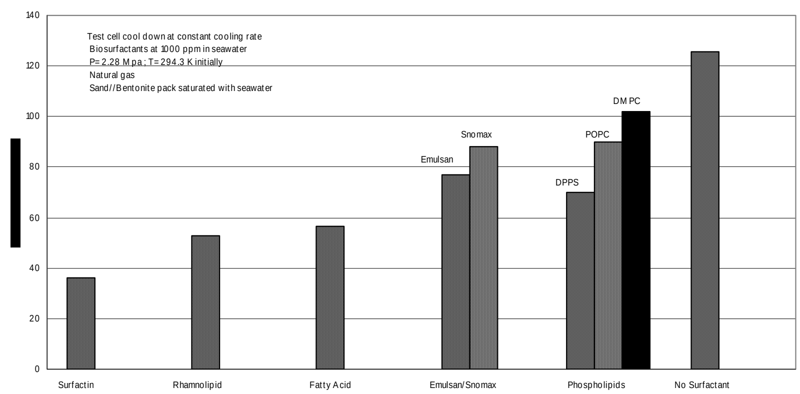


Fig 1. Defining induction time and formation rate

Induction Times



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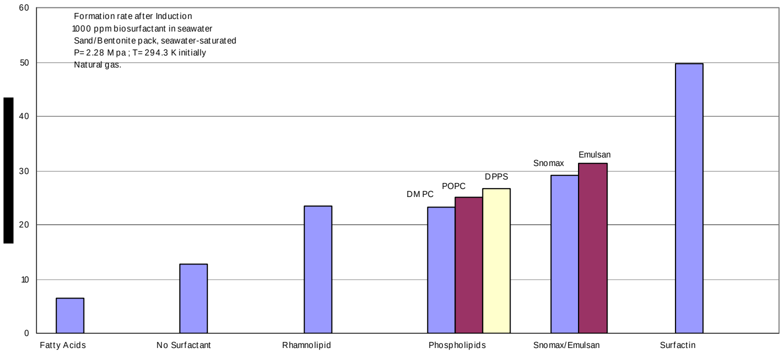
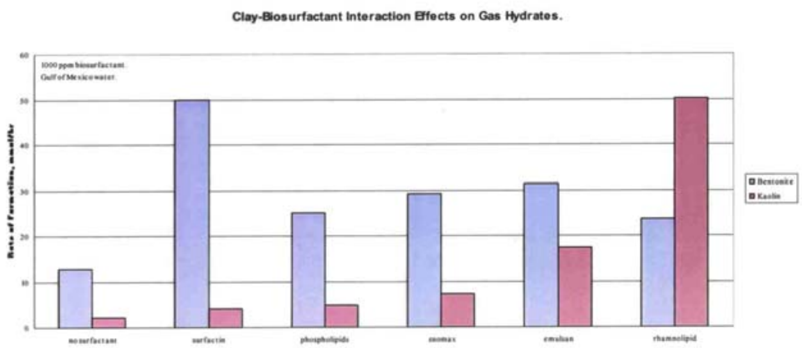
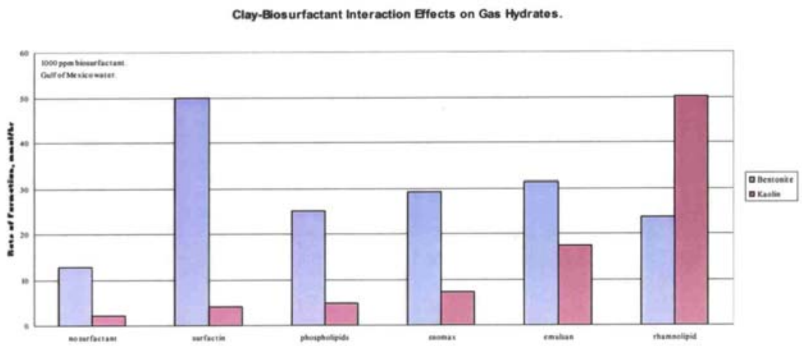
Rates of Formation



Comparison of Rates with Kaolin and Bentonite



Comparison of Rates with Kaolin and Bentonite



Conclusions

Minimal microbial activity in ocean sediments, even outside hydrate zone, greatly enhances hydrate formation!

SESSION III

Kinetics of Hydrate Formation and Dissociation

Chairman: Dr. John A. Ripmeester
Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottowa, Ontario, Canada

Rapporteur: Prof. P. Raj Bishnoi
Professor of Chemical Engineering
Department of Chemical and Petroleum Engineering
University of Calgary, Canada

Discussions on the Dynamic and Static Conditions in Hydrate Formation

I. Aya, R. Kojima and K. Yamane

National Maritime Research Institute, Japan

ABSTRACT

Prof. Makogon pointed out in his book(1) "There are two different cases in hydrate formation, that is: the dynamic and the static conditions." Through a lot of experiments, the speakers group also recognized these two cases in CO2 hydrate formation. And the group tried to explain what phenomenon should govern each case from the standpoint of dual nature of solubility in hydrate forming condition. The morphology between these two conditions is so much different that almost researchers tend not to believe the results obtained in a different condition. Therefore it is desirable for us to recognize these two different cases in hydrate formation and to consider which condition is prevailing in his experiment.

Reference

(1) Makogon, Y. F., Hydrates of Hydrocarbons, Penn Well Books, Tulsa, Oakland (1997).

Discussions on the Dynamic and Static Conditions in Hydrate Formation

I. Aya, R. Kojima and K. Yamane

National Maritime Research Institute, Japan

Purpose

- **To explain the essential difference between the dynamic and static conditions in hydrate formation pointed out by Prof. Makogon.**
- **Importance to recognize which condition prevails in individual experiment.**
- **This recognition helps us to understand deeper the results obtained from different system.**

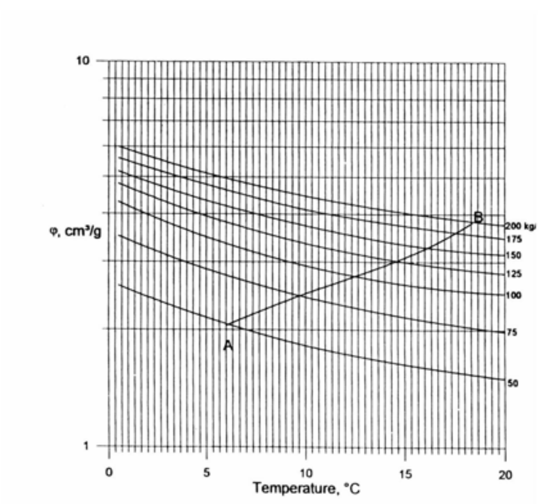


Fig. Dependence of the solubility of methane in water on pressure and temperature with a free interface.

Makogon 1996.

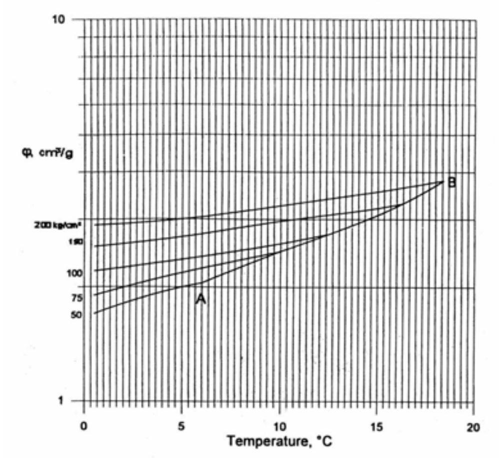
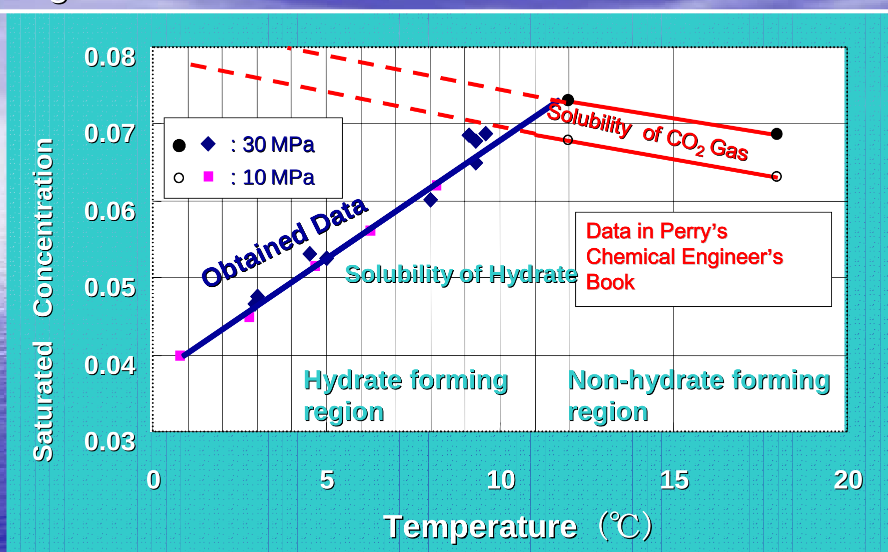


Fig. Dependence of the solubility of methane in water on pressure and temperature with hydrate present at the interface.

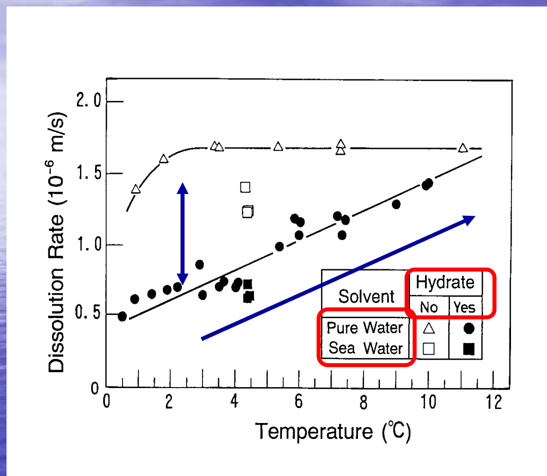
Makogon 1996.

Solubility of CO_2 in Hydrate and Non-hydrate Forming Region



Aya, Yamane and Nariai (1997)

The Dissolution Rate of CO_2 in case of Fresh Water and Seawater



Aya, Yamane and Nariai (1997)

The dissolution Rate of CO_2

with hydrate (R_h)< without hydrate (R_{Wh})

R_h=1/2~1/3 R_{wh}

Correlation

R_h ΔT (The subcooling from the dissociation temp)

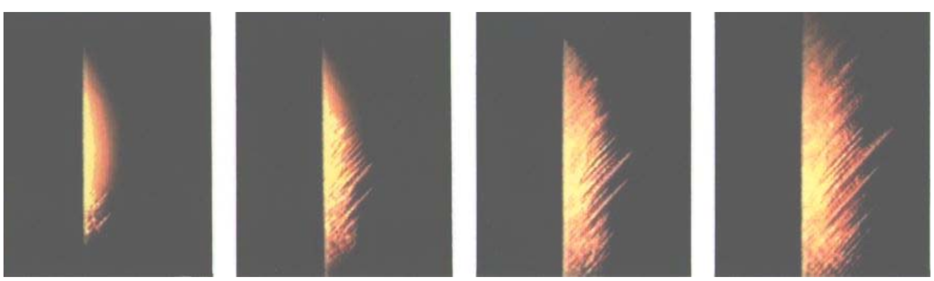
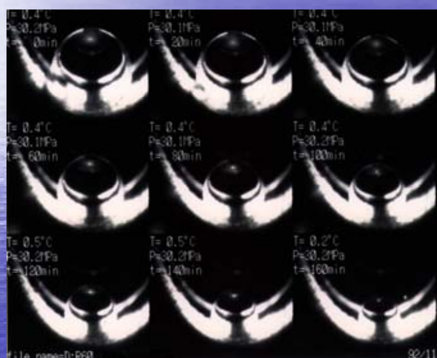


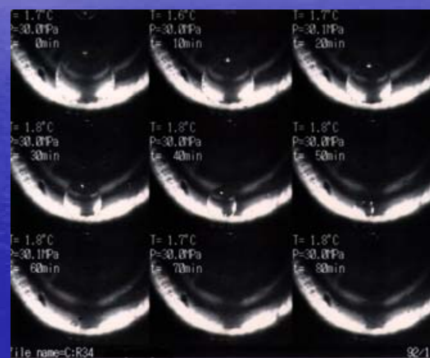
Fig. The rapidly growth of needle-like CO2 hydrate crystal at the surface of cooling pipe under unsaturated concentration.
Time span: 3sec., thickness of hydrate layer: 23mm, diameter of needle: 50 μm

The Dissolution Rate of a CO_2 Droplet

With Hydrate Film (20min. / frame)



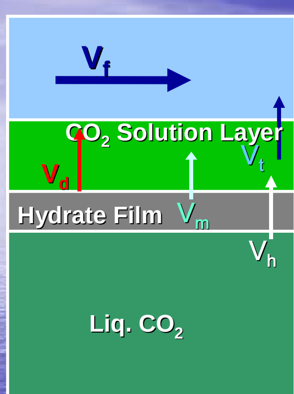
Without Hydrate Film (10min. / frame



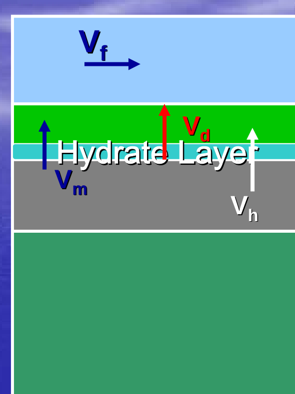
Yamane, Aya and Nariai (1997)

→ **The hydrate film influences very much.**

The Difference between Dynamic and Static System



- V_f : Current Flow
- V_t : Diffusion by Turbulence
- V_m : Molecular Diffusion in Solution
- V_h : Diffusion in Hydrate
- V_d: Dissolution Rate of Hydrate



V_d is governed by V_f

↓

$V_d \quad V_h = V_t >> V_m$

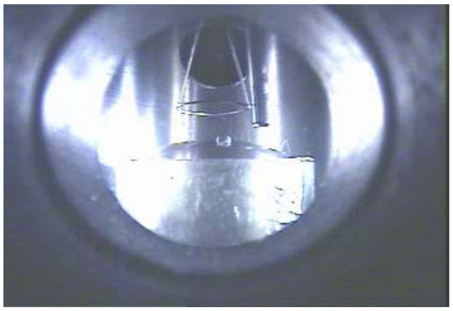
V_d is governed by V_m

↓

$V_h > V_d = V_m$

Morphology of Hydrate

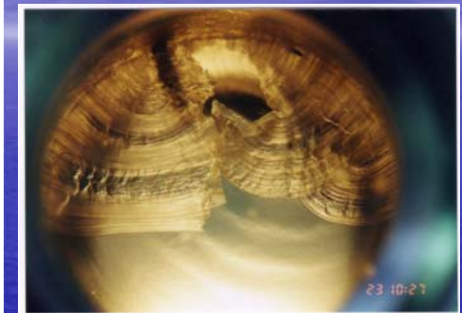
Dynamic State



Hydrate Film Formed on the Liquid-Water Contact
(P=300 bar, T= 276K)
Thickness of film is const.

Yamane, Aya.

Static State



CO_2 with Sea Water Whiskery Hydrate Crystals Formed in Liquid Sphere
(P=44.5 bar, T=273.3K)
Needle-like crystals are growing.

Texas A&M Prof. Y. F. Makogon

Concluding Remarks

1. Dynamic formation

The whole process is dominated by the diffusion process in the solution side.
And the thickness of hydrate membrane is determined,
so that the flux by diffusion in solution side is equal to the flux in membrane.
Then the membrane thickness is kept constant depending on the flow condition of solution side.

2. Static formation

The flux by diffusion in solution is smaller than the flux through the membrane.
The hydrate glows and various types of crystal as Prof. Makogon observed appear.
If direct contact or almost direct contact between the solution and guest molecules is attained, the rapid hydrate formation that we sometimes experienced occurs.
The driving force of rapid hydration is the difference of chemical potentials.

3. Recognition of dynamic and static hydrate formations

This helps us not only to understand the result obtained from different systems but also to understand our own experiment deeper.

Acknowledgements

The speaker would like to express his sincere thanks to Profs. Makogon and Kvamme for their useful discussions.

Proton Nuclear Magnetic Resonance Observation of Methane Hydrate Formation in Rock Samples in an ROV-Controlled Seafloor Laboratory

*Robert L. Kleinberg[1], Charles Flaum[1], Peter G. Brewer[2], George Malby[2], Edward Peltzer[2], Gernot Friederich[2] and James P. Yesinowski[3]**

[1]Schlumberger-Doll Research, Ridgefield, Connecticut 06877; [2]Monterey Bay Aquarium Research Institute, Moss Landing, California 95039; [3]Naval Research Laboratory, Washington, DC 20375

We have successfully demonstrated the use of proton nuclear magnetic resonance (NMR) at 2 MHz to measure changes in the liquid water content of sediment and rock resulting from methane hydrate formation in the deep ocean. Laboratory proton NMR experiments on synthetic samples of hydrates indicated that the proton NMR signal from the solid hydrate should be unobservable under the experimental conditions used in the deep ocean NMR experiments. Hydrates were artificially formed at the seafloor (1034m depth, 3.8C) in Monterey Bay, California by introducing methane into tubes containing sediments or rock saturated with seawater. After several weeks' exposure to methane the samples were revisited by a remotely operated vehicle (ROV) on which NMR equipment was mounted. Independent hydrate mass estimates were obtained by flying the vehicle above the hydrate phase boundary, decomposing the hydrates, and collecting the evolved gas. For rocks with disseminated hydrate, NMR and mass balance assays of hydrate volume are in good agreement. We have thereby established that proton NMR can be used to observe quantitatively and non-invasively the formation of methane hydrate in spatially-selected regions (a cylinder approximately 15 cm long and 4 cm^2 in cross-sectional area, centered 2.5 cm from the face of the NMR instrument) of opaque sediment samples. NMR is also potentially useful for quantifying pore size control of hydrate formation, and for estimating *in situ* hydraulic permeability of hydrate-affected earth formations. Such direct experimental information about the formation of hydrates in pore spaces of rocks is needed for the development of realistic models of the natural occurrence of hydrates.

Proton Nuclear Magnetic Resonance Observation of Methane Hydrate Formation in Rock Samples in an ROV-Controlled Seafloor Laboratory

R. L. Kleinberg, C. Flaum, C. Straley,
Schlumberger-Doll Research

P. G. Brewer, G. Malby, E. Peltzer,
G. Friederich,
Monterey Bay Aquarium Research Institute

J. P. Yesinowski,
Naval Research Laboratory

2nd Workshop of the International Committee on Gas Hydrates,
Washington DC, Oct. 29-31, 2002

OUTLINE

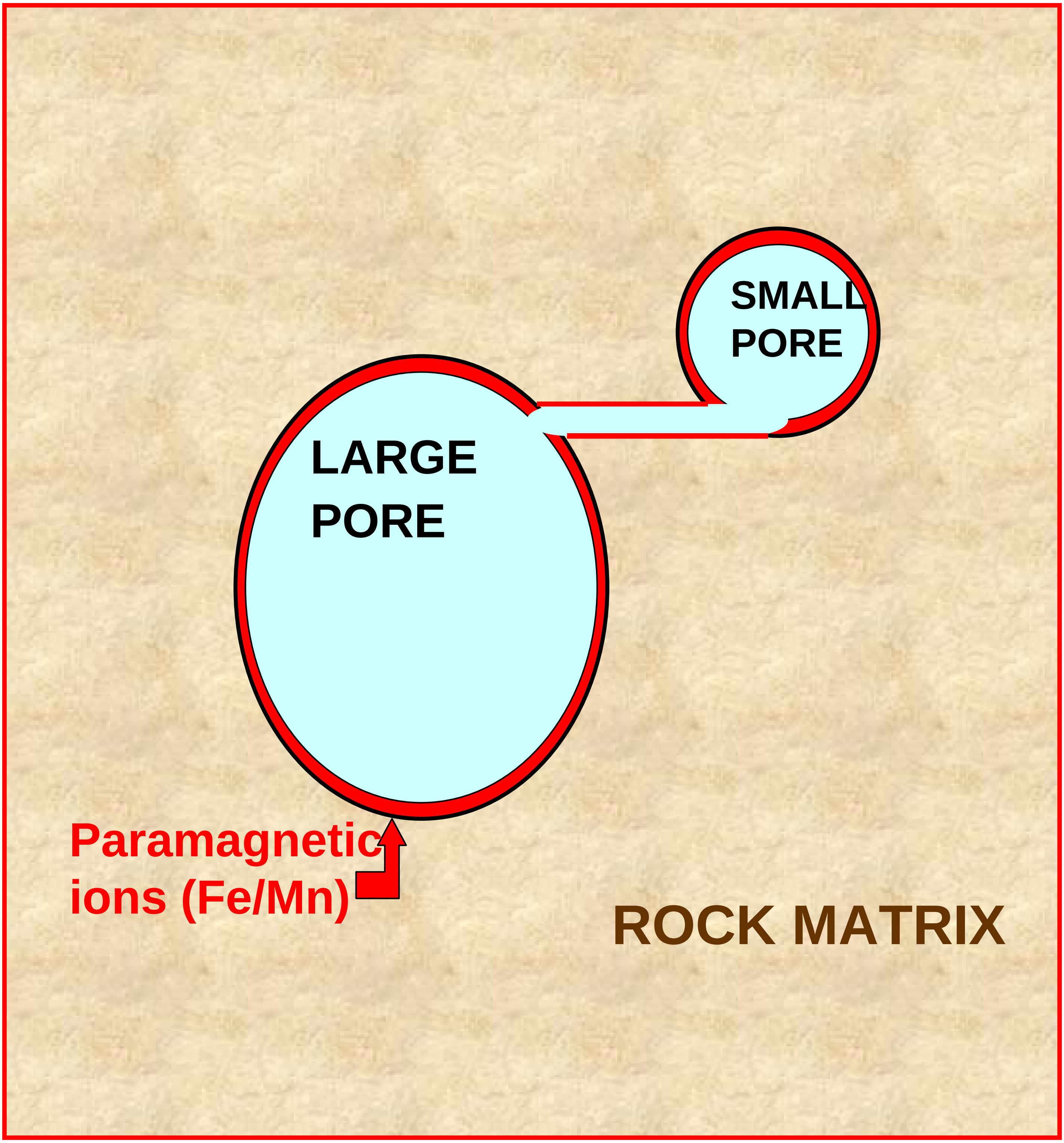
- **Basis of NMR technique for Porous Media**
  - **Direct quantitation of liquid water signal, (indirect quantitation of methane hydrate)**
  - **NMR relaxation times T_1 and T_2 for water, methane hydrate, and methane gas**
  - **T_2 distribution yields pore size distribution**

- **Experimental "Apparatus"**
  - **Remotely-Operated-Vehicle (ROV) carrying Low-field NMR for Deepsea "Laboratory"**

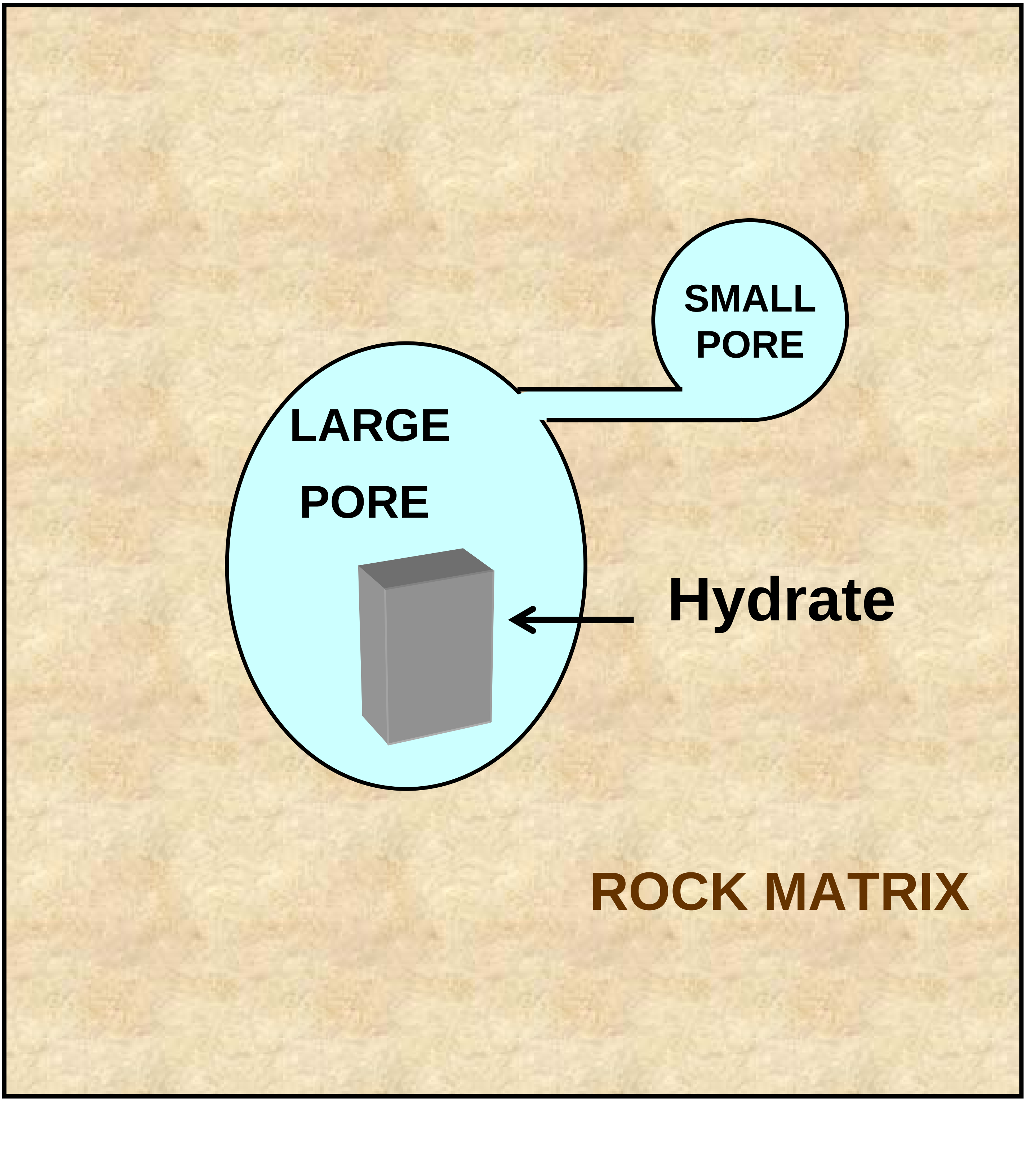
- **Results**
  - **Validation of porosity and T_2 measurements: lab vs. seafloor**
  - **NMR detection of hydrate formation in sandstone (model for unconsolidated sediment with overburden pressure), and pore size preference**

- **Future Prospects and Issues**

- **Video of Deepsea NMR Experiments**



NMR OBSERVES LIQUID WATER SIGNAL ONLY



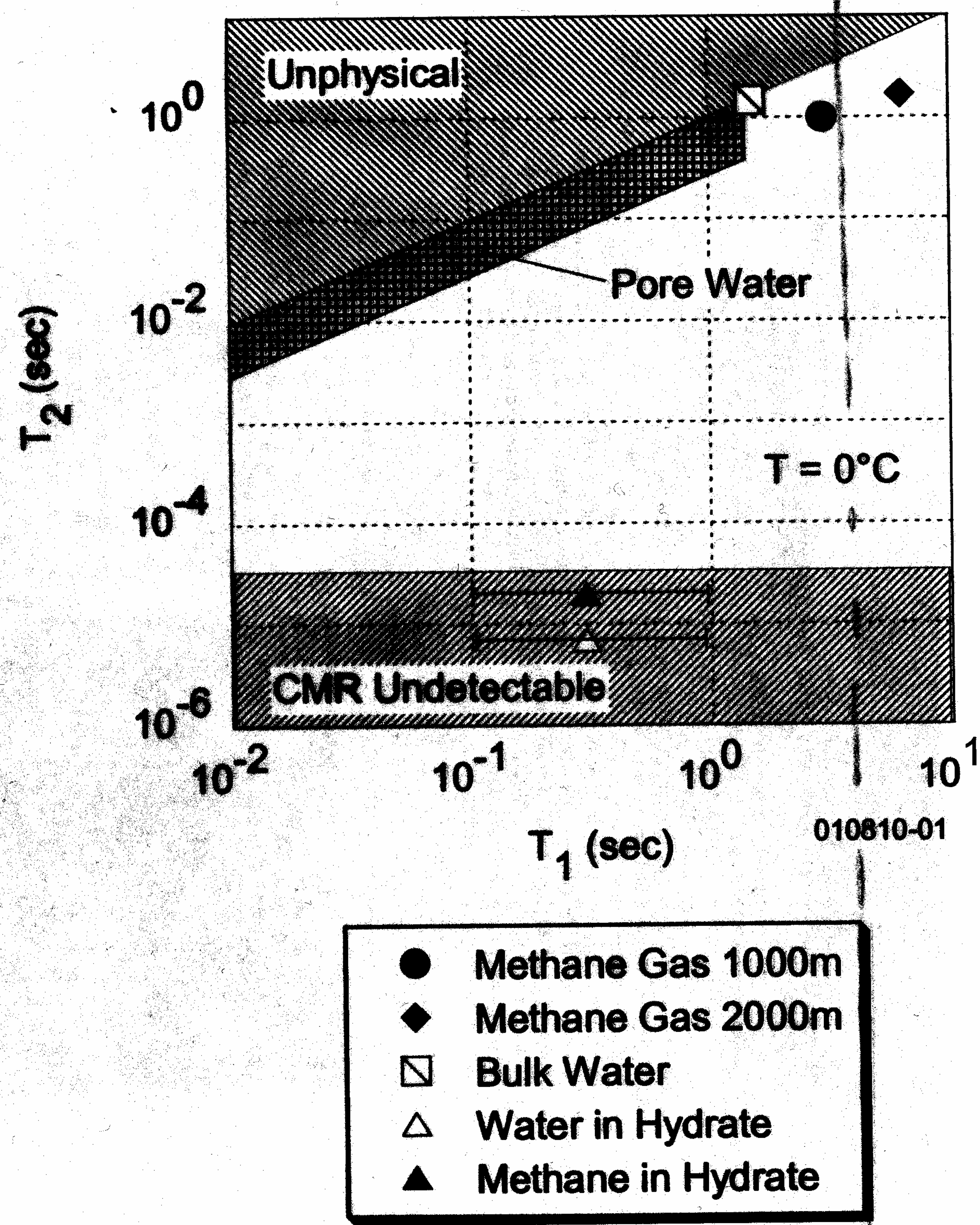
NMR OBSERVES LIQUID WATER SIGNAL ONLY

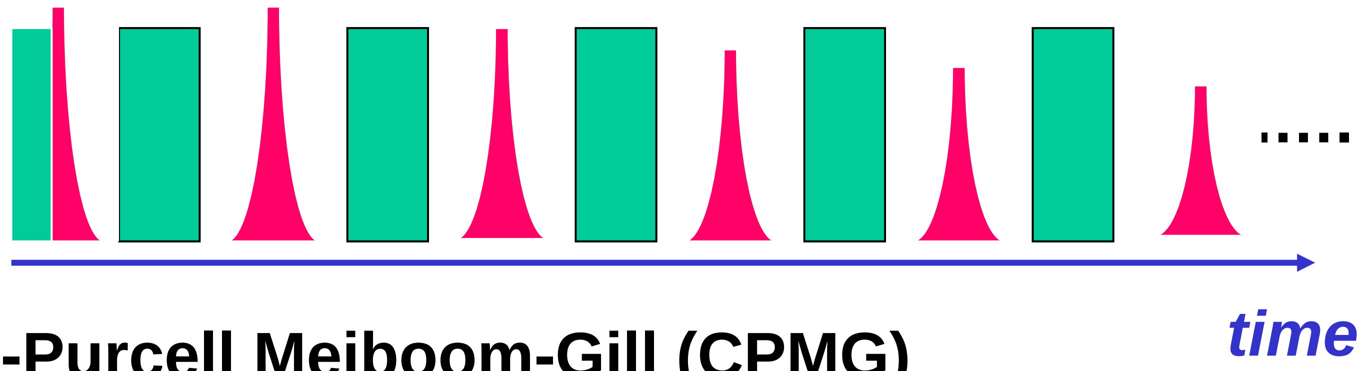
LOW-FIELD PROTON NMR

(2.2 MHz AT 52 mT FIELD)

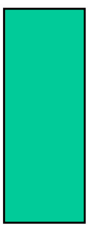
RELAXATION TIME T_1
GOVERNS HOW FAST
EXPERIMENT CAN BE
REPEATED TO IMPROVE
SIGNAL:NOISE RATIO)

RELAXATION TIME T_2
MEASURES HOW LONG
SIGNAL LASTS

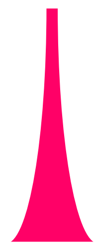

Unphysical
Pore Water
T = 0°C
CMR Undetectable
T_2 (sec)
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-2}
10^{-1}
10^0
10^1
T_1 (sec)
010810-01
Methane Gas 1000m
Methane Gas 2000m
Bulk Water
Water in Hydrate
Methane in Hydrate



Carr-Purcell Meiboom-Gill (CPMG)
Pulse Sequence
(90_x - ☺ - 180_y - 2☺ - 180_y ....)



Radiofrequency (rf) pulse (180_y)



Spin-echo NMR signal (Decays with time)

5000 Spin Echoes
Echo spacing = 0.2 ms
Wait time between CPMG repeats = 8 s (for T_1 recovery)
Typical 15 Minutes Total Acquisition
Calibration with Doped Water Standard

$$\frac{1}{T_{2S}} = \rho_2 \left(\frac{S}{V}\right)_{pore}$$

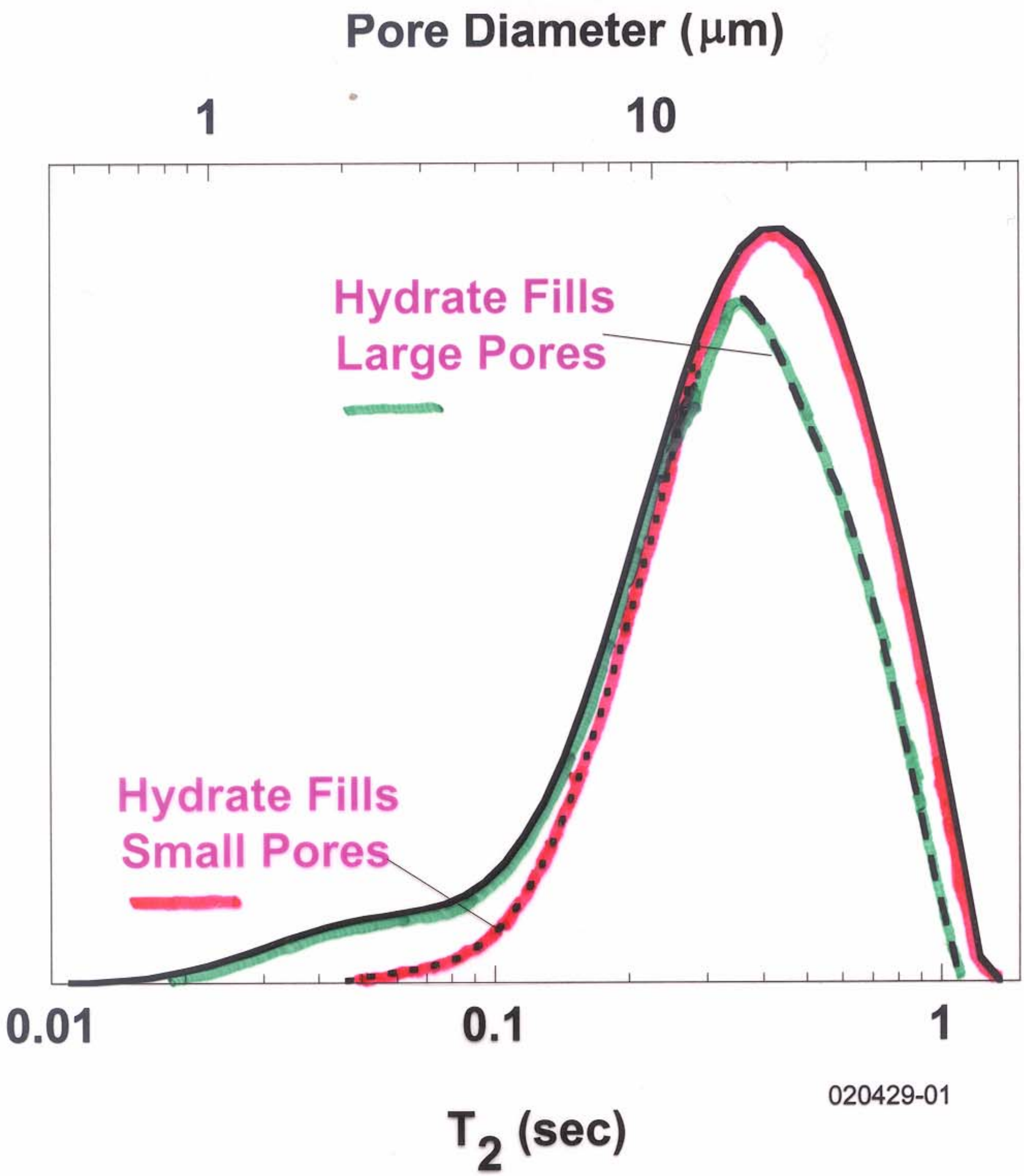
SURFACE RELAXATION = CONSTANT x (SURFACE / VOLUME)

$$M(t) = \sum_{i=1}^{50} m(T_{2i}) \exp\left(-\frac{t}{T_{2i}}\right)$$

OBSERVED SIGNAL = SUM OVER T_2 DISTRIBUTION (50 VALUES FIT, 0.3 – 5000 ms)

$$T_{2LM} = 10^{\left[\frac{1}{\phi}\sum_i m(T_{2i}) \log_{10}(T_{2i})\right]}$$

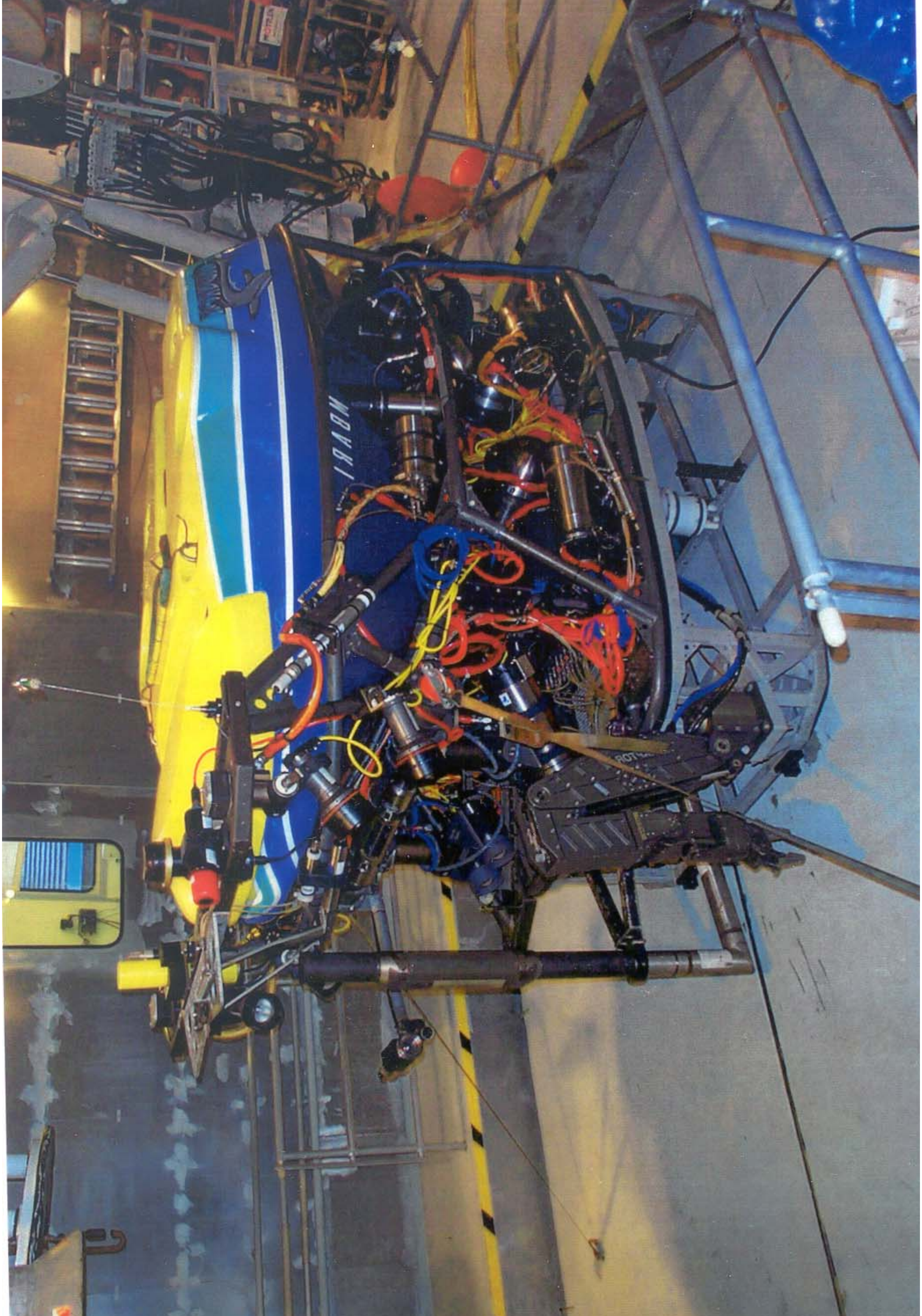
DEFINITION OF LOG-MEAN T_2

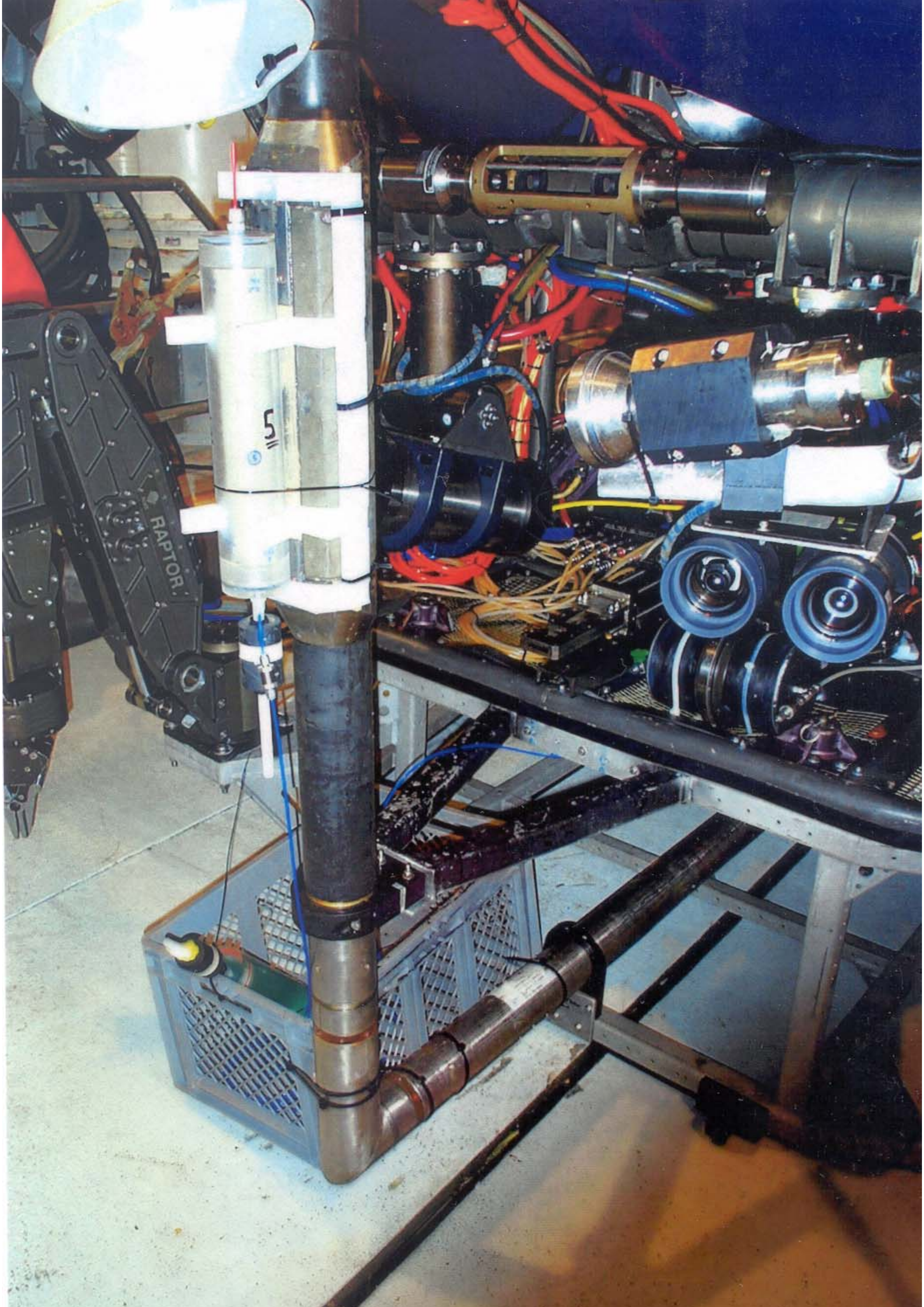


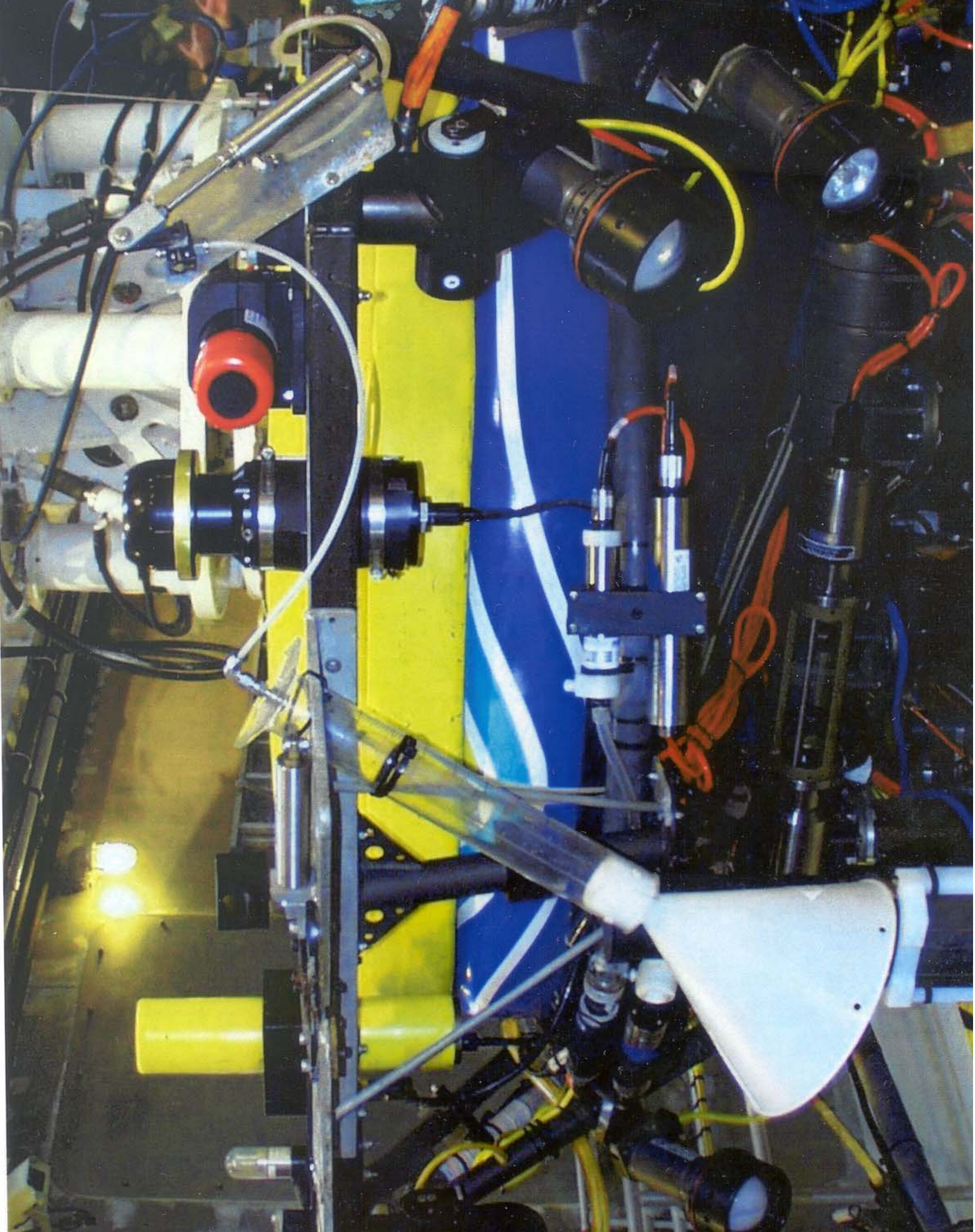
Measured NMR T_2 Distribution in Sandstone Yields Distribution of Pore Sizes (Solid Curve)

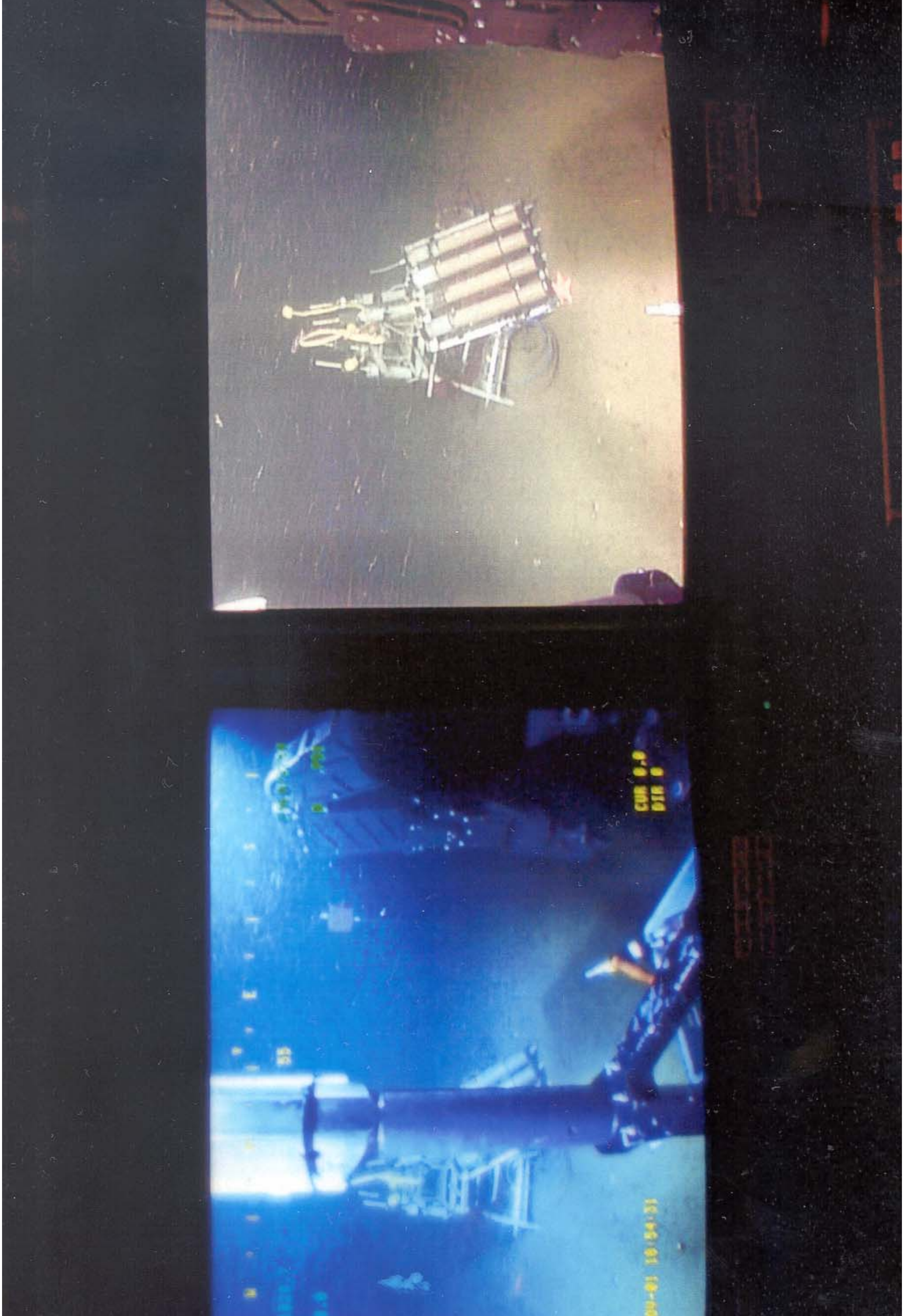
Dashed and Dotted Lines: *Hypothetical* deviations from solid curve due to hydrate formation (curves merge with solid line)

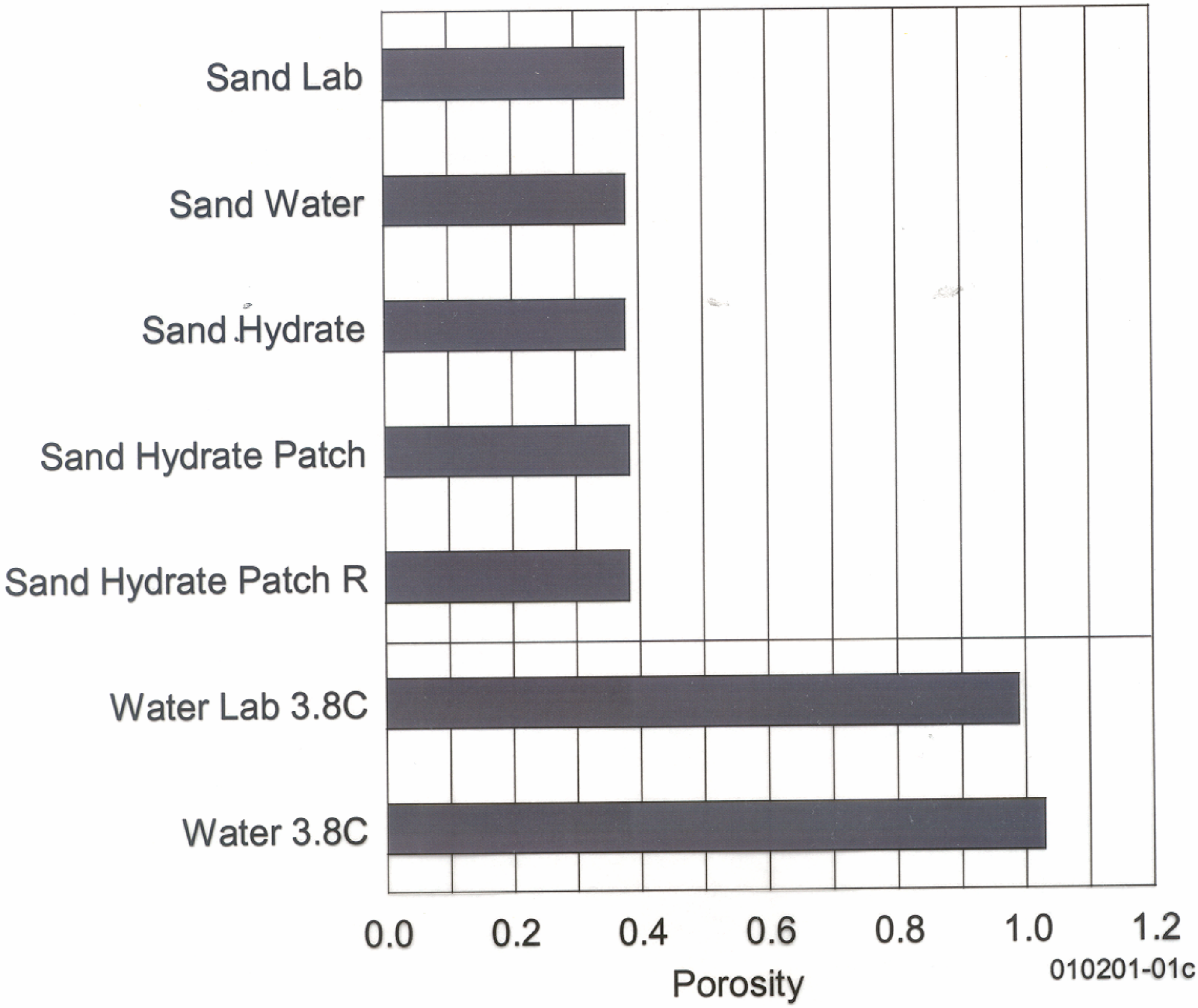

MBARI
WESTERN FLYER


MBARI


RAPTOR



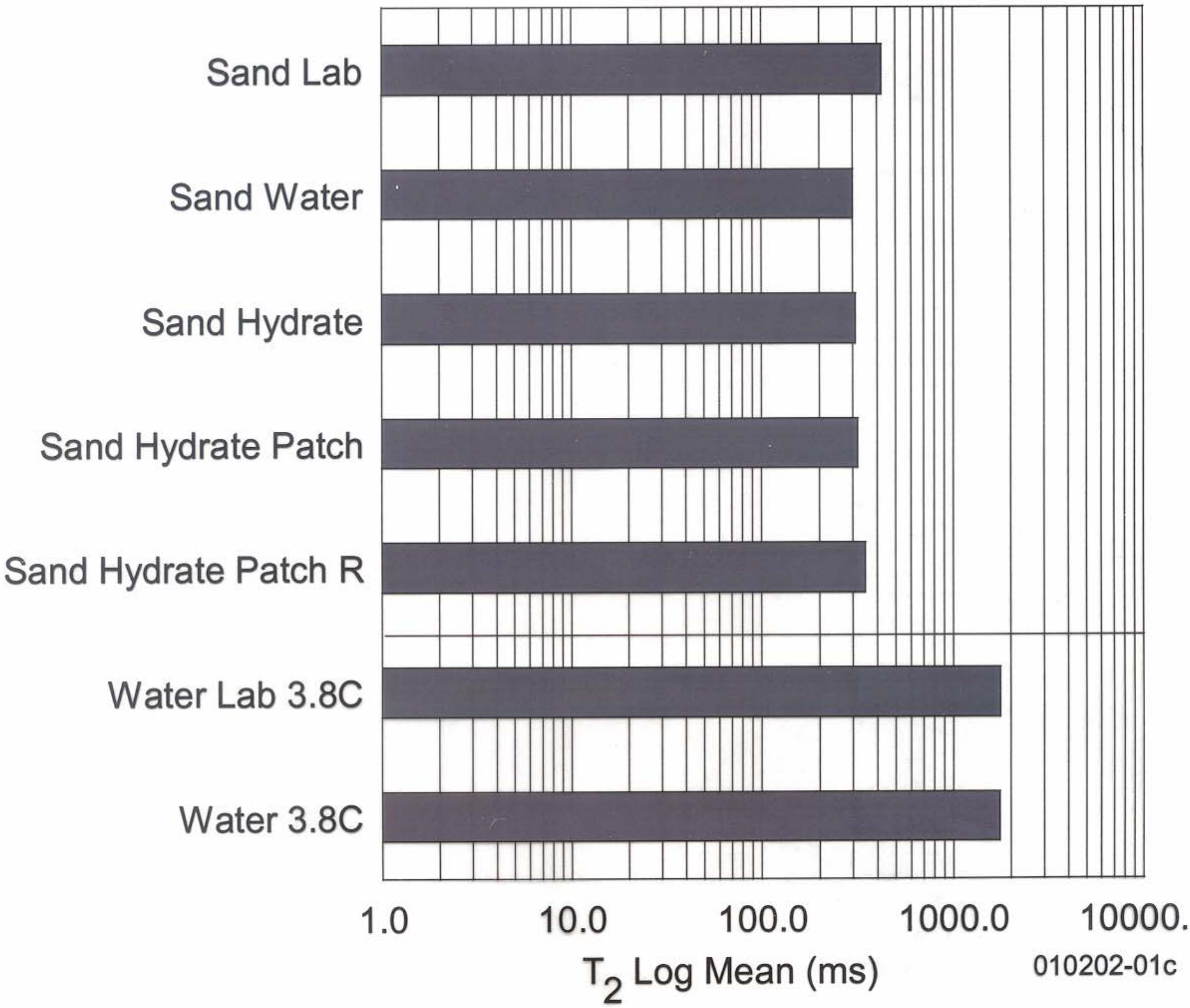

CUR 0.0
DIR 0



VALIDATION OF SEAFLOOR NMR-DERIVED POROSITY MEASUREMENTS

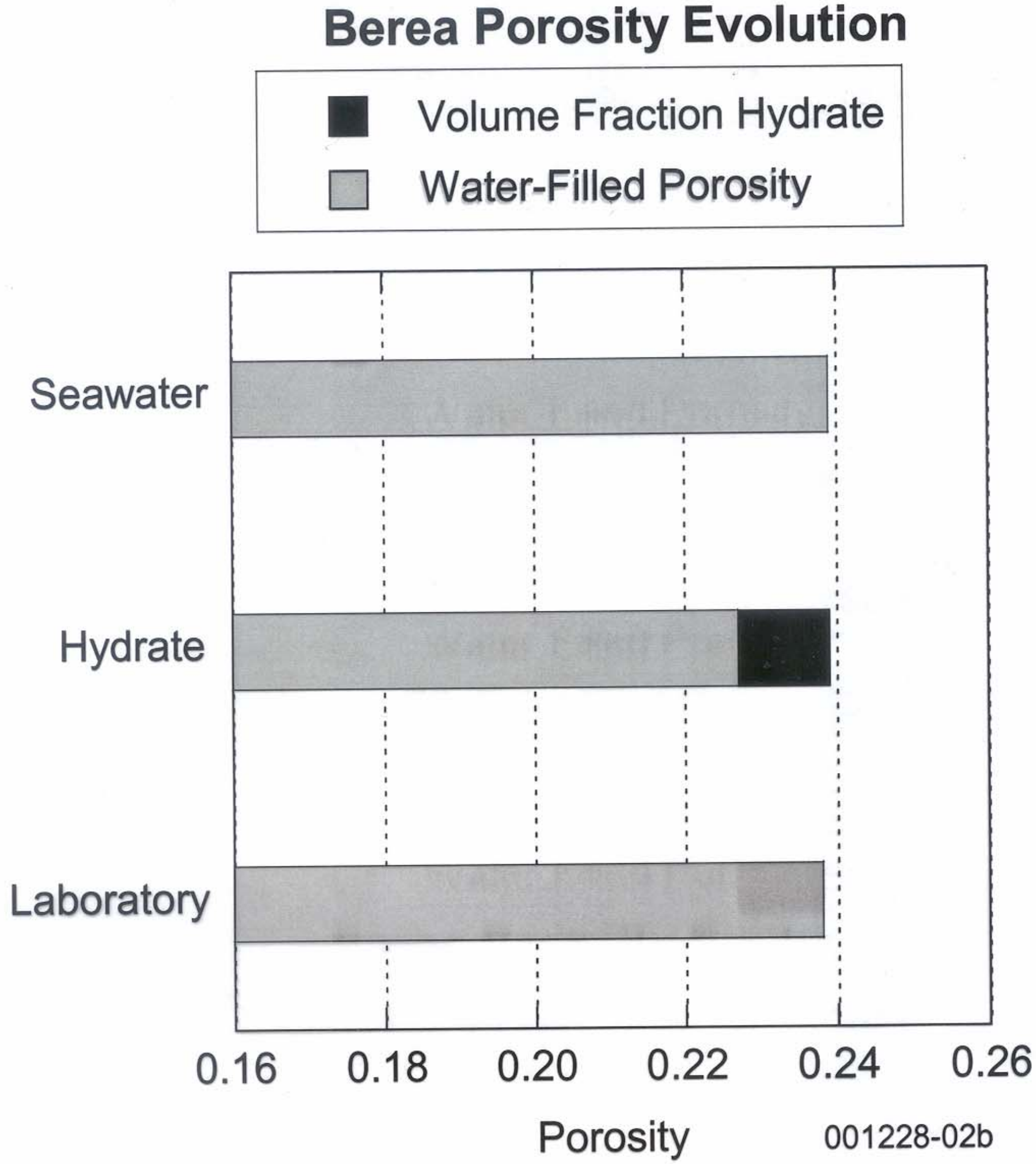
Two "LAB" measurements made at 1 atm

"POROSITY" = VOLUME FRACTION LIQUID WATER



VALIDATION OF SEAFLOOR NMR LOG-MEAN T_2 MEASUREMENTS

Two “LAB” measurements made at 1 atm



NMR Porosity Measurements of Sandstone with Seawater and with Hydrate (Formed after 41 Days Exposure to Methane at 1034 Meters)

Reduction in NMR Porosity Due to Hydrate Formation Agrees with Dissociation Expt.

"REAL-TIME" FORMATION OF HYDRATE IN SANDSTONE

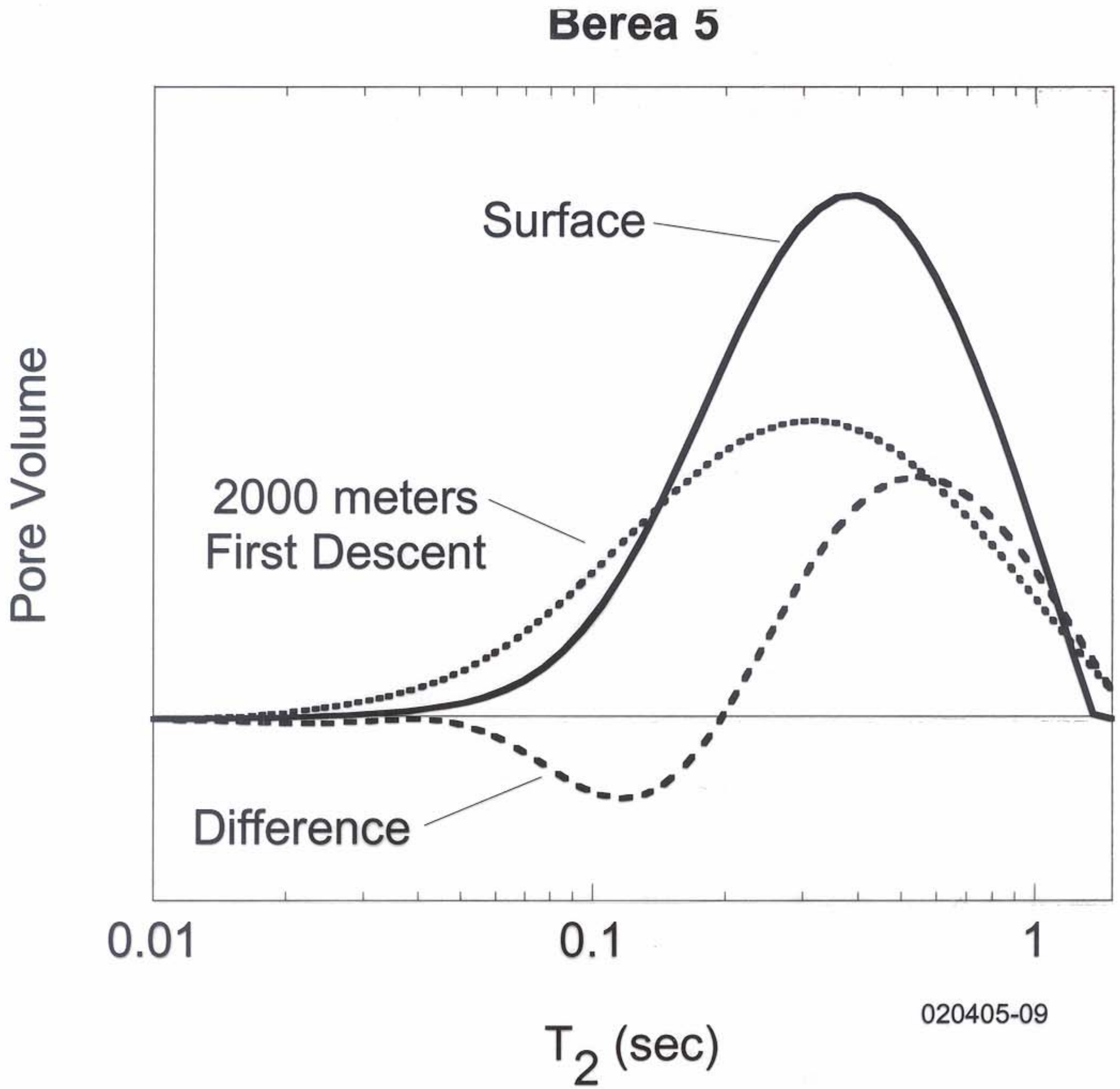
AND OBSERVATION BY NMR

BUBBLE METHANE GAS INTERMITTENTLY THROUGH SAMPLE DURING DESCENT TO 2000 METERS

MAKE NMR MEASUREMENT AT 2000 METERS

MAKE ADDITIONAL NMR MEASUREMENTS AT LESSER DEPTHS TO CHECK FOR PRESENCE OF METHANE GAS SIGNAL

BRING ABOVE THE HYDRATE STABILITY ZONE AND MEASURE (PARTIAL) DISSOCIATION

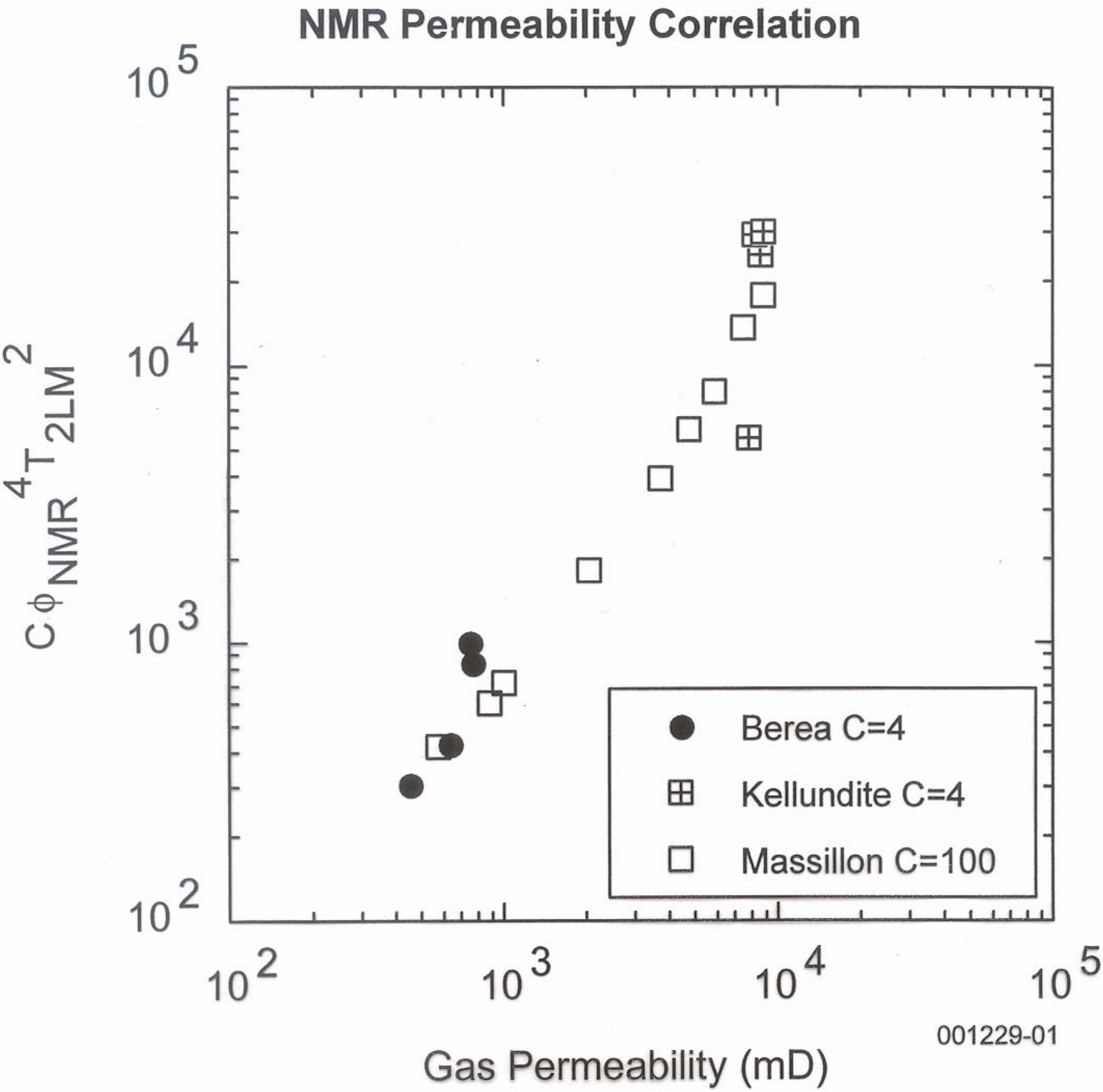


Berea sandstone, Porosity = 0.23

Surface: T_2 distribution in laboratory

2000 meters: same sample with methane hydrate formed *in 1 hour*.
Fraction pore space filled with hydrate = 0.20 ± 0.03.

Difference: derived from difference of raw data, note volume reduction in largest pores and increase at intermediate pore sizes due to partial occlusion of large pores with hydrate.


NMR Permeability Correlation
$C\phi_{NMR}^{4}T_{2LM}^{2}$
10^5
10^4
10^3
10^2
Berea C=4
Kellundite C=4
Massillon C=100
10^2
10^3
10^4
10^5
001229-01
Gas Permeability (mD)

CONCLUSIONS

NMR MEASUREMENTS OF POROSITY AND T_2 CAN BE CARRIED OUT IN THE DEEP OCEAN

AMOUNT AND PORE-SIZE PREFERENCE OF HYDRATE FORMATION CAN BE MEASURED

ADVANTAGES OF NEW DEEPSEA NMR APPROACH:

- QUANTITATIVE
- NON-DESTRUCTIVE, CAN MONITOR THE SAME SAMPLE FOR KINETIC STUDIES
- RELATIVELY RAPID
- (PRELIMINARY) DATA IN REAL TIME
- LARGE-VOLUME & LONG-TERM EXPERIMENTS UNDER OCEAN CONDITIONS

FURTHER ADVANTAGES:

- SPATIALLY SELECTIVE OVER SMALL REGION
- PORE SIZE INFORMATION (RELATED TO HYDRAULIC PERMEABILITY)
- CAN DETECT HYDRATE NOT VISUALLY OBSERVED IN OPAQUE SAMPLES
- APPLICABLE TO OTHER HYDRATES

Two-step formation process of methane-propane mixed gas hydrates in the batch-type reactors

T. Uchida[1], M. Moriwaki[2], S. Takeya[1], I. Y. Ikeda[1], J. Nagao[1], R. Ohmura[1], H. Minagawa[1], T. Ebinuma[1], H. Narita[1], K. Gohara[2] and S. Mae[2,3]*

[1]Institute for Energy Utilization, Natl. Inst. of Adv. Sci. and Tech. (AIST), Sapporo 062-8517, Japan; [2]Faculty of Engineering, University of Hokkaido, Sapporo 060-8628, Japan; [3]Asahikawa Natl. College of Tech., Asahikawa 071-8142, Japan

ABSTRACT

Vapor compositions of methane and propane mixed gas in a batch-type reactor were measured by gas chromatography during hydrate crystallization at 274 K with molar ratios of propane below 10%. The molar ratio of propane in vapor decreased as the hydrates crystallized. When the initial propane concentration was between 4 and 8%, rapid gas consumption occurred for about 1 hour causing an initial pressure drop, and after a temporary stabilization of the pressure, a second pressure drop occurred; that is, hydrate crystallization occurred in two-steps. X-ray diffraction and Raman spectroscopic analyses on both samples taken from the reactor at each step revealed that the structure II methane-propane mixed gas hydrates crystallized in the first step and structure I methane hydrates in the second step. This process observed only when the partial pressure of methane was above the equilibrium of methane hydrate at the end of the first step.

021030 Fiery Ice WS-2

Two step formation process of CH_4-C_3H_8 mixed gas hydrates in a batch-type reactor

T. Uchida [(1)]*, S. Takeya[(1)], J. Nagao[(1)], T. Ebinuma[(1)], H. Narita[(1)], M. Moriwaki [(2)], K. Gohara [(2)] S. Mae[(2)(3)]

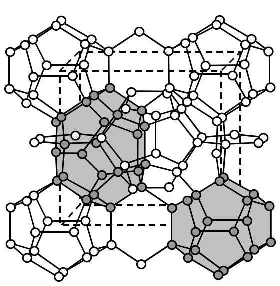
[(1)] Gas Hydrate Research Group,Inst. for Energy Utilization, AIST, JAPAN
[(2)] Faculty of Engineering, Hokkaido University, JAPAN
[(3)] present address: Asahikawa National College of Technology, JAPAN

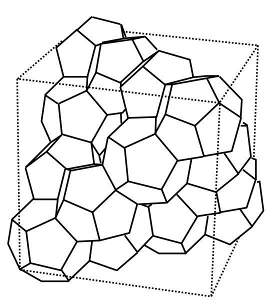
Introduction: mixed-gas hydrates

Mixed-gas including CH_4: composition & structure

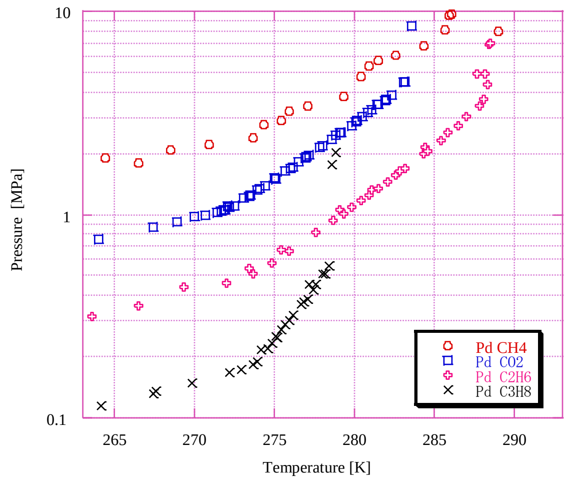
$CH_4 - C_2H_6$
$CH_4 - C_3H_8$ } Natural gas component：sI⇔sII

$CH_4 - CO_2$ Industrial utilization：sI





Phase diagram of pure gases



(Sloan, 1998)

Objectives

1. Formation process observations of CH_4-C_3H_8 mixed-gas hydrates via Gas Chromatograph
2. Observations of gas fractionation
3. Physical property measurements of formed gas-hydrate samples via XRD and Raman spectroscopy

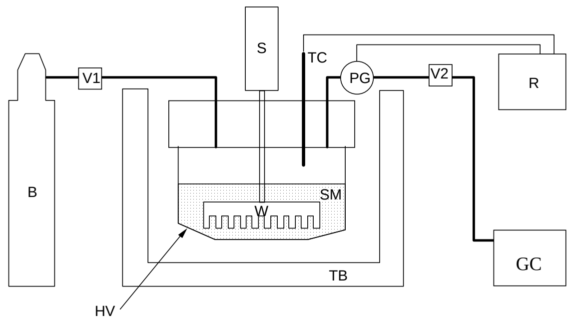
Experimental Setup

High pressure vessel (batch-type reactor)

V～200 cm^3, T = 274 K, R = 500 rpm

High speed Gas Chromatograph

→ Gas composition measurements in each 5 min.



Experimental procedures

Distilled de-ionized water (18.2 MΩ cm) ～50 cm^3

Initial conditions of mixed gas

	composition	pressure
C_1-C_3	y_{C1}= 0.04～ 0.1	P_{tot}～ 7.0MPa

Purity: C_1: 99.95%, C_3: 91.2%

t=0 (starting stirring) →starting gas sampling

P(t), T(t), gas composition C(t) → partial pressure

Sample taking out at 170 K, 1 atm → XRD, Raman

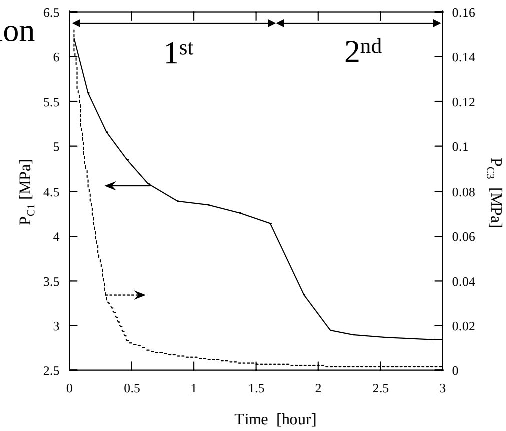
Results: Partial pressure change

Pressure drop with hydrate formation

→ two-step drop of P_{C1}

- 1st: rapid gas consumption and preferential consumption of C_3
- 2nd: C_1 consumption after temporary pressure stabilization

(initial composition: y_{C1} = 94%)



Sample analyses

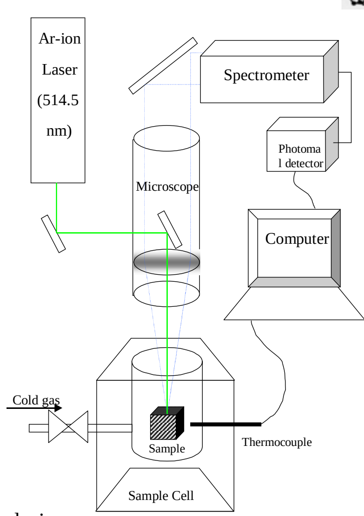
Sampling from each step

1st step: cooling start just after the beginning of hydrate formations

2nd step: cooling after finishing the hydrate formations

→ samples were stored at 77K

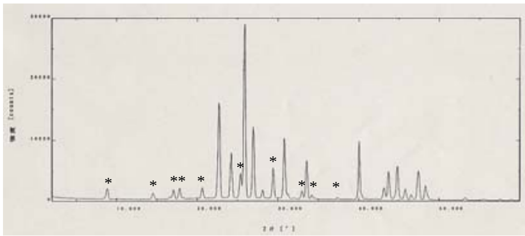
Sample analyses via
XRD (structure) and
Raman (cage occupancy)



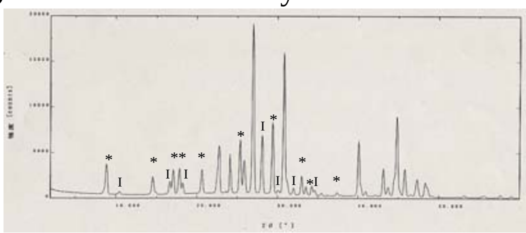
Experimental setup for Raman spectroscopic analysis

Results of XRD measurements

- 1st: C_1-C_3 mixed-gas hydrate (sII:*)



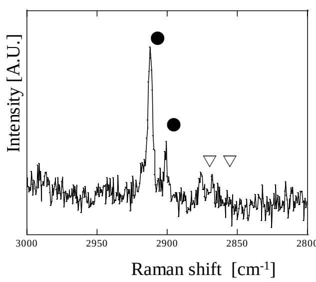
- 2nd: C_1 hydrate (sI:I) formed in the same system



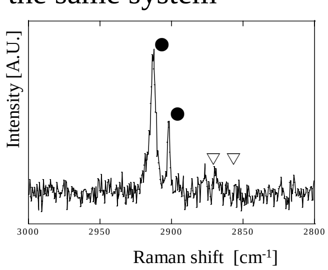
Raman spectroscopic measurements

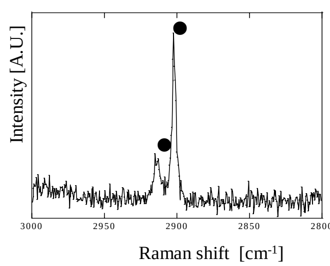
- 1st: C_1-C_3 mixed-gas hydrates (sII)

(C-H stretching mode)
● : CH_4 molecule in cages
▽: C_3H_8 molecules in cages



- 2nd: C_1 hydrate (sI) formed in the same system





Discussions

Formation process of mixed-gas hydrates in a batch reactor:

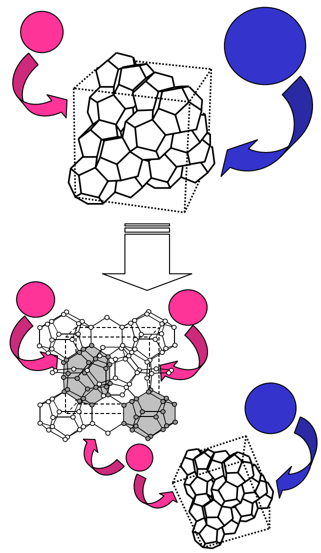
- 1st: C_1-C_3 mixed-gas hydrate (sII)
- 2nd: C_1 hydrate (sI) formation due to gas composition became C_1-rich

Interesting phenomenon:

Existing of temporary stabilization (‘second’ induction period)

↓

- sII hydrate isn’t nucleus of sI?
- sI formation has large energy barrier?



Conclusions

Formation process observations of CH_4-C_3H_8 mixed-gas hydrates: gas composition change in vapor phase

- Two-step formation process was observed at P(t) change
- 1st step: Formation of CH_4-C_3H_8 mixed-gas hydrates (sII)
- 2nd step: CH_4 hydrate (sI) formed in the same system
- ‘second’ induction period was observed between steps

\# Effects of initial pressure on the formation process

\# Observations of formation processes in other mixed-gas hydrates

Acknowledgments

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by the international joint project entitled "Research and Development on Natural Gas System utilizing Gas Hydrate Technology" collaborated with the Institute of Applied Energy.

We greatly acknowledge Mr. S. Date and Ms. M. Akaike for their supports of the experiments.

This paper has submitted to AIChE Journal.

Additives' effects on dissociation rates of hydrates

Toshiharu Okui

Japan National Oil Corporation

Some chemical compounds are known as effective additives for control of gas hydrate formation and dissociation. In this report, effects of typical chemicals on kinetic properties of gas hydrates are reported. One of the purposes of this study is to develop useful additives for drilling fluids for gas hydrates.

The 500cc autoclave vessel was immersed in the cooling bath. A piston connected to the vessel keeps pressure inside during measurement of hydrate dissociation. For measuring dissociation rate of the synthetic pure methane hydrate, first, pure methane hydrate was previously synthesized and sample solution of an additive was introduced. Pressure was decreased and then kept constant by the piston. Dissociation rate was measured as released gas volume. Gas amount was also measured with the piston. Dissociation of natural gas hydrate samples was measured at a constant pressure and temperature as well, in the similar manner.

It was indicated that some polymer compounds influenced kinetic properties distinctively, whereas they did not affect thermodynamic properties so much. Especially PVCap decelerated both formation and dissociation rates. The same trend was observed in drilling fluids. Such property is suitable for drilling fluids for gas hydrate because those fluids should have both functions to preserve natural gas hydrates and to inhibit new hydrate formation.

The effect of lecithin in a drilling fluid on natural gas hydrate samples obtained from natural sediments was different from that on synthetic methane hydrates. Lecithin preserved natural gas hydrates obviously whereas such a trend was not observed about synthetic methane hydrates. The difference might be caused by the grain size of hydrates that is directly related to surface area.

In summary, it was suggested that formation and dissociation behavior of gas hydrates are controllable by chemical and physical treatments. Potential problems in natural gas hydrates development as a natural gas resource can be solved by technical improvements.

30 October 2002

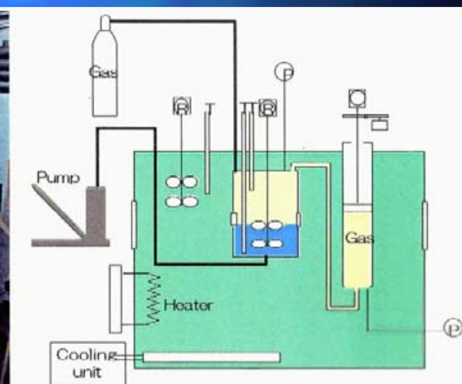
Additives' effects on dissociation rates of hydrates

Toshiharu Okui
Japan National Oil Corporation

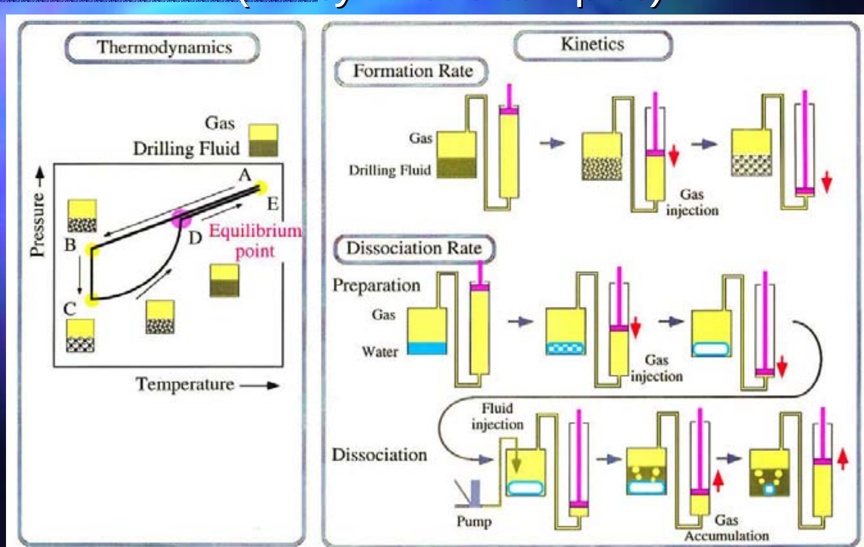
Outline

- Equipment
- Synthetic hydrates samples
  Procedure, Results and Discussion
- Natural hydrate samples
  Procedure, Results and Discussion
- Conclusions

Equipment



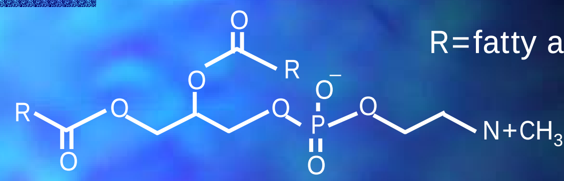
Procedure
(for synthetic samples)



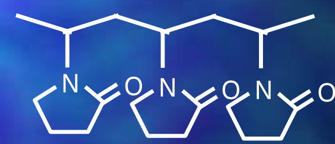
Chemical Additives

R=fatty acid

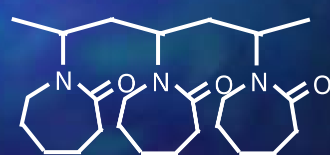
Lecithin



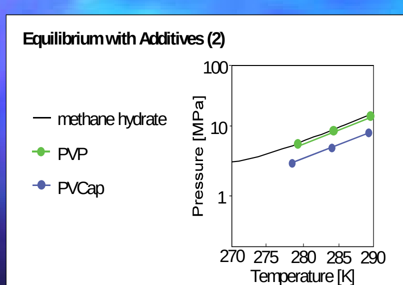
Polyvinylpyrrolidone (PVP)

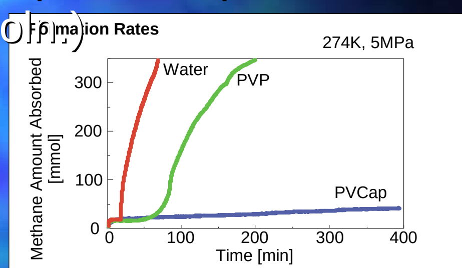


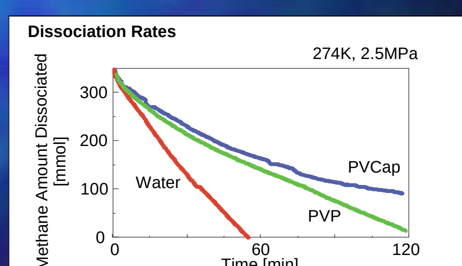
Polyvinylcaprolactam (PVCap)



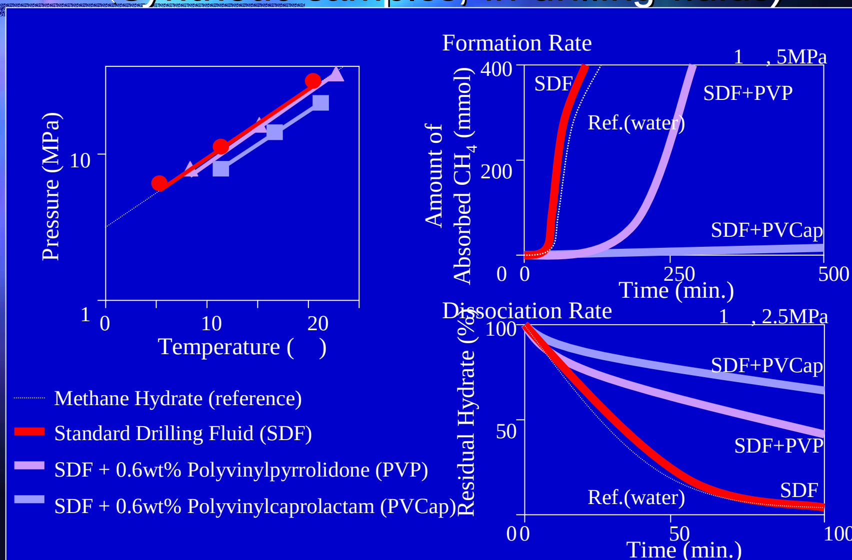
Data
(Synthetic samples, in aqueous soln.)



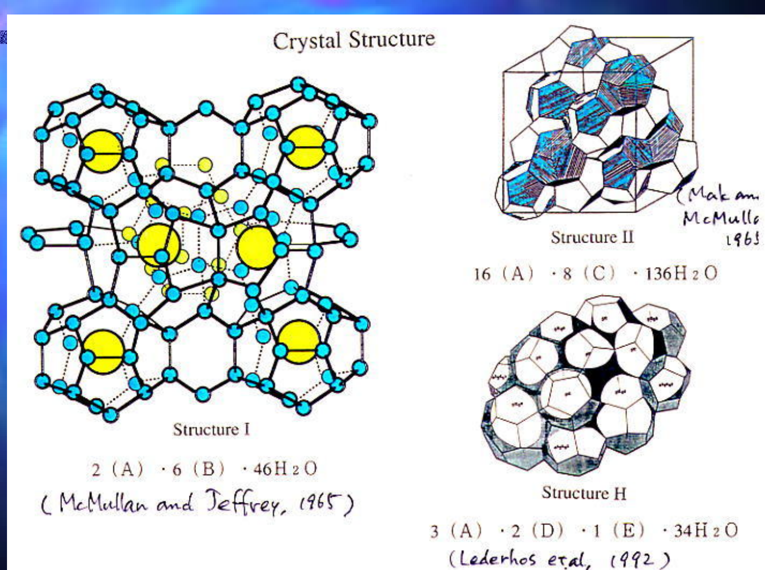




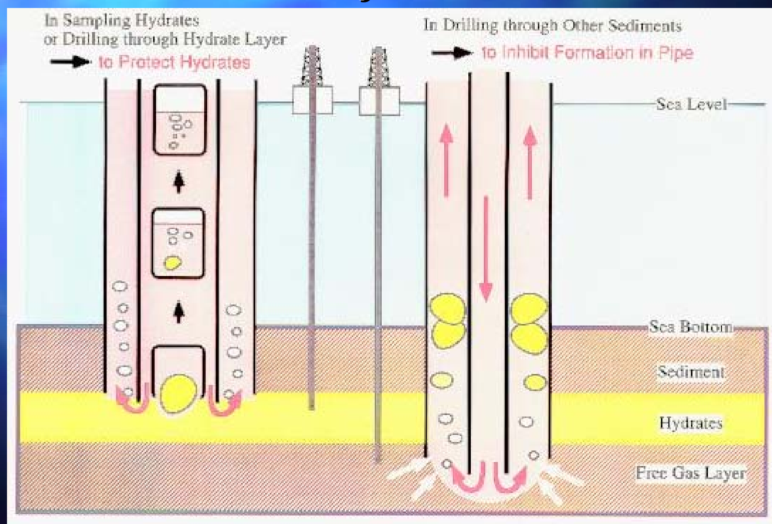
Data
(Synthetic samples, in drilling fluids)



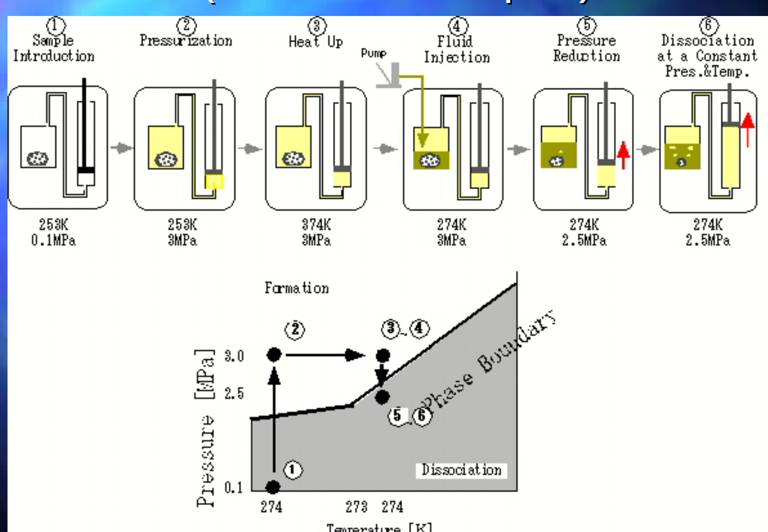
Crystal Structures

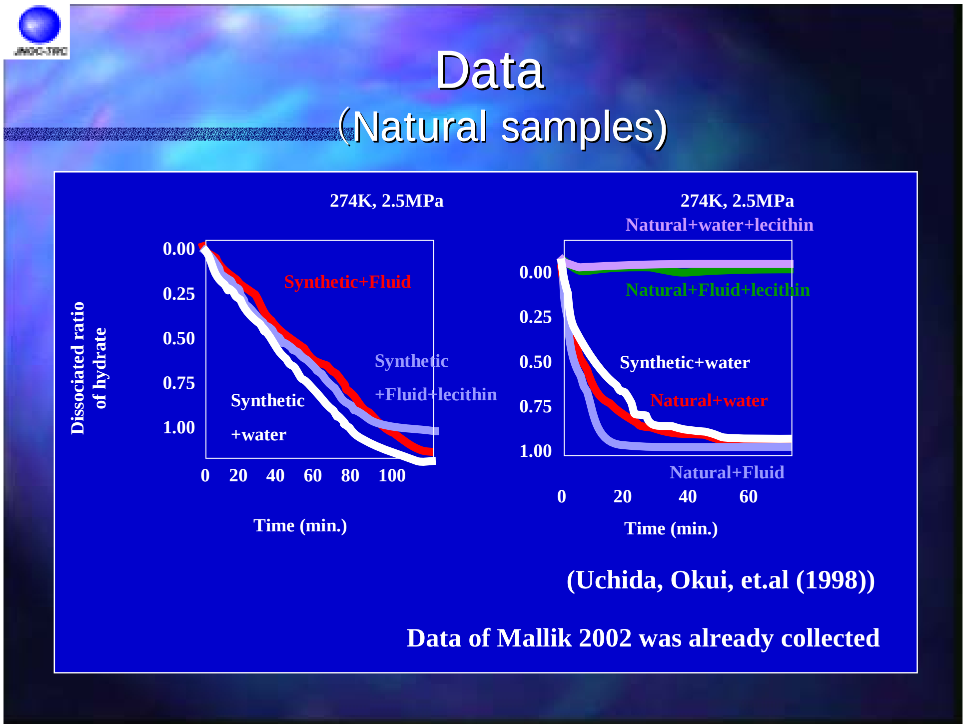


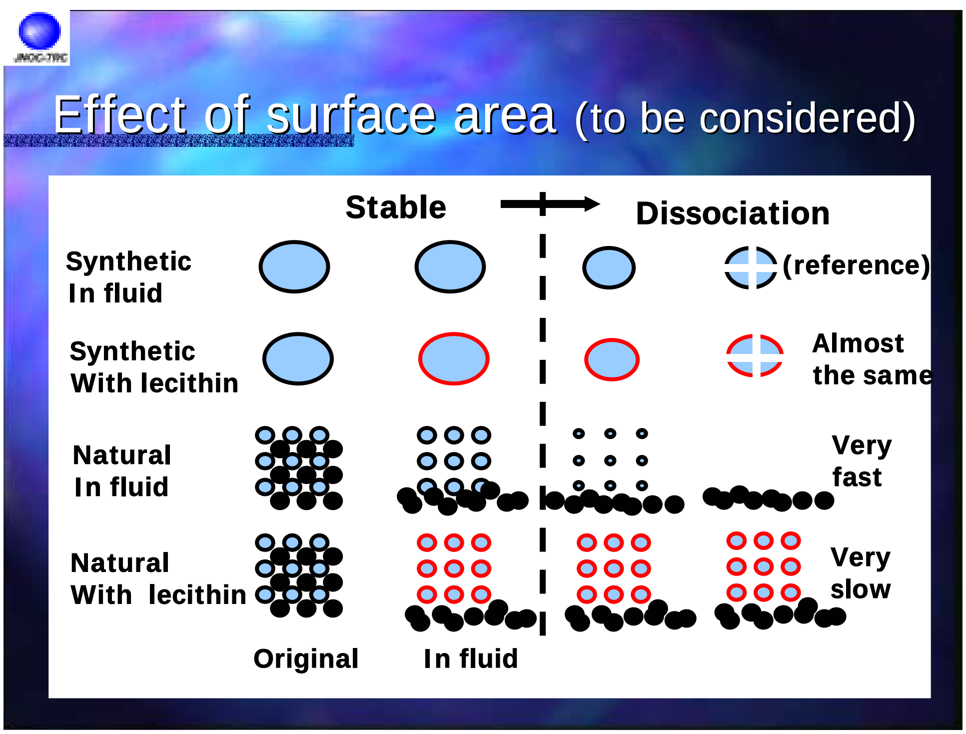
Requirements for drilling fluids for hydrates



Procedure (for natural samples)




JNOC-TRC
Data
(Natural samples)
274K, 2.5MPa
Dissociated ratio of hydrate
0.00
0.25
0.50
0.75
1.00
Synthetic+Fluid
Synthetic +Fluid+lecithin
Synthetic +water
0 20 40 60 80 100
Time (min.)
274K, 2.5MPa
Natural+water+lecithin
Natural+Fluid+lecithin
Synthetic+water
Natural+water
Natural+Fluid
0 20 40 60
Time (min.)
(Uchida, Okui, et.al (1998))
Data of Mallik 2002 was already collected


JNOC-TRC
Effect of surface area (to be considered)
Stable
Dissociation
Synthetic In fluid
(reference)
Synthetic With lecithin
Almost the same
Natural In fluid
Very fast
Natural With lecithin
Very slow
Original
In fluid

Conclusions

Formation and dissociation behavior of gas hydrates are controllable by chemical and physical treatments.

Kinetic behavior was considered to be caused by chemical additives and physical appearance of hydrates.

KINETICS in GAS HYDRATE PRODUCTION & TRANSPORT TECHNOLOGY

Dr. Yuri F. Makogon

Texas A&M Universyty

Abstract

Gas Hydrate are metastable mineral whose formation, stable existence and dissociation depend upon pressure, temperature, composition and other properties of the gas and water. Gas hydrates are clathrate inclusion compounds in which molecules of gas volatile liquids no larger than 0.83 nm are hosted in crystalline lattice formed by hydrogen-bonded water molecules. Scientists have known about gas hydrates for over 200 years (Priestley, 1778). Serious research on gas hydrates by the oil and gas industry dates back over 60 years (Hammershsmidt, 1934). Natural gas hydrates, which are widespread on our planet, where discovered over 30 years ago (Makogon, 1966).

Gas hydrate forms in a technological oil-gas production and transport system, and in nature. From one side gas hydrates are very expensive problem – for prevention formation of solid gas hydrate plugs in the wells and pipelines industry spent over two million US$ awry day; from another side gas hydrate presented very high energy resource – proven reserves of hydrated gas are more then 2.1×10^{12} tons oil equivalent (present time total proven reserves of free gas, oil and coal is 693×10^{9} t.o.e.).

One of the most important and complicate problem in hydrates is kinetic it formation and dissociation. There is different mathematics models for prediction conditions of hydrate formation and dissociation in the pipelines and porous media for pure gases and water. However, very necessary more experimental study for this, especially for natural gases and minerals water.

In this paper we will show some results of experimental research kinetic of hydrate formation and dissociation in static and dynamic conditions with pure and natural gases and different water solution, including thermodynamic and kinetic inhibitors. We will show how we can use kinetics parameters of hydrate in gas hydrate production and transport technology.

KINETICS in GAS HYDRATE
PRODUCTION & TRANSPORT TECHNOLOGY

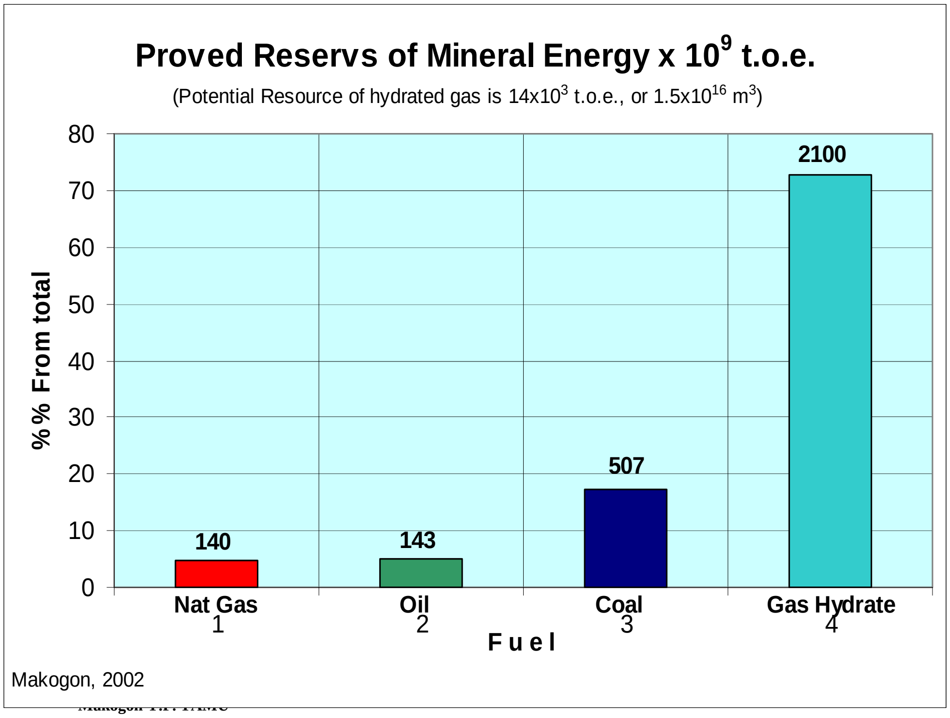
Dr. Yuri F. MAKOGON
Texas A&M University

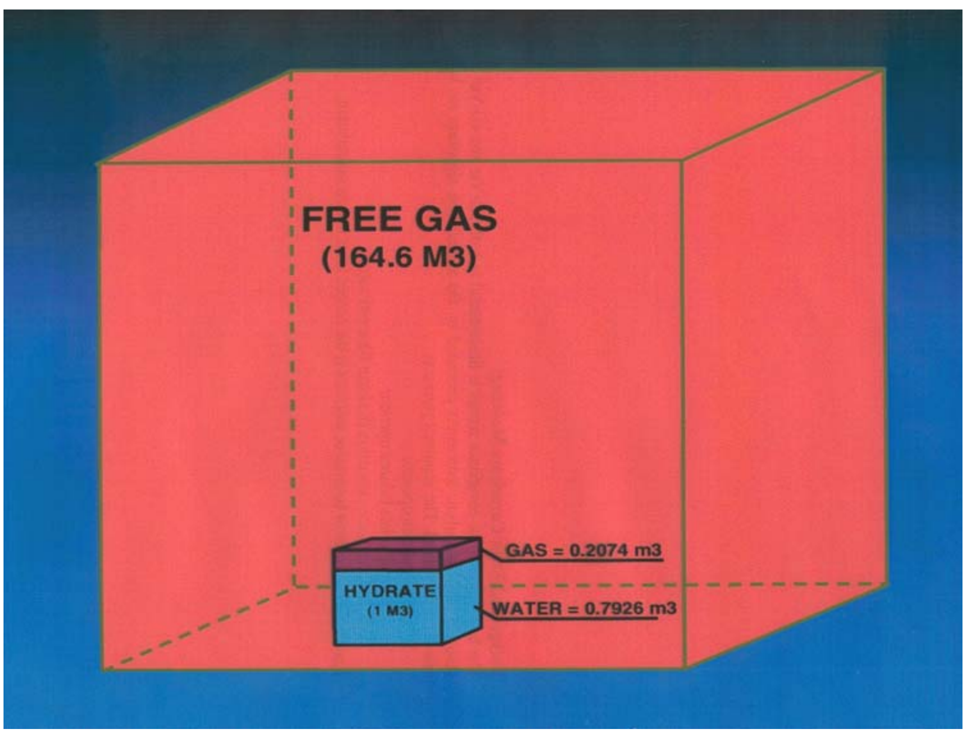
Contact address:
makogon@spindletop.tamu.edu

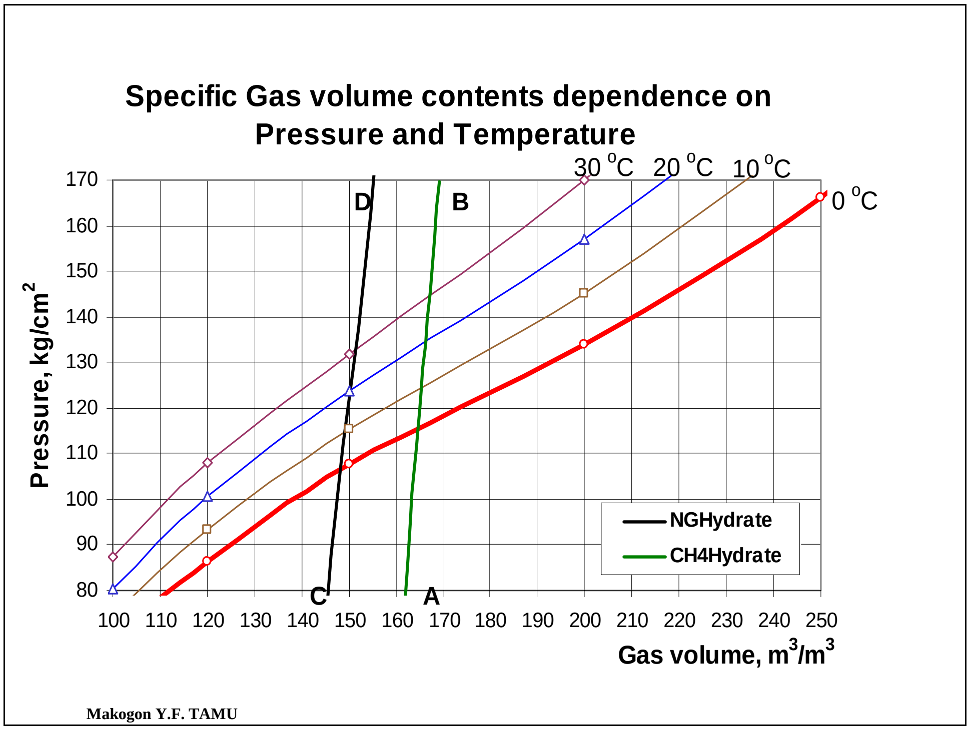
2 Int. NGH Workshop, Washington, Oct.-2002

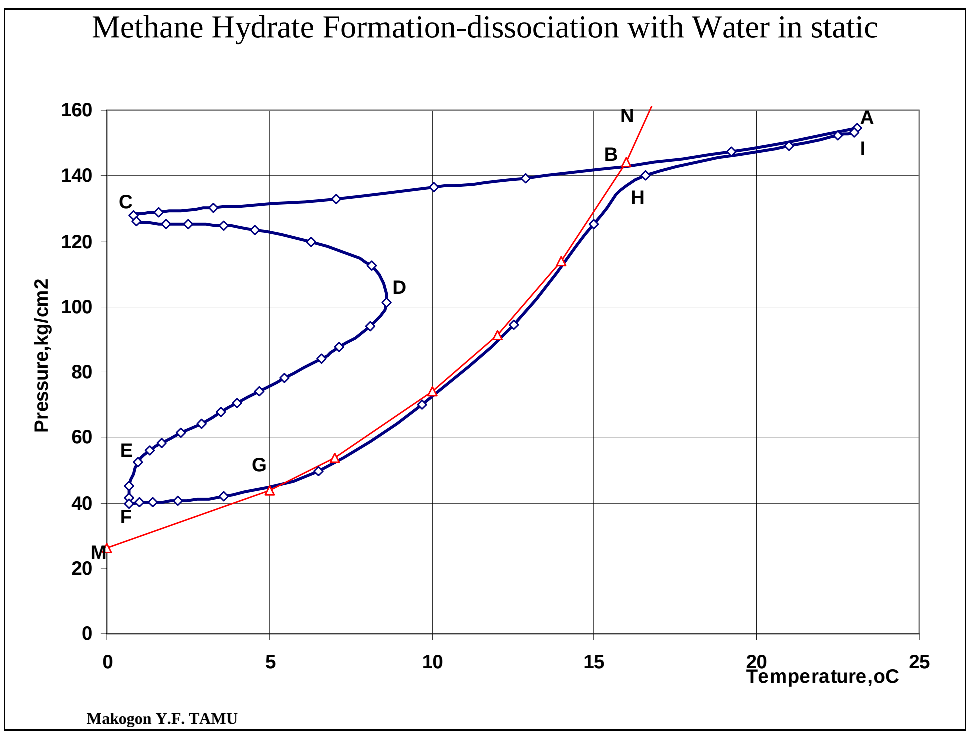
General History of Gas Hydrates

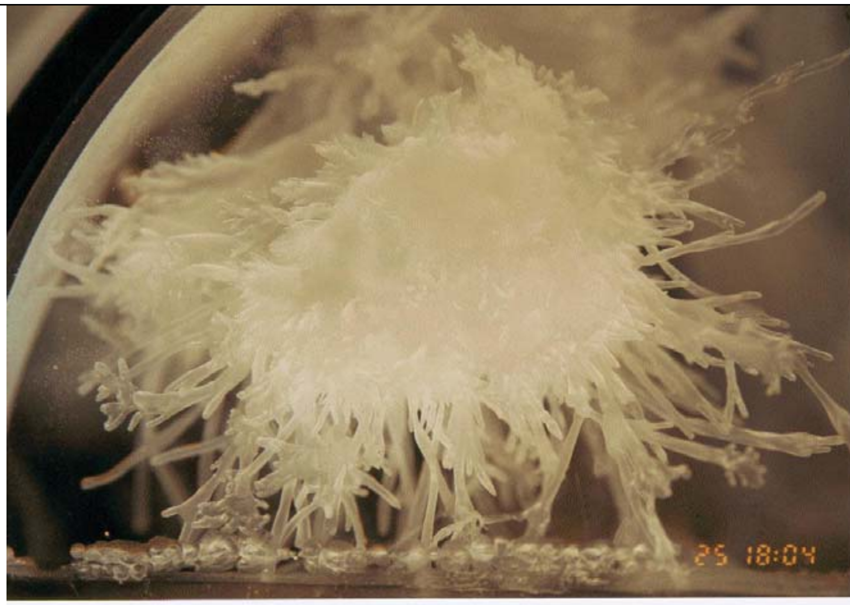
- **1811** – **Davy** Gas Hydrate **in Laboratory**
- **1934** –**Hammershmidt**–Gas Hydrate **in Industry**
- **1966** – **Makogon** – Gas Hydrate **in Nature**
- **1969** – Gas Production from first Gas
- Hydrate Deposit-**Messoakhy**


Proved Reservs of Mineral Energy x 10^9 t.o.e.
(Potential Resource of hydrated gas is 14x10^3 t.o.e., or 1.5x10^16 m^3)
% % From total
80
70
60
50
40
30
20
10
0
140
143
507
2100
Nat Gas
1
Oil
2
Coal
3
Gas Hydrate
4
F u e l
Makogon, 2002


FREE GAS
(164.6 M3)
HYDRATE
(1 M3)
GAS = 0.2074 m3
WATER = 0.7926 m3


Specific Gas volume contents dependence on Pressure and Temperature
Pressure, kg/cm2
Gas volume, m3/m3
30 oC
20 oC
10 oC
0 oC
NGHydrate
CH4Hydrate
A
B
C
D
Makogon Y.F. TAMU

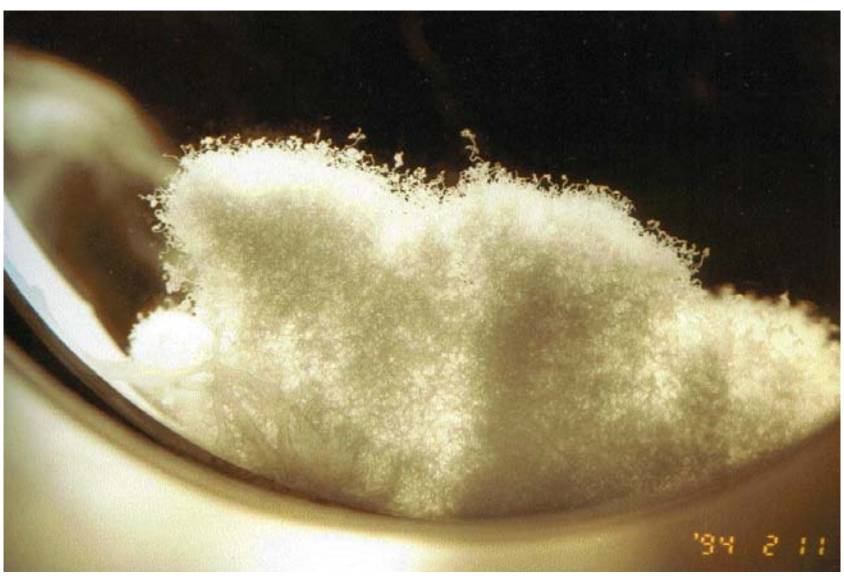

Methane Hydrate Formation-dissociation with Water in static
Pressure,kg/cm2
Temperature,oC
A
B
C
D
E
F
G
H
I
M
N
Makogon Y.F. TAMU



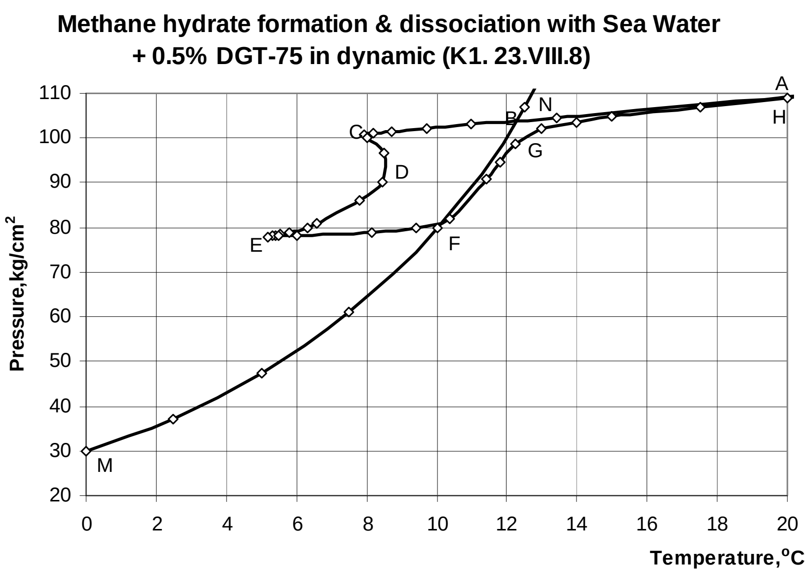
Methane massive hydrate formed from vapor water. P=86.1 bar; T=276.4 K

Makogon Y.F. TAMU

Massive Natural Gas Hydrate Crystals formed with Kinetic Inhibitor



Makogon Y.F. TAMU



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Gas Hydrate formed in Dynamic conditions

Natural gas Hydrate crystals formed in Water+Kinetic Inhibitor

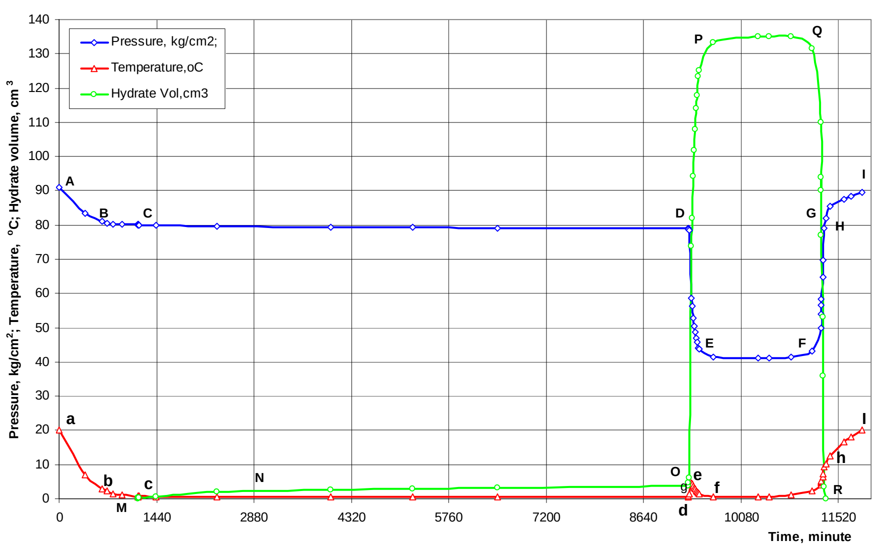
Gas Hydrate Crystals formed in Dynamic flow

Removal of Hydrates–(Petrobras)

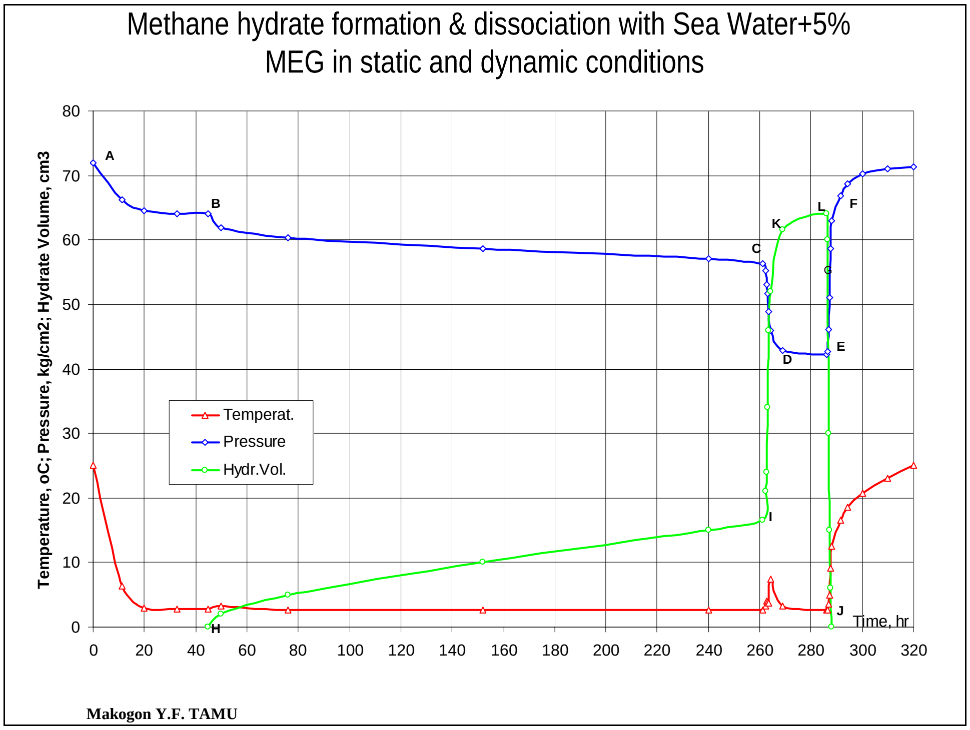
- Hydraulic – depressurization of line
- Chemical – inject methanol or glycol if flows
- Thermal – direct heating in topsides only
- Mechanical – coiled tubing, drilling

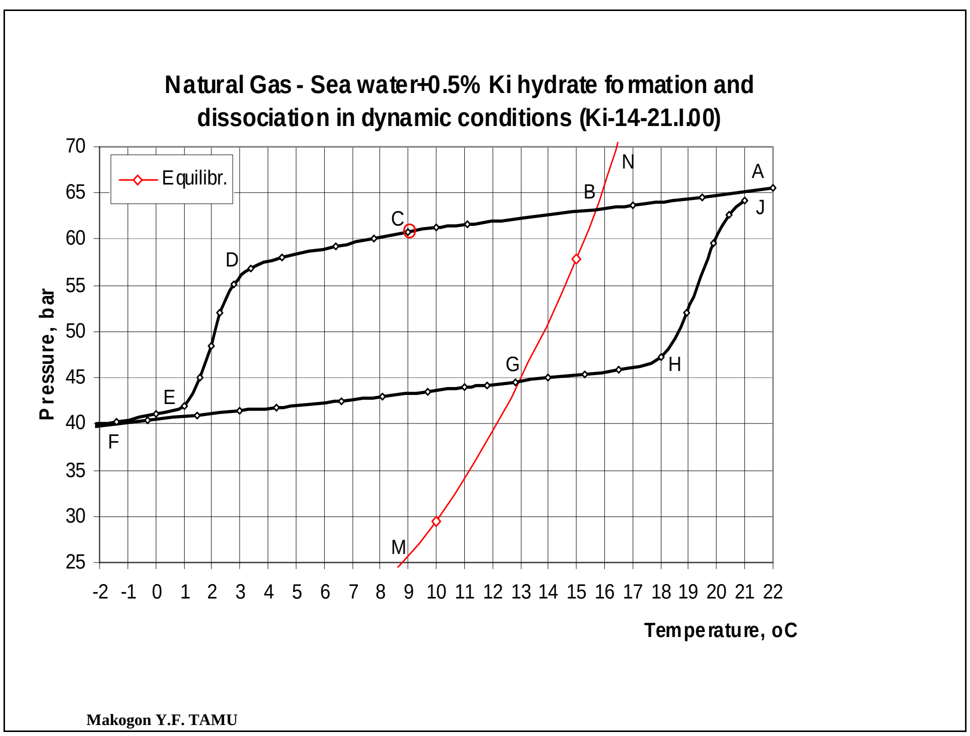
Makogon Y.F. TAMU

Methane hydrate formation-dissociation in static & dynamic with water + 5% Methanol & 1%VP-4-67

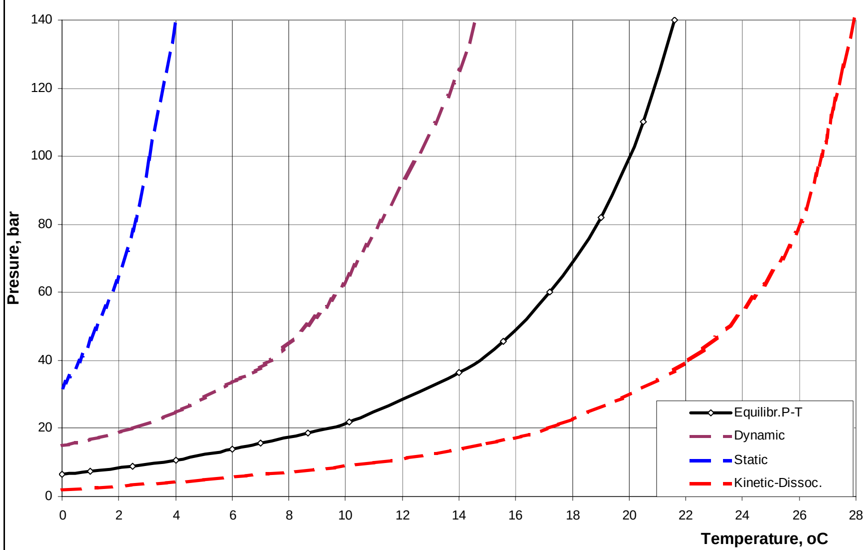


Makogon Y.F. TAMU


Methane hydrate formation & dissociation with Sea Water+5% MEG in static and dynamic conditions
Temperature, oC; Pressure, kg/cm2; Hydrate Volume, cm3
Time, hr
Temperat.
Pressure
Hydr.Vol.
A
B
C
D
E
F
G
H
I
J
K
L
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
Makogon Y.F. TAMU

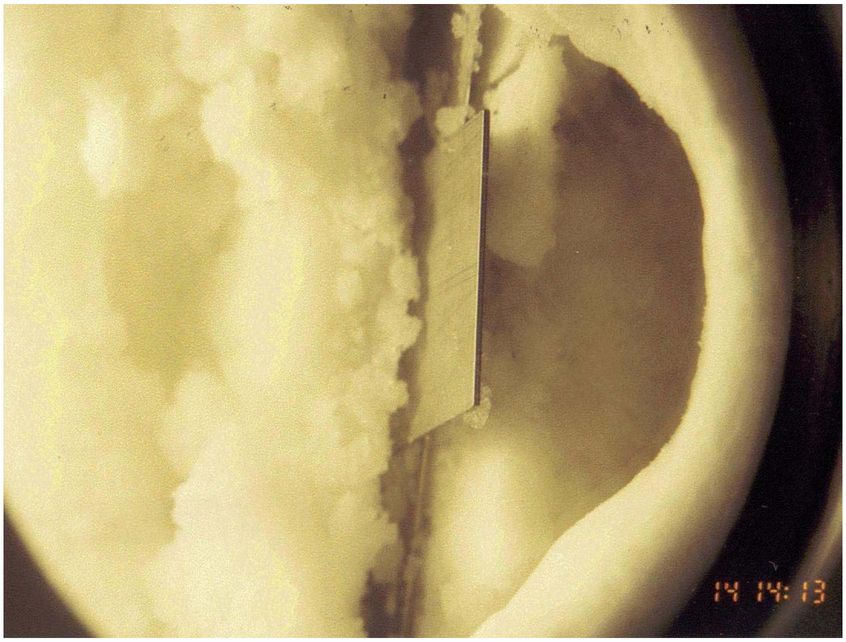

Natural Gas - Sea water+0.5% Ki hydrate formation and dissociation in dynamic conditions (Ki-14-21.I.00)
Pressure, bar
Temperature, oC
Equilibr.
A
B
C
D
E
F
G
H
J
M
N
25
30
35
40
45
50
55
60
65
70
-2 -1 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Makogon Y.F. TAMU

There are three Metastable Zones



Makogon Y.F. TAMU

Hydrate formed without adhesion on the steel



Makogon Y.F. TAMU

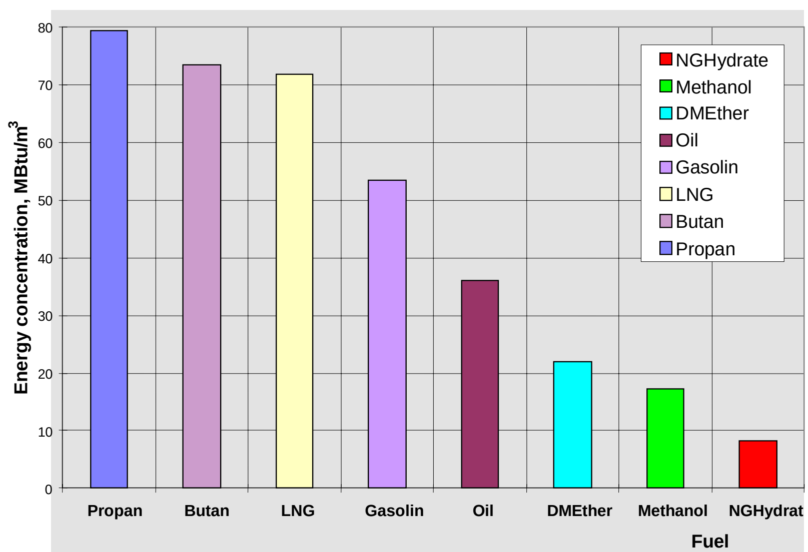
TRANSPORT of GAS

- Free state ?

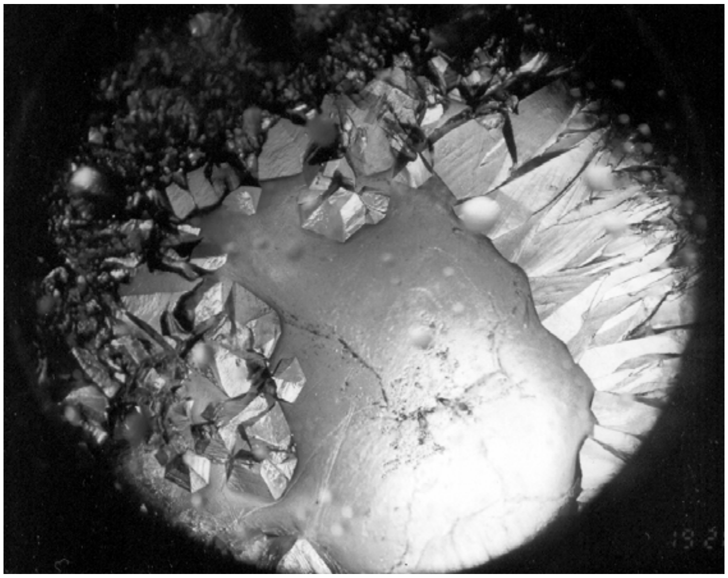
- Liquid state ?
- LNG
- Methanol
- Dimetilether

- Hydrate state ?
- Solid hydrate blocks by pipelines
- Solid hydrates by ships
- Solid hydrate slurries by pipelines

Fig. 3 Specific Energy concentration in Fuel, MBtu/m^3



High Energy Concentration Hydrate Crystals



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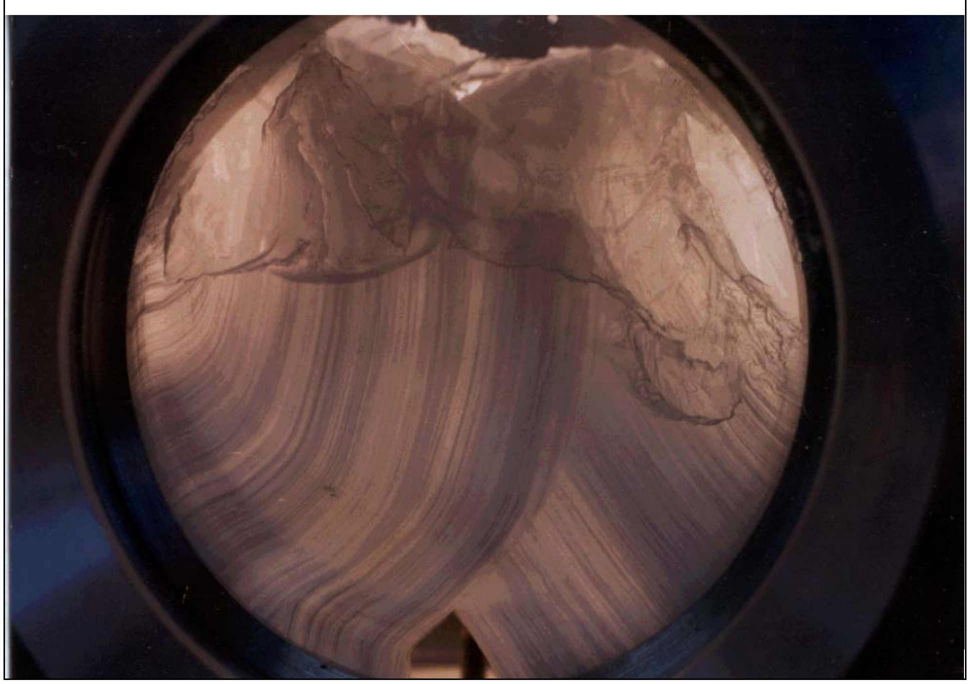
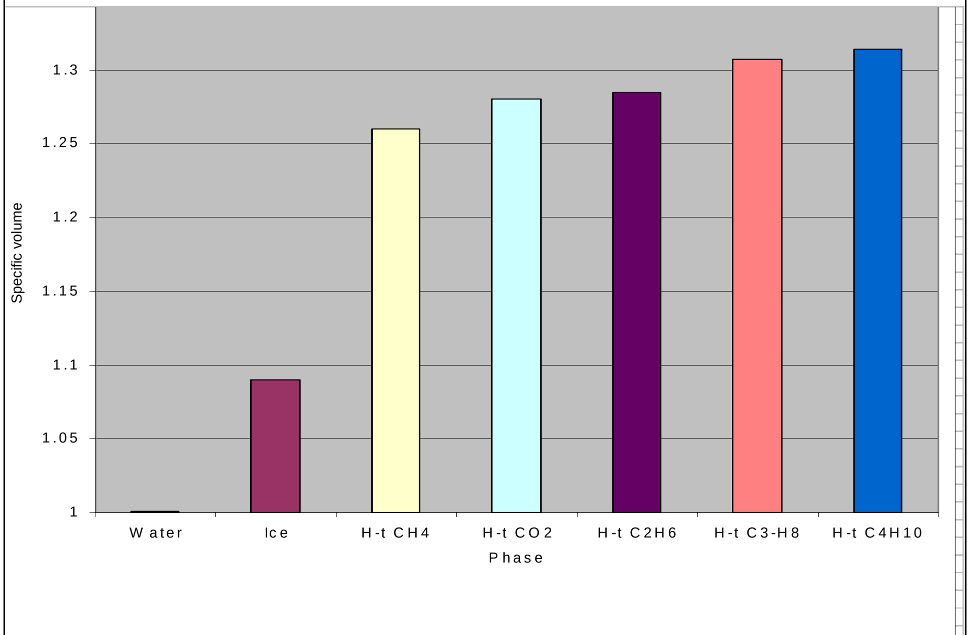
High Energy Concentration Methane Hydrate Whiskery Crystals



Specific Volume of Water in Ice & Hydrate Phases



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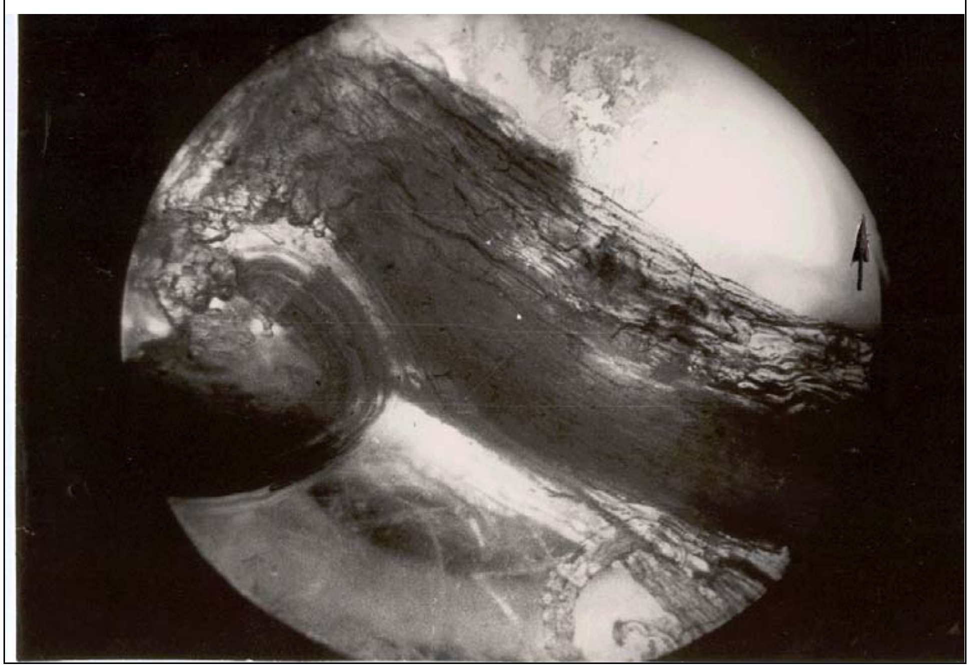
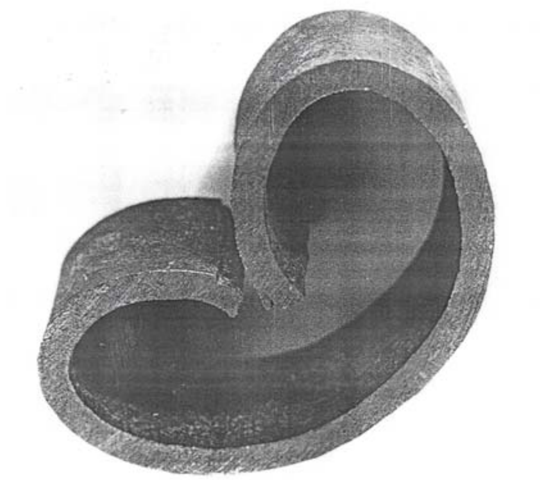
Very hard Whiskery Liquid Propane-Water Hydrate Crystals



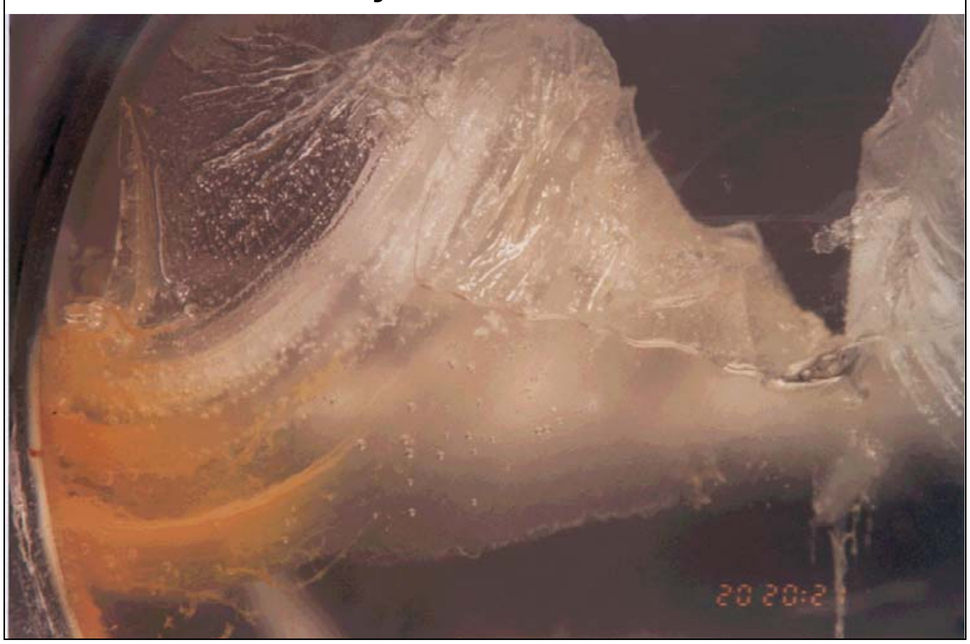
Collapse of Tubing as result of Hydrate growth between Casing and Tubing

(P=110 atm; T=8 ºC; $P_{col.}$>800 atm)



Makogon Y.F

Stainless Steel Electro Corrosion by Whiskery Crystal formation



Stainless steel corrosion by hydrate crystal formation

Makogon Y.F. TAMU

Electro Corrosion of Stainless Steel by Methane-Water Hydrate Crystal Formation

Makogon Y.F. TAMU

Conclusions

- Gas from natural gas hydrates could provide large volumes of energy by 2010-2050
- Additional research will be required over the next 5-20 years to recover the gas hydrate resource and to develop the technologies to extract the resource and transport of produced gas
- Transportation of gas in the hydrate state for long distances is not feasible
- The industry needs more laboratory work to understand the kinetics and properties of gas hydrates

Laboratory observations of sI and sII gas-hydrate decomposition using accurate gas flow measurements, x-ray tomography, cryogenic SEM and seafloor measurements

Stephen Kirby[1], *Laura Stern*[1], *Susan Circone*[1], *William Durham*[2], *Tim Kneafsey*[3], *Barry Freifeld*[3], *Liviu Tomutsa*[3], *Peter Brewer*[4], *Ed Pelzer*[4] *and Gregor Rehder*[4]

[1]US Geological Survey, Menlo Park, CA; [2]Lawrence Livermore National Lab, Livermore, CA; [3]Lawrence Berkeley National Lab, Berkeley, CA; [4]MBARI, Moss Landing, CA

ABSTRACT

Characterizing the decomposition rates of natural hydrocarbon clathrate hydrates is potentially relevant to such issues as optimizing hydrate recovery in drill core, natural-gas production modeling from hydrate-bearing sediments, developing strategies for dealing with gas-line blockages, investigating the fates of gas hydrates in submarine debris flows, evaluating the responses of hydrates to climate changes and considering the lifetimes of seafloor exposures of hydrocarbon hydrates to undersaturated seawater.

Decomposition rates of synthetic aggregates of pure sI methane hydrate, sI CO2 hydrate and sII methane-ethane hydrate were studied using accurate gas-flow measurements, x-ray tomography and seafloor images of hydrate dissolution. These aggregates are extremely well characterized and very reproducible and these attributes make measured decomposition rates also very reproducible. Their porous and permeable structure also tends to minimize rate effects associated with sample-to-sample variations in the pathways of gases or liquids released by decomposition.

We discuss three temperature-dependent regimes observed in experiments on gas-saturated porous sI methane hydrate decomposed by pressure drops below its equilibrium line at constant bath temperature or by 1-atm temperature ramping:(1) **"Normal" dissociation regime**: Heating from temperatures below the 1 atm dissociation temperature (195 K) to 240 K produces rapid dissociation beginning at 200-205 K and completed by 220 K. Similarly, pressure drop experiments at fixed bath temperature also show a sharp increase dissociation rates in this temperature interval. (2)**Anomalous preservation Regime** from 240 K to 272.5 K in which long-term dissociation rates are many orders of magnitude slower than those extrapolated from lower-temperature behavior. Minimum decomposition rates occur near 269 K. (3) **High-temperature regime** in which decomposition takes place rapidly at bath temperatures above 272.5 K and sample temperatures drop to and are buffered at about 272.5 K due to the endothermic reaction. Rates increase with increasing bath temperature and are largely governed by heat flow through the pressure vessel wall. Decomposition rates at elevated pressures are slightly slower than those at 1 atm and mirror the steep temperature effect seen at high temperatures and 1 atm methane pressure. sII methane ethane hydrate does not show anomalous preservation behavior at 269 K. We also report on the a recent collaborative x-ray tomography study of Regime 1 (above) that imaged a dissociation front by exploiting differences in the x-ray properties of ice and sI methane hydrate. Finally, we report on seafloor measurements of the dissolution rates sI methane and CO2 hydrates, rates that are proportional to *in situ* solubilities of these hydrate formers and consistent with diffusive-boundary-layer theory.

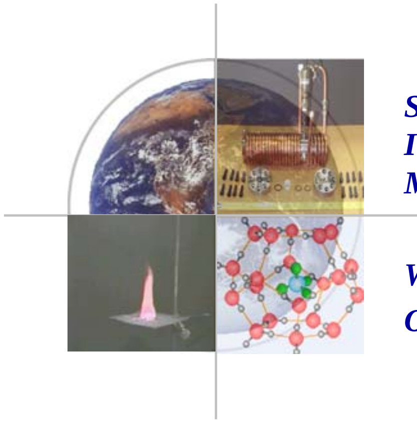
Formation Studies Of Methane Hydrates With Surfactants

Charles E. Taylor

U.S. Department of Energy, National Energy Technology Laboratory

Important characteristics for formation of methane hydrates have been investigated. Characteristics such as temperature and pressure profiles for methane hydrate formation and dissociation in pure water, simulated seawater, and surfactant-water systems have been established. A hysteresis effect has been observed for repeated formation/dissociation cycles of the same methane-water system. In an attempt to maximize the uptake of methane during methane hydrate formation, the addition of sodium dodecyl sulfate provided methane uptake of over 97 % of the theoretical maximum uptake. Additional surfactants were tested for their ability to enhance the uptake of methane for hydrate formation. Successful demonstration of efficient methane storage using hydrate formation enhanced by addition of surfactants could provide a safe, low-cost alternative method for storage of natural gas at remote locations.

Formation Studies of Methane Hydrates with Surfactants



Second Workshop of the International Committee on Methane Hydrates

Washington, DC
October 29-31, 2002

Charles E. Taylor, Leader, Methane Hydrate Team
National Energy Technology Laboratory

Storage of Methane in Hydrates Staffing

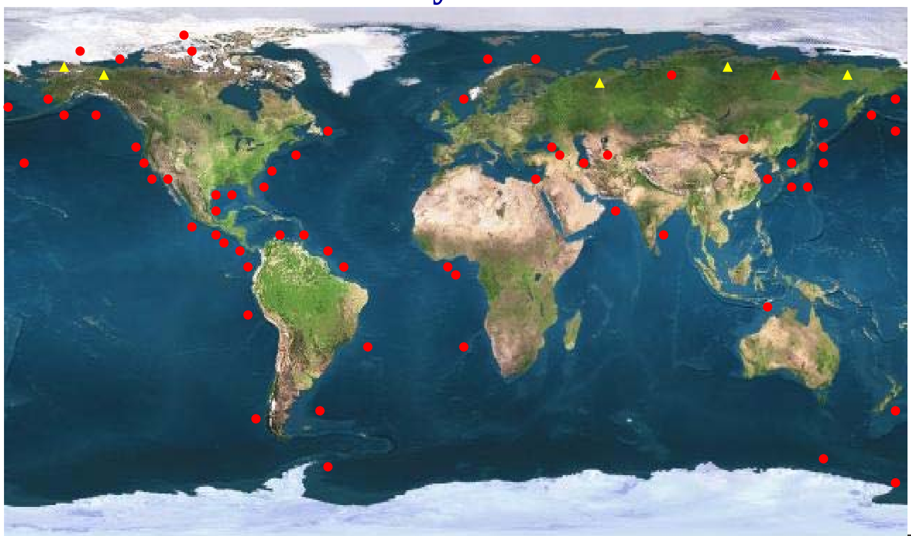
Heather A. Elsen

Edward P. Ladner

Jonathan W. Lekse

Dirk D. Link

Global Gas Hydrate Locations



● Ocean Sediment △ Permafrost

NETL

USGS Estimates Of U.S. In-place Methane Contained Within Gas Hydrates (tcf)

NETL

Storage of Methane in Hydrates Background

- **Previous research focused on the conversion of methane in methane hydrates.**
- **During the course of the conversion studies, it was observed that the quantity of methane converted to hydrate varied.**
  - Reaction conditions
  - Physical mixing
  - Additives
- **Preliminary experiments revealed high conversion of methane to hydrates is possible.**

NETL

Storage of Methane in Hydrates Background

- **Majority of research on the use of additives and hydrates is focused on inhabitation of hydrate formation.**
- **Literature survey revealed several papers on the use of additives to enhance methane uptake during hydrate formation.**
  - Kalogerakis *et al*., *Soc. Pet. Eng*. 25188, p. 375, 1993.
  - Zhong and Rogers, *Chem Eng. Sci*. **55**, p. 4175, 2000.
  - Irvin et al., *Annl. N. Y. Acad. Sci*. **912**, p. 515, 2000.
  - Karaaslan and Partlaktuna, *Annl. N. Y. Acad. Sci*. **912**, p. 735, 2000.

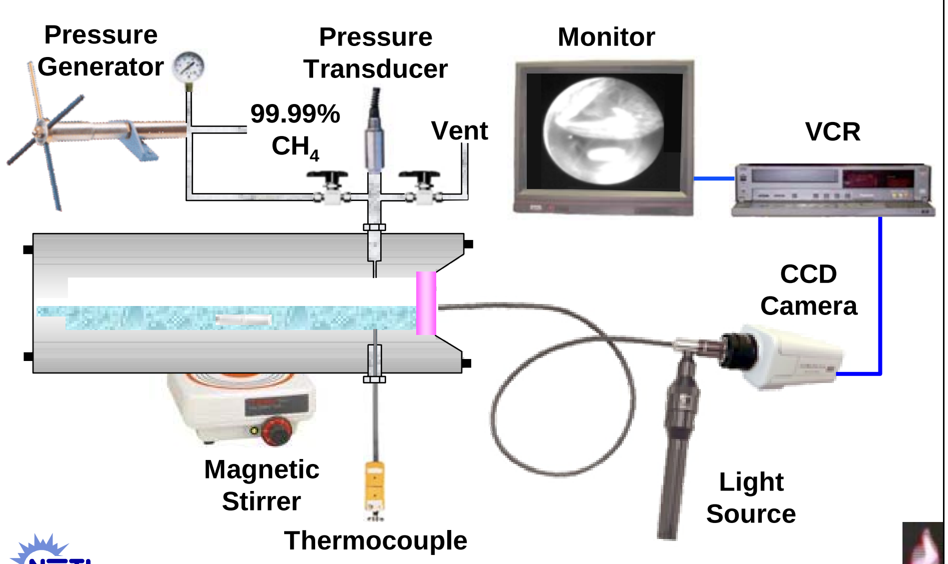
NETL

03HydrateMeritReview – CET/ST-50/0802

FY-02 Research for the Storage of Methane in Hydrates

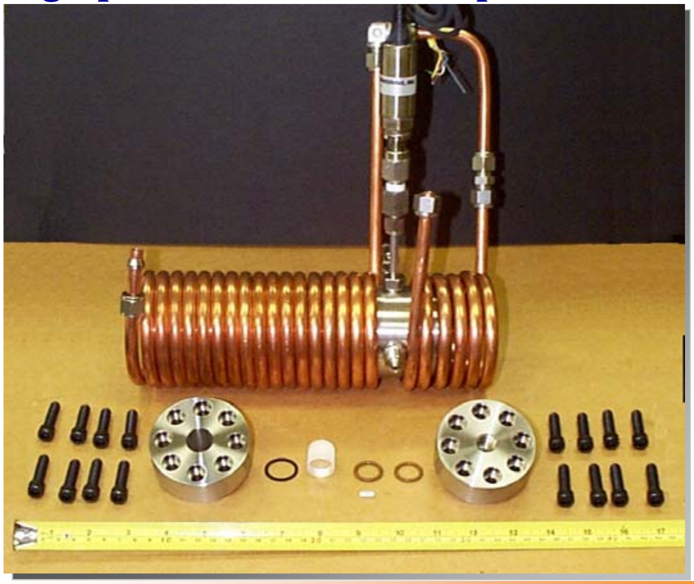
- **Research to focus on methods for forming methane hydrates in the shortest time and with the maximum methane uptake.**
  - The high-pressure view cell currently on hand will be used for preliminary screening studies.
  - Effects of additives, formation rate, etc. will be investigated.
- **A second high-pressure view cell to be constructed.**
- **A large-volume cell will be designed and constructed similar to cells in use at the Naval Research Laboratory and the University of Hawaii.**

High-pressure View Cell Schematic

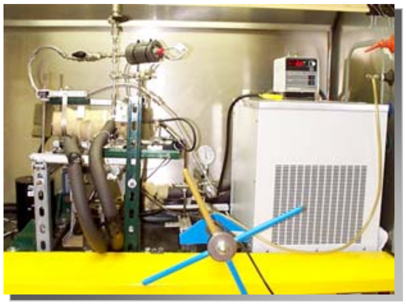


NETL 03HydrateMeritReview – CET/ST-50/0802

High-pressure View Cell Exploded View

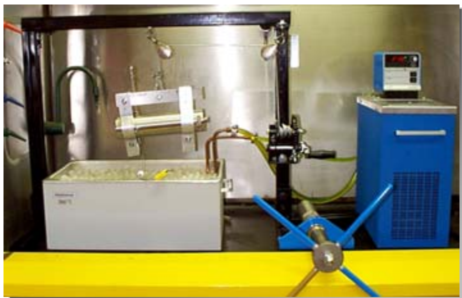


Two High-pressure View Cells Available

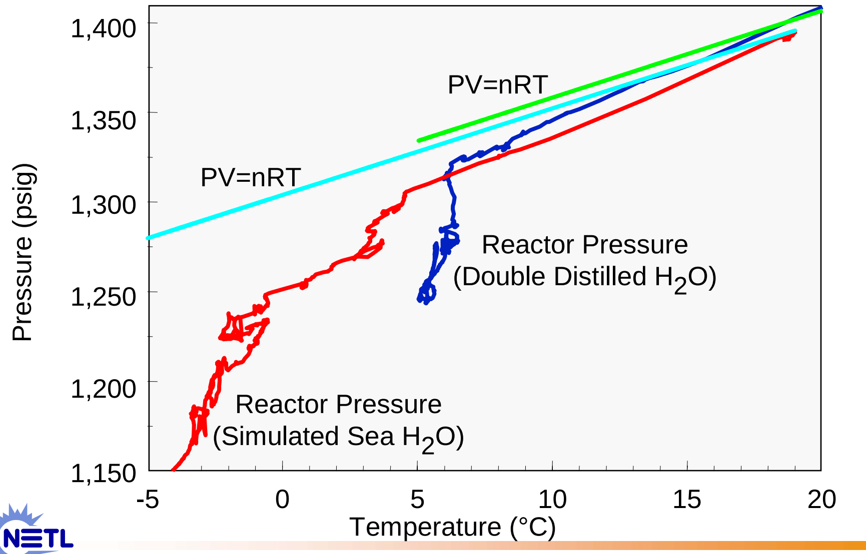


Original view-cell cooled via external chiller and cooling coil around cell (operates in either horizontal or vertical position).

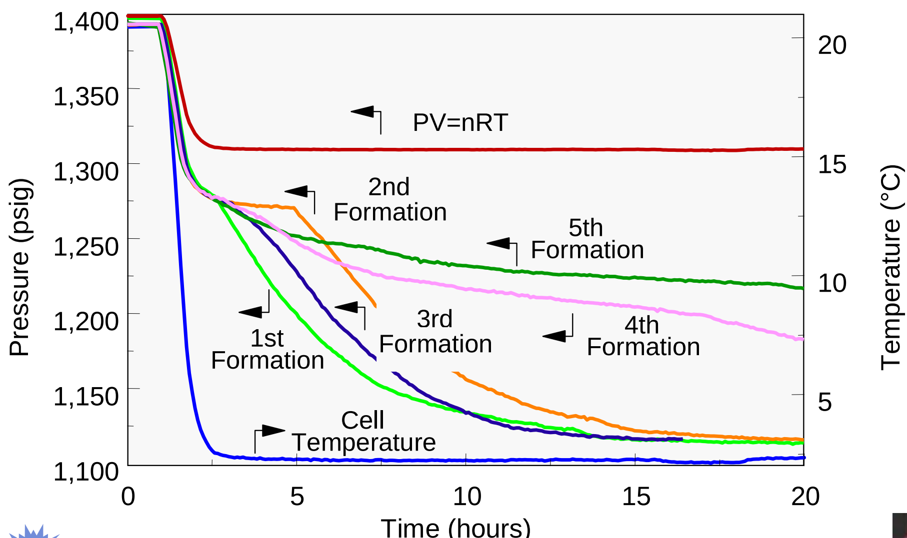
Second view-cell cooled via external chiller and immersion bath (operates in horizontal position).



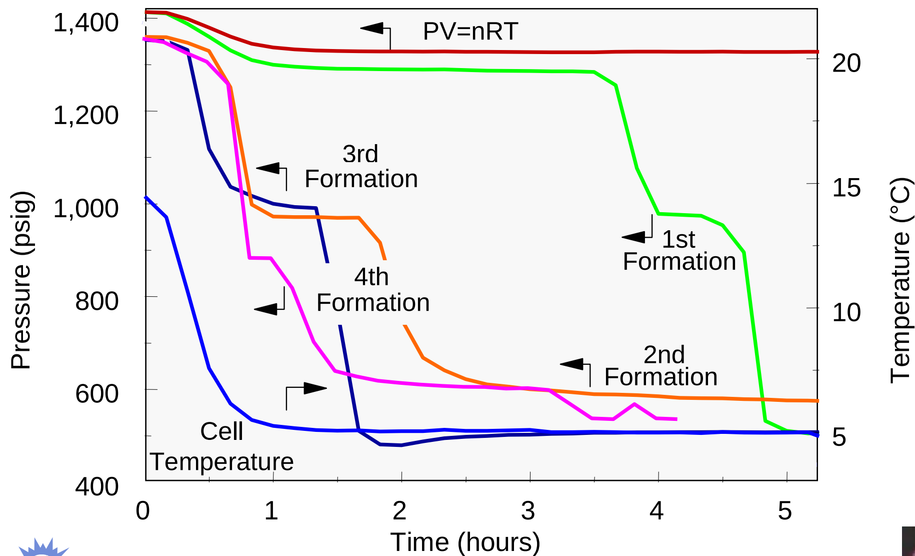
Pressure-temperature Profile Of Hydrate Formation



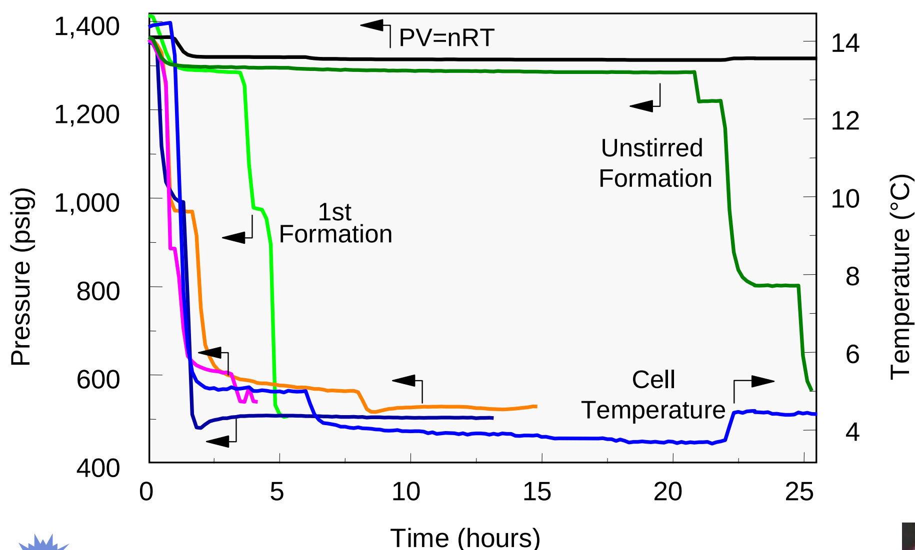
Hysteresis Effect During Hydrate Formations



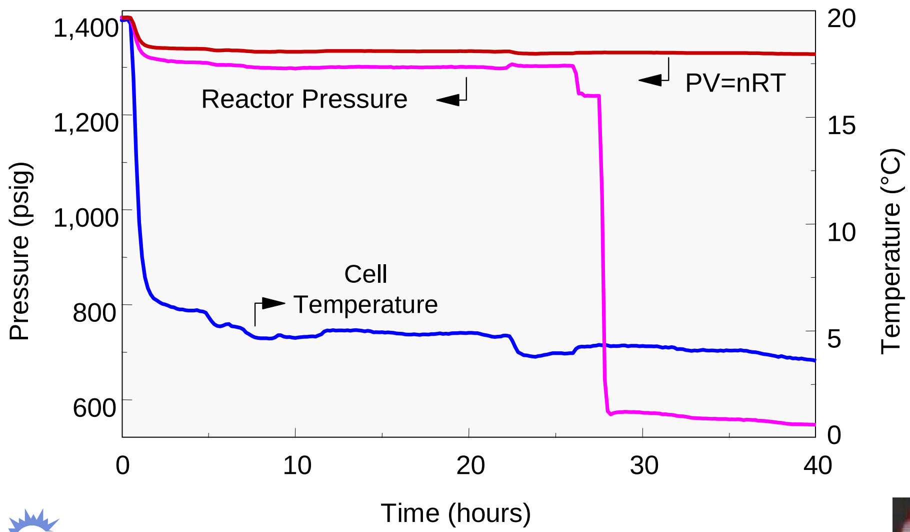
Hysteresis Effect During Hydrate Formations



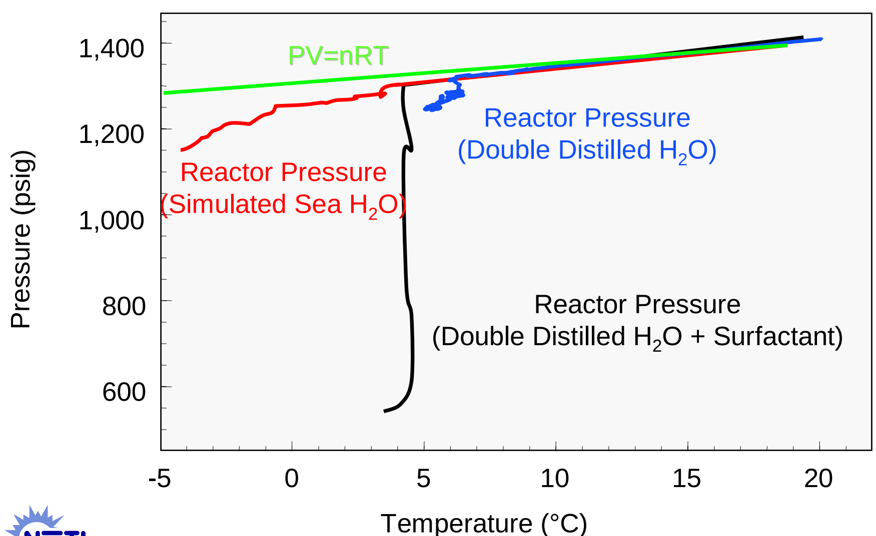
Hysteresis Effect During Hydrate Formations



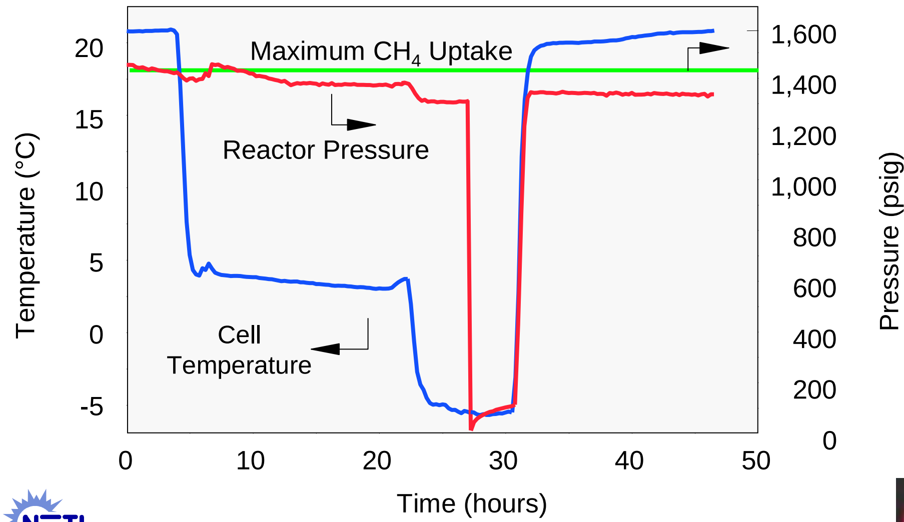
Hydrate Formation With Surfactant Added



Pressure-temperature Profile Of Hydrate Formation



Hydrate Formation Under Constant Methane Pressure (Sodium DodecylSulfate)



Methane Storage Experimental Procedure

1. **Fill the cell with ~10 mL (± 0.1 mL) of double-distilled water, surfactant (~220 ppm) mixture and a magnetic stir bar.**
2. **Purge the cell several times with methane.**
3. **Apply a constant head pressure of 1400 psig.**
4. **Lower the cell temperature until formation of methane hydrate observed**
5. **Isolate the cell from the manifold and vent the unabsorbed methane.**
6. **After release of the head pressure, re-seal the cell and warm to room temperature.**
7. **Determine methane uptake based on the amount of pressure that built up inside the cell due to dissociation of the hydrate.**

Sodium DodecylSulfate

Constant Head Pressure	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
No	-4.0	10	101.25
No	-4.5	10	90.75
Yes	-5.5	15	97.26
Yes	-4.0	30	37.30
Yes	-4.5	30	39.41

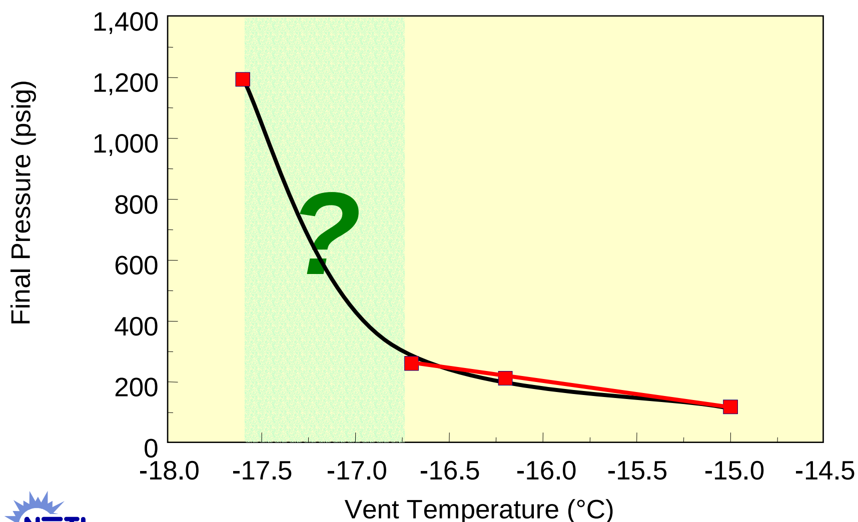
Other Surfactants Tested

Surfactant	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
Dodecylamine	-10.8	10	9.91
Dodecyl Trimethyl Ammonium Chloride	-15.5	10	13.92
Sodium Lauric Acid	-15.2	10	39.54
Sodium Lauric Acid	-16.1	10	77.35
Sodium Oleate	-13.7	10	70.47
Superfloc 16	-14.0	10	19.59
Superfloc 84	-15.1	10	20.05

Commercial Surfactant Test

Cycle Number	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
First	-17.6	10	99.10
Second	-16.2	10	22.75
Third	-16.7	10	27.96
Fourth	-15.0	10	12.71

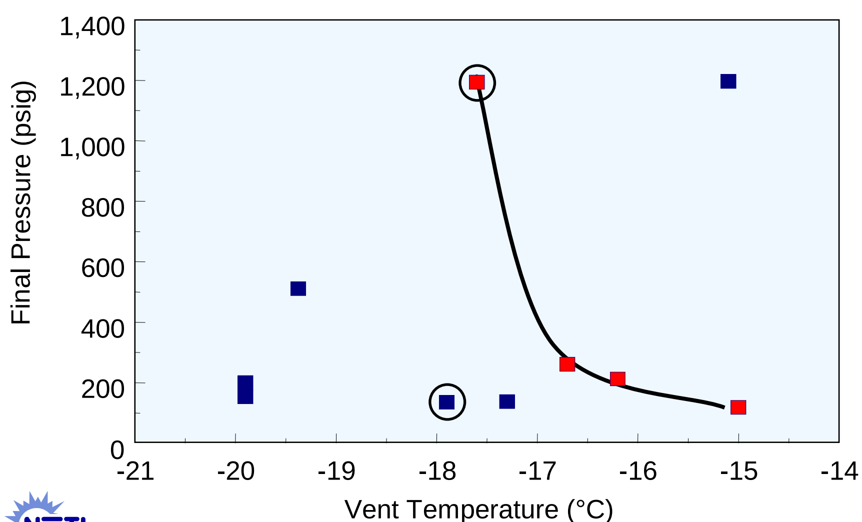
Final Pressure as a Function of Venting Temperature for Commercial Surfactant



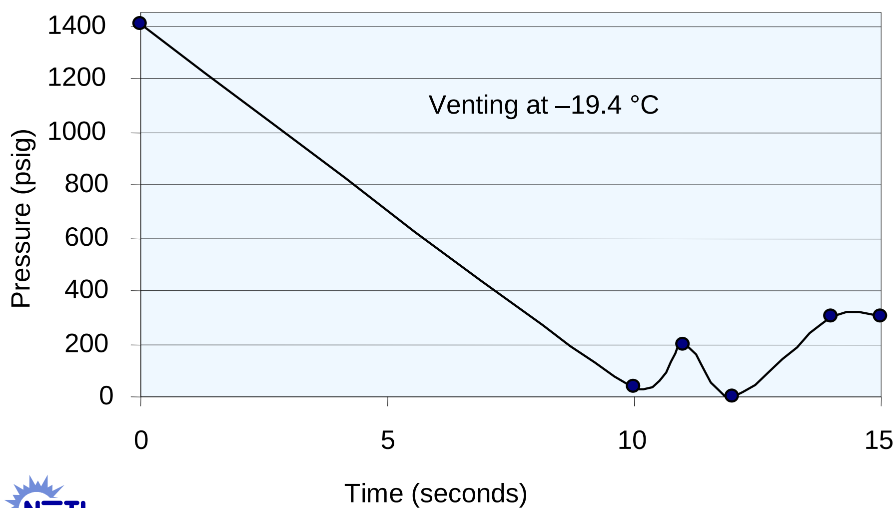
Commercial Surfactant Test (2nd Set)

Cycle Number	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
First	-17.9	10	14.51
Second	-15.1	10	99.10
Third	-19.9	10	16.47
Fourth	-17.3	10	14.76
Fifth	-19.9	10	21.47
Sixth	-19.4	10	54.35

Final Pressure as a Function of Venting Temperature for Commercial Surfactant



Pressure as a Function of Time During the Venting of Commercial Surfactant Experiment



New Collaborations in FY-02

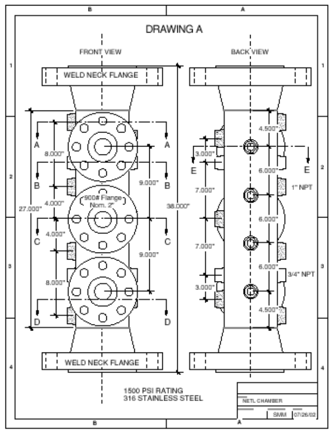
- Dr.s Faruk Civan and Richard G. Hughes, Mewbourne School of Petroleum and Geological Engineering Univ. of Oklahoma.

- Dr. Stephen M. Masutani, Hawaii Natural Energy Institute School of Ocean and Earth Science and Technology University of Hawaii.

- National Laboratories' Methane Hydrate (MH) Working Group.

New Hydrate Facility

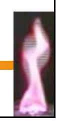
- 12.2L Hydrate View Cell, Environmental Chamber, and Assorted Hardware.



Raman Spectrometer to Study Hydrates

FY-03 Planned Research

- **Continuation of surfactant screening study**
  - Addition of second view cell to assist in study
- **Construction of 12.2L hydrate cell**
  - Most major components ordered
  - Location of unit determined
  - SARS begun
  - Study hydrate formation using a NETL-developed ultrasonic technique
- **Collaborate with National Laboratories Methane Hydrate Working Group**
- **Expand associations with U. Oklahoma and U. Hawaii**



COMMERCIAL

2003 AIChE Spring National Meeting Symposium on

GAS HYDRATES (TBa05)

March 30 - April 3, 2003 in New Orleans, LA

This Symposium will feature work on all aspects of gas hydrates. Papers on experimental, engineering, theoretical, exploration, production, and environmental aspects of gas hydrates of natural gas, CH_4, CO_2, or other compounds are welcome.

Symposium Organizers:

Charles E. Taylor
U.S. DOE/NETL
P.O. Box 10940
Pittsburgh, PA 15236-0940
Phone: 412-386-6058
Fax: 412-386-5920
charles.taylor@netl.doe.gov

Jonathan Kwan
Anadarko Petroleum
1201 Lake Robbins Dr.
The Woodlands, TX 77380
Phone: 832-636-1388
Fax: 832-636-8006
jonathan_kwan@anadarko.com

Visit www.AIChE.Org/Springapp/ for more details

Mechanical Property of Methane Hydrate

Masayuki Hyodo, Yukio Nakata, Norimasa Yoshimoto

Department of Civil Engineering, Yamaguchi University, Japan

ABSTRACT

Methane hydrate has been regarded as a new natural gas resource for the next generation, and the expectation is recently increasing markedly. In order to utilize such natural resources, mechanical properties such as compressive strength are the essential information for the drilling and production stage. In this study, compressive strength was measured and the effect of temperature and pressure was investigated. The sample methane hydrate was synthesized from pure methane(99.9999%) and pure water(18.3 MΩ・cm) with stirring at 10□ and 10MPa. Then the powdery product was put into a high pressure crystallization equipment (10□ and 160MPa), free water was removed, and solid cylindrical shaped sample was obtained. The sample ice, as a reference, was made of water which was purified by distillation and ion-exchange treatment. Cold and high pressure three spindle compressing machine was used for measuring compressive strength. The controllable range of temperature and pressure is from ambient to -34□ and 10 MPa respectively. In this equipment, compressive stress was given by the controlled strain, and the strain rate was controlled at 1.0%/min. The sample size was approximately φ15mm×30mm. The pressure and the temperature range to be measured was 0, 4, 6, 8, MPa and 5, -5, -10, -30□, respectively. 5 to 10 samples were tested in each condition. It was confirmed that compressive strength of both methane hydrate and ice were dependent on temperature and pressure. At the lower temperature and at the higher pressure, they showed the higher compressive strength. Methane hydrate showed a little lower shearing strength than ice.

Mechanical properties of methane hydrate-sand mixture

M. HYODO and Y.NAKATA
Yamaguchi University
hyodo@yamaguchi-u.ac.jp

OBJECTIVE

1. Although there has been considerable research on the physical and chemical properties of methane hydrate, the mechanical properties have yet to be fully investigated.
2. It is important to know these properties in order to allow the extraction of this material under stable condition.

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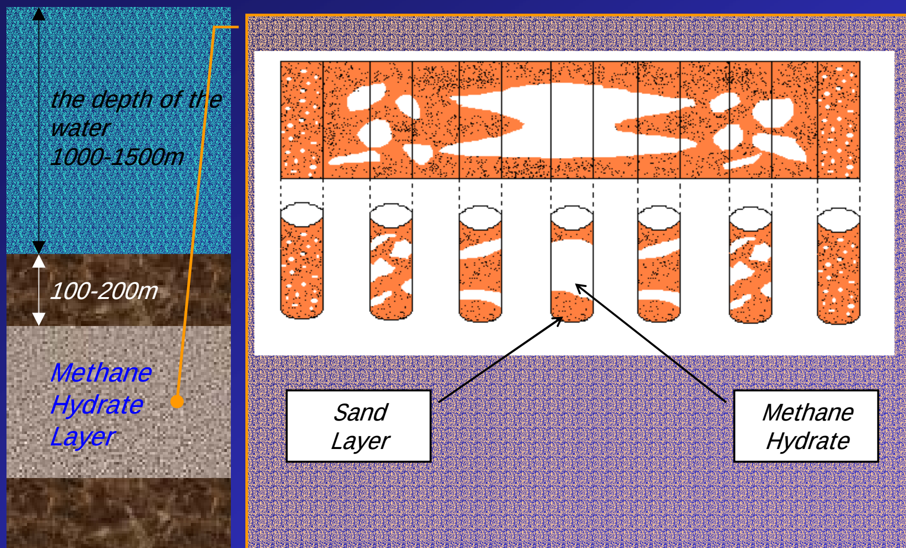
The distribution of methane hydrate in seabed



To produce the hydrate ……

- Stability and deformation of the seabed ground during the process
- The mechanical properties of methane hydrate
  - Have effects of many factors
  - Hydrate (temp., pressure, saturation etc)
  - Geomaterial (type, fractions, density, stress etc)

In this presentation .....

- The effects of soil grains fraction
  - The ratio of soil grains volume to total volume

- Temperature
- Strain speed
- Gas quantity in methane hydrate

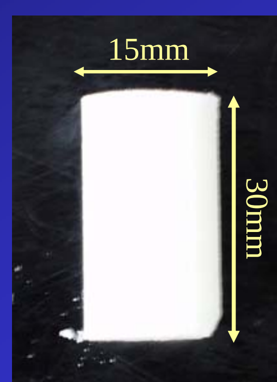
- Low temperature high confining triaxial compression apparatus developed

Contents of presentation

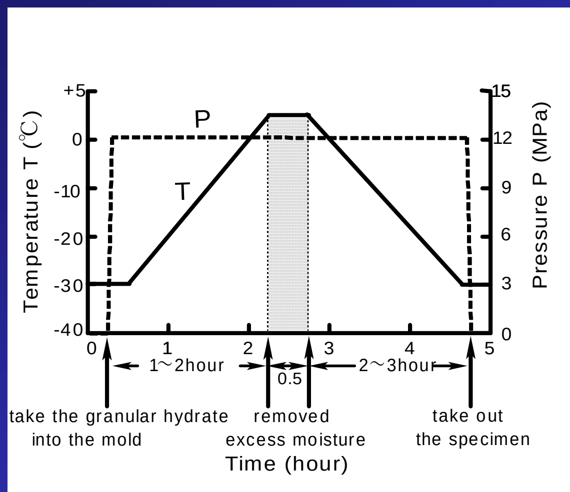
- Equipments for testing
- Procedure for test
- Test conditions
- Results
- Summary

Equipment for producing granular methane hydrate

High pressure crystallization equipment



Process of crystallization



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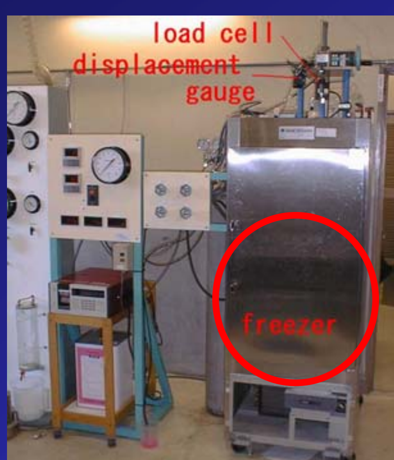
Low temperature, high pressure triaxial testing equipment



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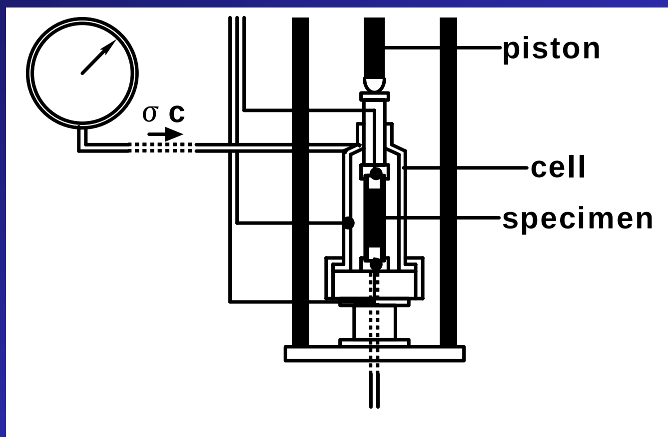
Cross section of triaxial compression cell



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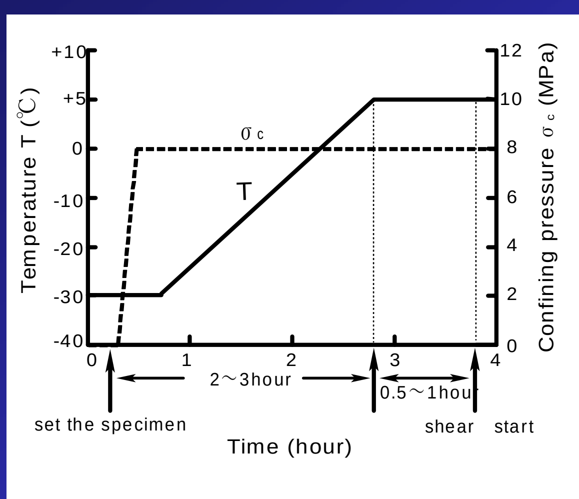
Process before mechanical test



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Test conditions

				A				B	
				Methan hydrate A		Sand mixture		Methan hydrate B	
				Strain rate (%/min)					
				0.1	1.0	0.1	1.0	0.1	1.0
Temperature (℃)	+5	Confinig pressure (MPa)	8		○		○	○	○
	-10		8				○		
	-30		1.5				○		
			4				○		
			8	○	○	○	○		

Gas quantity in methane hydrate

70cm^3/g for A, 100cm^3/g for B

Sand fraction in the methane hydrate is defined as the ratio (Vs/V) of sand volume to total volume (0-1.0)

Vs/V=0 methane hydrate specimen

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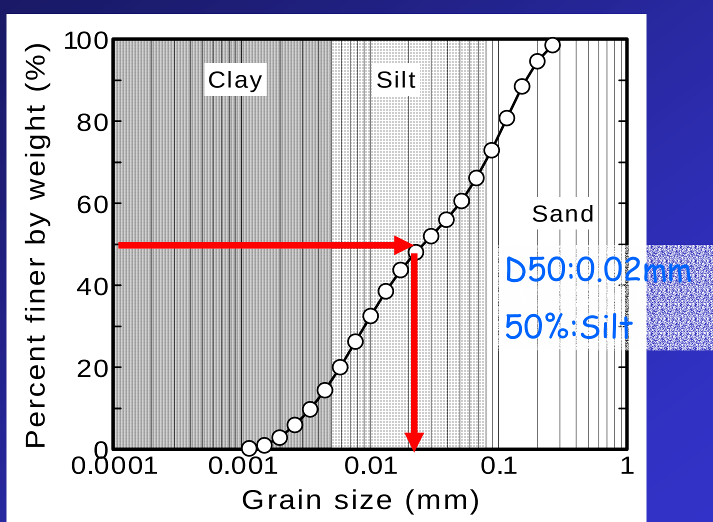
Grain size distribution for sand used



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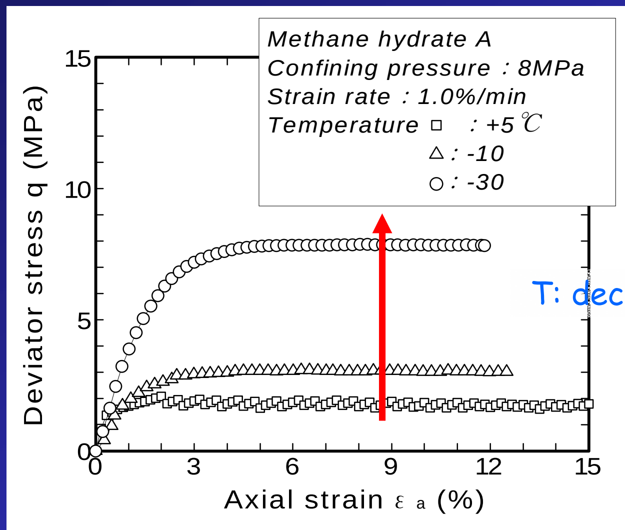
Effect of temperature (hydrate A)

Gas quantity in methane hydrate A = $70cm^3/g$



T: decrease

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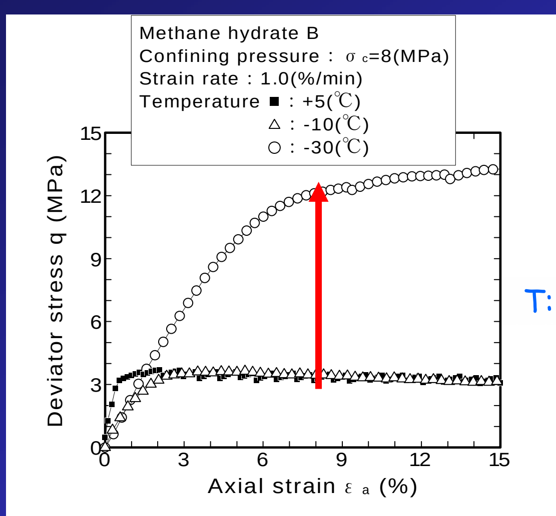
Effect of temperature (hydrate B)

Gas quantity in methane hydrate B = $100cm^3/g$



T: decrease

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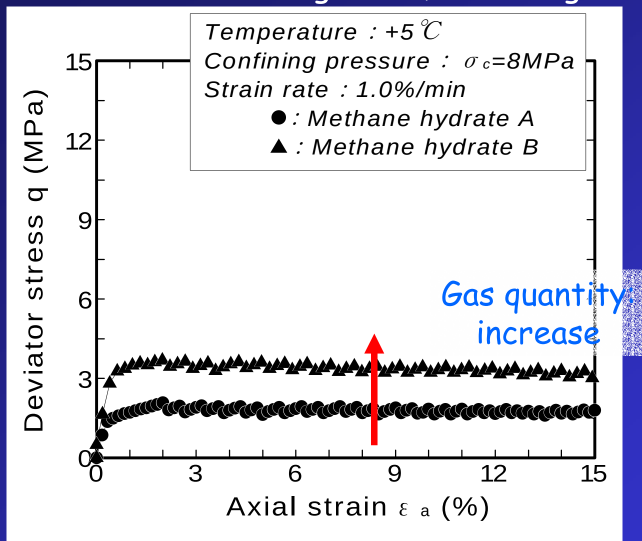
Effects of gas quantity in methane hydrate

70cm³/g for A, 100cm³/g for B



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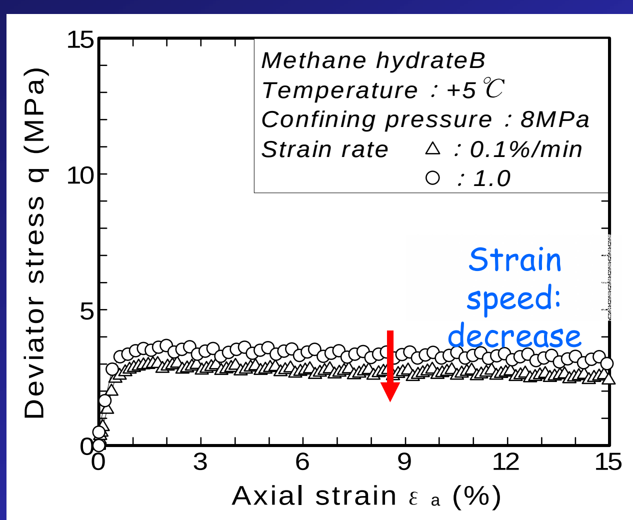
Effect of strain speed (+5℃)



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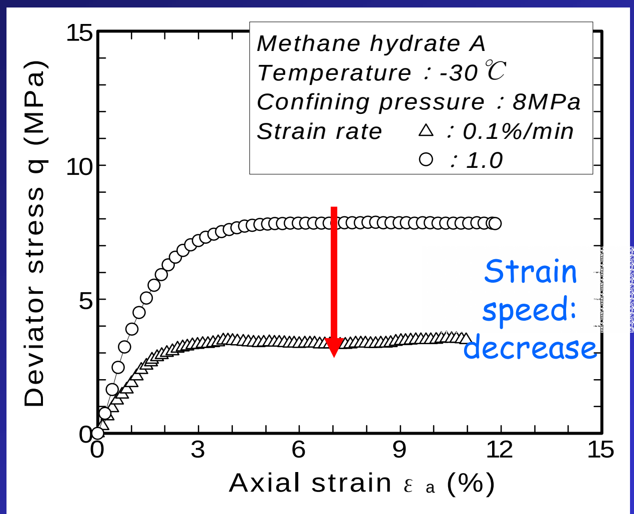
Effect of strain speed (-30℃)



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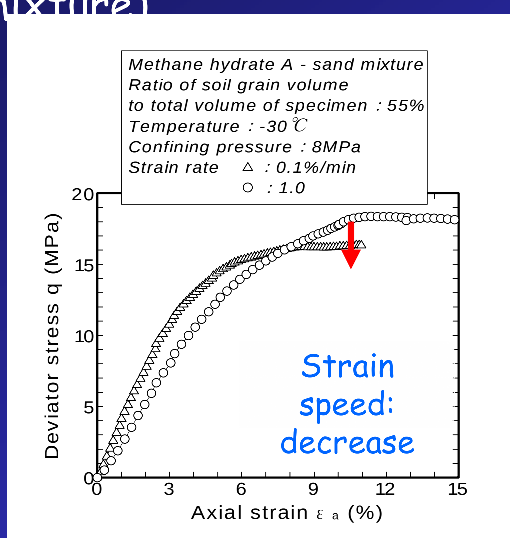
Effect of strain speed (-30℃, Methane hydrate-sand mixture)



Vs/V=0.55;

Grain skeletons developed

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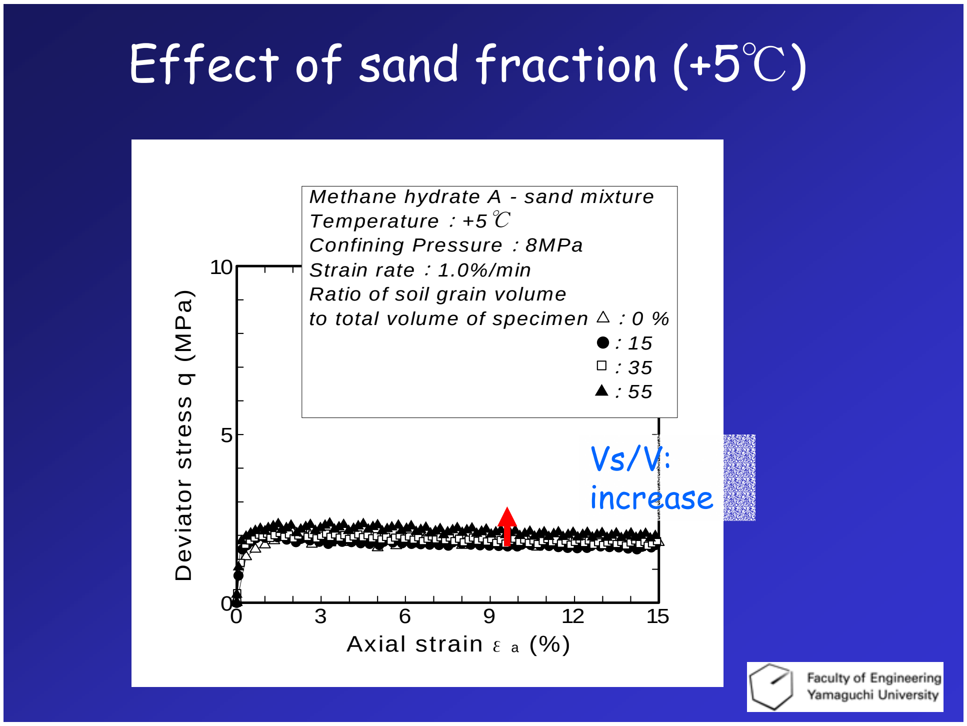
Effect of sand fraction (+5℃)
Methane hydrate A - sand mixture
Temperature : +5℃
Confining Pressure : 8MPa
Strain rate : 1.0%/min
Ratio of soil grain volume
to total volume of specimen △ : 0 %
● : 15
□ : 35
▲ : 55
Deviator stress q (MPa)
10
5
0
0
3
6
9
12
15
Axial strain ε a (%)
Vs/V:
increase
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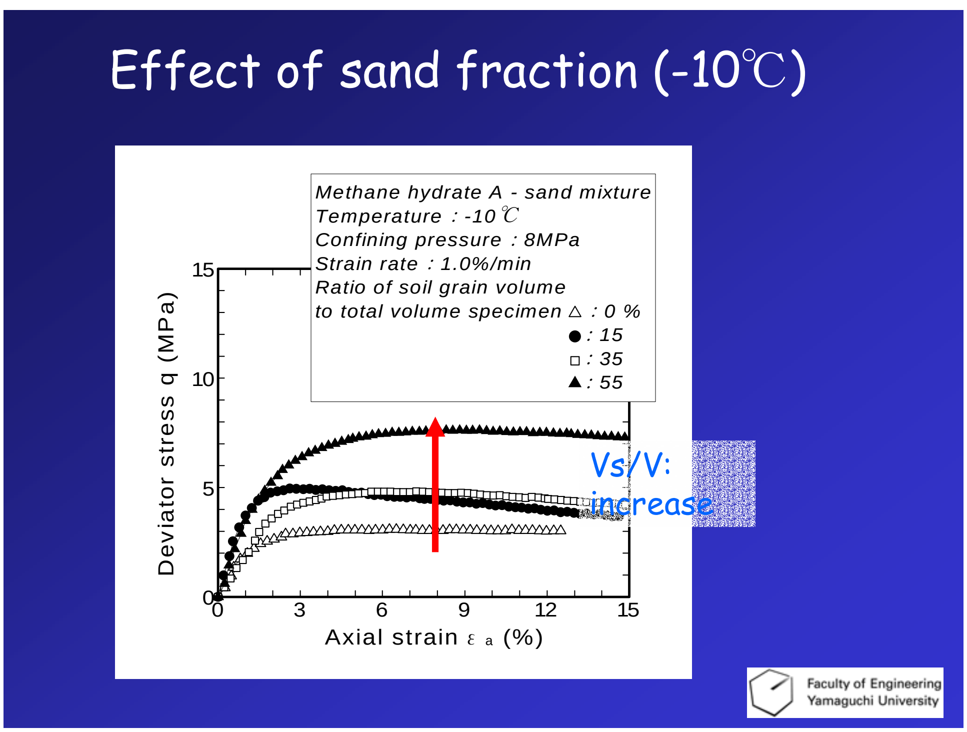
Effect of sand fraction (-10℃)
Methane hydrate A - sand mixture
Temperature : -10℃
Confining pressure : 8MPa
Strain rate : 1.0%/min
Ratio of soil grain volume
to total volume specimen △ : 0 %
● : 15
□ : 35
▲ : 55
Deviator stress q (MPa)
15
10
5
0
0
3
6
9
12
15
Axial strain ε a (%)
Vs/V:
increase
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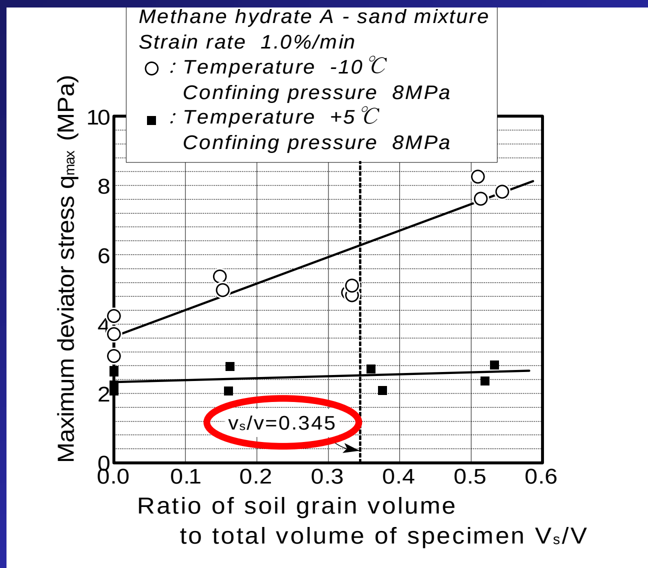
Dependency on sand fraction



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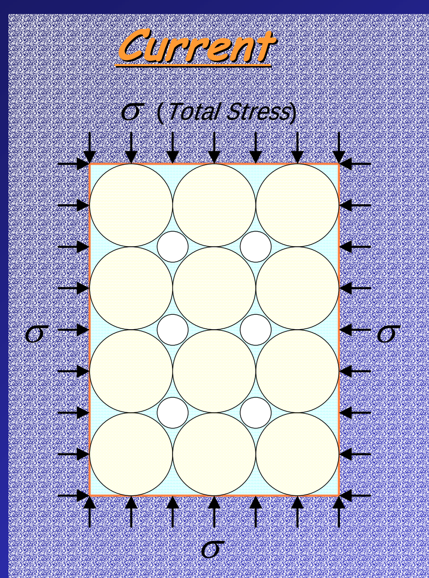
Stress condition during test



σ=known

If T < 0

u=0
σ'=σ-u=σ

If T > 0

u=unknown
>0
σ'=unknown
<σ

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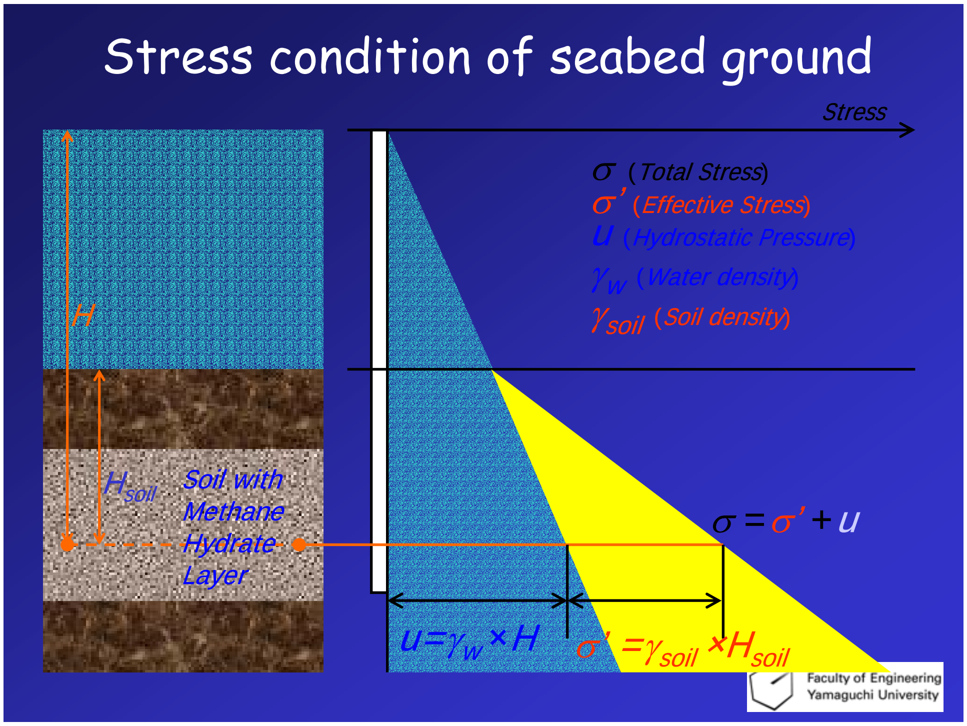
Stress condition of seabed ground
Stress
σ (Total Stress)
σ' (Effective Stress)
u (Hydrostatic Pressure)
γw (Water density)
γsoil (Soil density)
H
Hsoil
Soil with Methane Hydrate Layer
σ = σ' + u
u=γw×H
σ' =γsoil ×Hsoil
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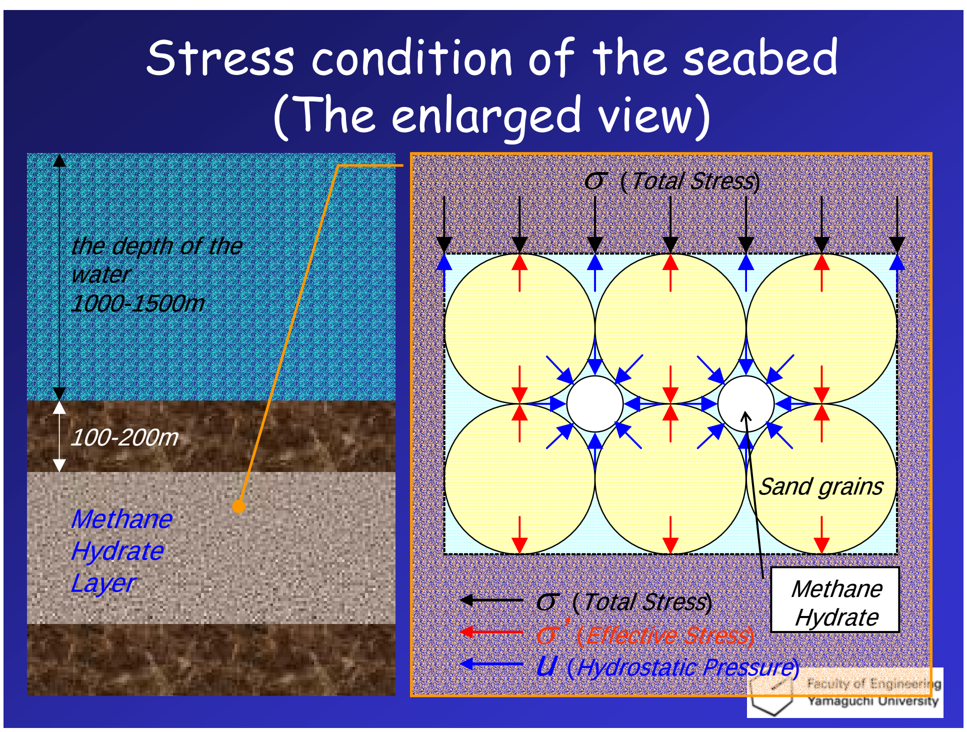
Stress condition of the seabed
(The enlarged view)
the depth of the water 1000-1500m
100-200m
Methane Hydrate Layer
σ (Total Stress)
Sand grains
Methane Hydrate
σ (Total Stress)
σ' (Effective Stress)
u (Hydrostatic Pressure)
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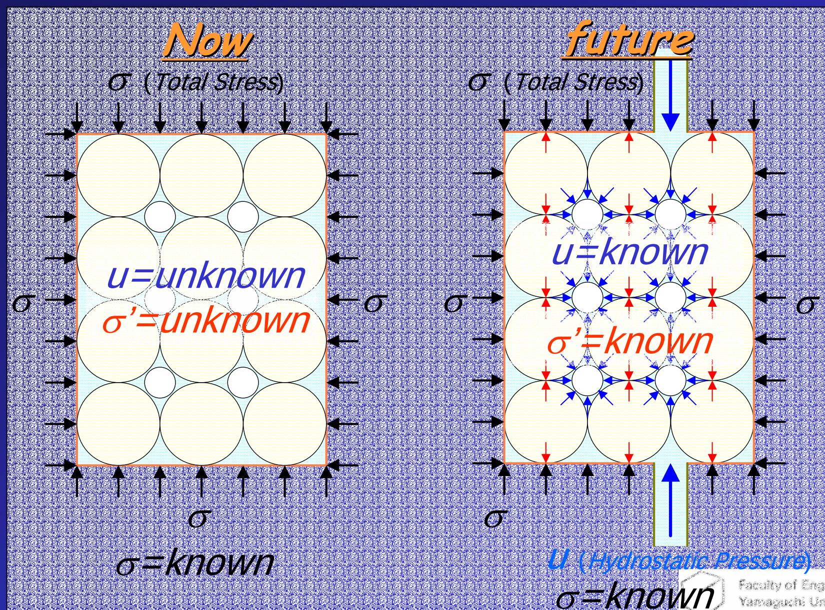
Stress condition under experiment



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Summary

- Primitive investigation on mechanical behaviour
- Low temperature high confining triaxial compression apparatus developed
- The effects of soil grains fraction
  - The ratio of soil grains volume to total volume
- Temperature
- Strain speed
- Type of hydrate(saturation of hydrate)

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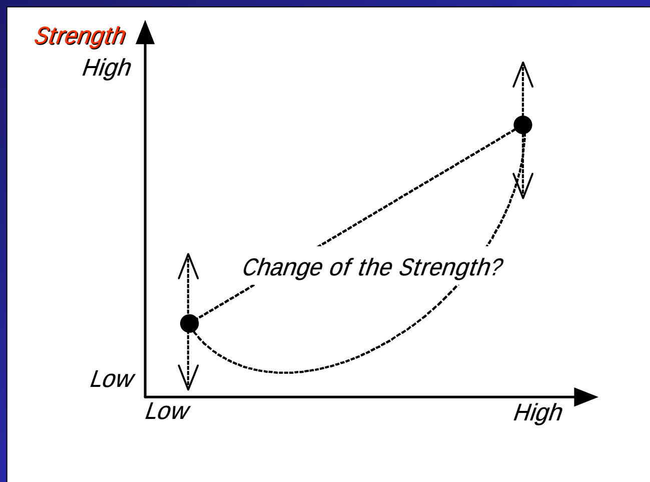
The relationship between Saturation rate of Methane Hydrate and Strength



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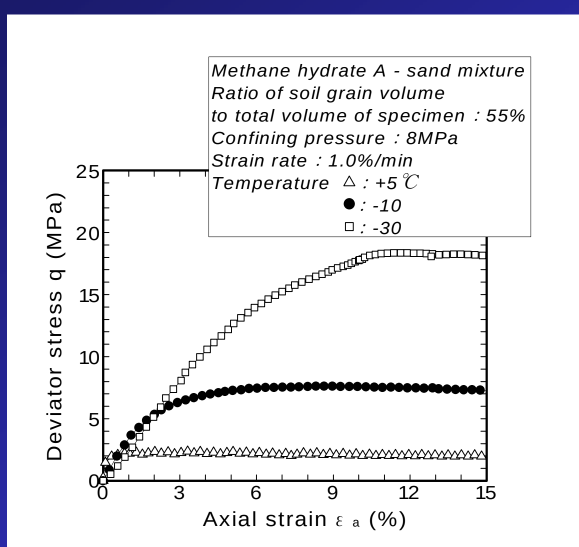
Effect of temperature (methane hydrate - sand mixture)



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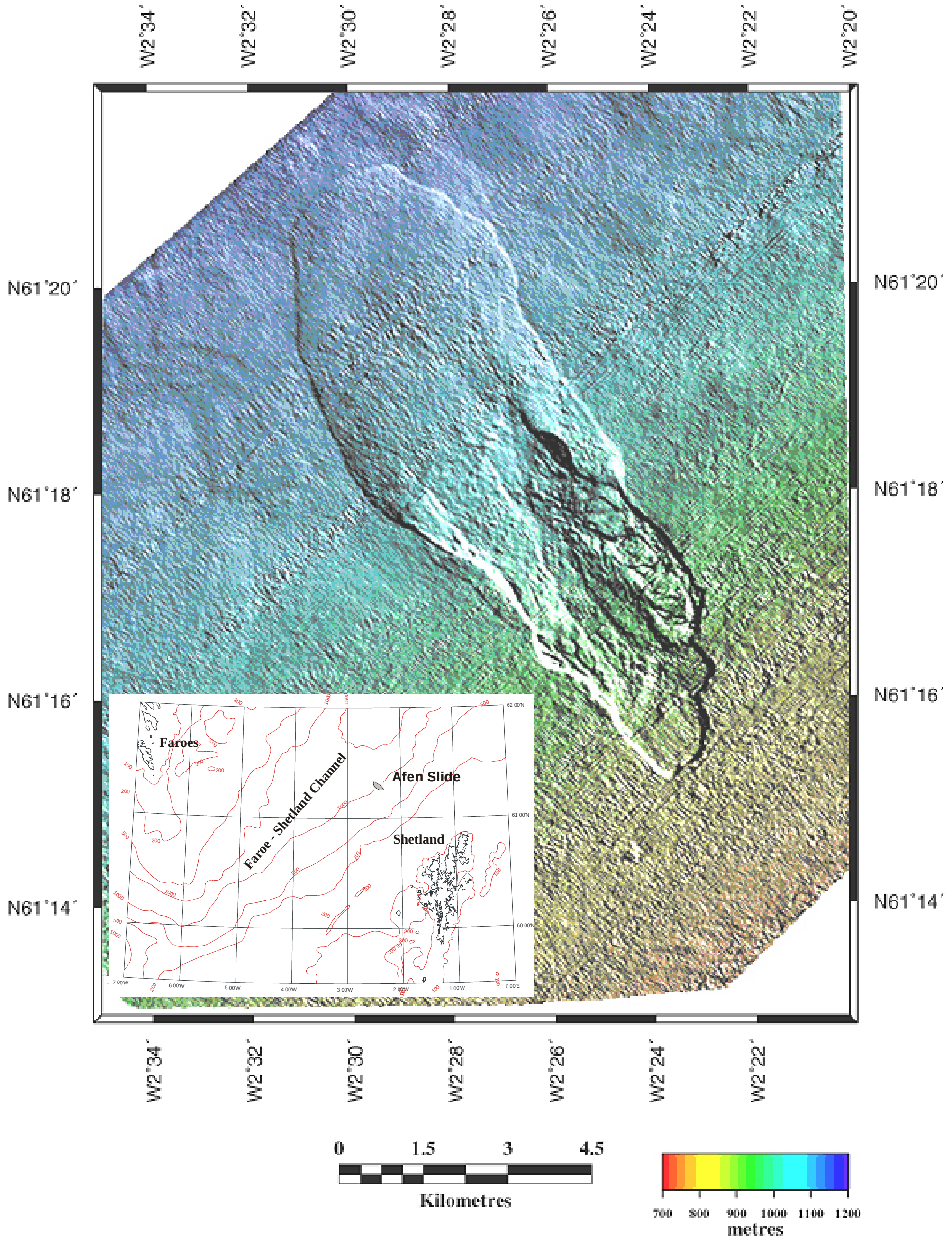
Extended Abstract for the Second Workshop of the International Committee on Gas Hydrates Washington DC
DA Gunn, PD Jackson, D Long, MA Lovell[1], CA Rochelle, K Bateman, L Nelder, J Rees.
MA Lovell – Professor of Petrophysics, University of Leicester and Visiting Research Associate at BGS.

Towards improved ground models for slope instability through better characterisation of gas-hydrate sediments.

The conditions for gas-hydrate stability exist and the presence of gas-hydrates have been confirmed or inferred on many continental margins word-wide. In the exploitation of methane-hydrate there are implications for stability on seafloor engineering operations. We consider a requirement of hydrate research is in the provision of seafloor hazard susceptibility maps in project risk assessments. To this end we have developed a capability that models geophysical and geotechnical property profiles and the effect of seismicity on instability within the sediment column. This model can be applied to low-slope environments where there is little lateral variation over large distances.

World estimates for the amount of methane in oceanic gas hydrate deposits have changed over the last two decades; from around 10^{15} to 10^{18} m^3 in the 1980s, to 10^{15} to 10^{16} m^3 in the 1990s, with 10^{15} m^3 being a common estimate in 2000. Assessments of the level of stability of the seafloor and its potential impact on seafloor installations are required, whether they be for the exploitation of this potential resource or for other activities. The effect of seismic loading on stability can be under-assessed if the ground accelerations from regional seismic hazard analyses are used without considering the site effects of the sediment column. In particular, there is a need to fully investigate the control of the sediment property profile on the peak ground acceleration in the near-seafloor zone that is important to site investigation. As part of this understanding there is a need for further geophysical and geotechnical property models that can account for sediment-hosted methane-hydrates.



Extended Abstract for the Second Workshop of the International Committee on Gas Hydrates Washington DC

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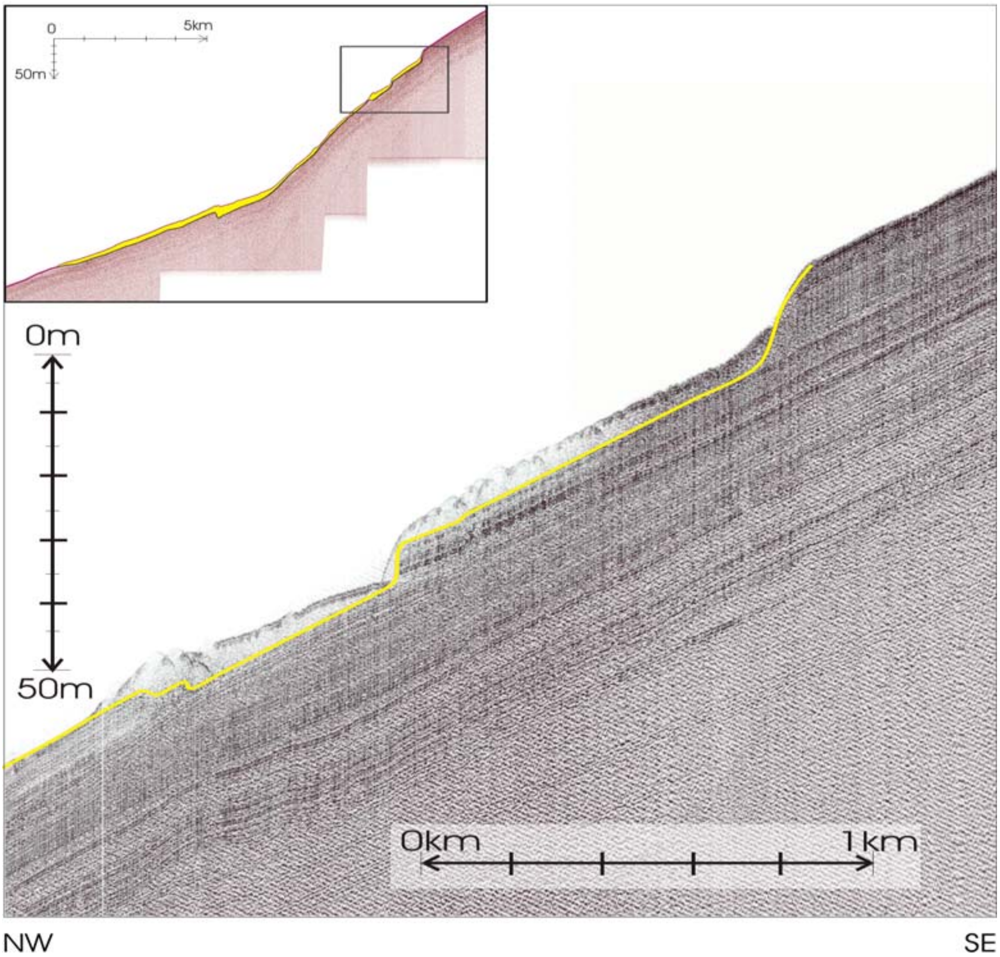
The Afen Slide, a mid Holocene event west of Shetland on the UK margin, is presented as a case history to demonstrate that slip planes can be developed within 10m of the seafloor. Also, submarine landslides can occur on low slope angles, e.g. 1^{o} to 2^{o}, and that whole sediment blocks can move en masse.



A methodology is presented for a seismically induced instability assessment along the continental slope. This will demonstrate the application of the infinite slope approximation and factors of safety are calculated from modelled undrained shear strengths and ground accelerations.

The development of the models involves an appreciation of the controls of lithology and effective stress on geophysical and geotechnical properties of sediments. Newly developed ground models are required that account for the control lithology and hydrate morphology on sediment properties such as shear wave velocity and density. Also, further models are required to account for the properties of sediments in which dissociation has occurred.

The potential for slip plane formation is investigated using hypothetical geophysical properties of sedimentary sequences. The properties of an original sedimentary sequence for the continental slope near the AFEN slide are modified to account for the presence of free gas and hydrate. In this way the effect of gas hydrates on the stability of the sediment column is investigated via a comparison of the factors of safety.

Reviews of current data from which new ground models will be devised indicate very broad ranges of sediment properties. Thus, it is very difficult to model the effects of gas-hydrates on stability with a large degree of constraint. There are several laboratory programmes within the UK operating to address this lack of data. A review of the activities of LU, BGS, Geotek Ltd and Heriot-Watt is presented to show how we a trying to address this situation and offer some ways forward.

Towards improved ground models for slope instability through better characterisation of gas-hydrate sediments.

British Geological Survey

PD Jackson, DA Gunn, D Long,
CA Rochelle, K Bateman,
R Holmes, R Musson, L Nelder,
PRN Hobbs & JG Rees

University of Leicester

MA Lovell

GEOTEK

P. Schultheiss

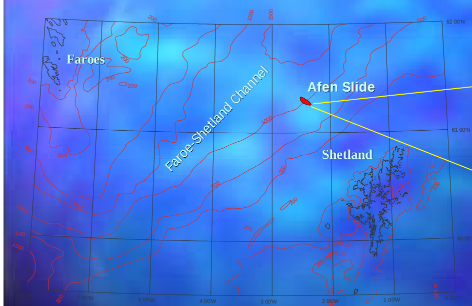
Ground Models for Slope Instability

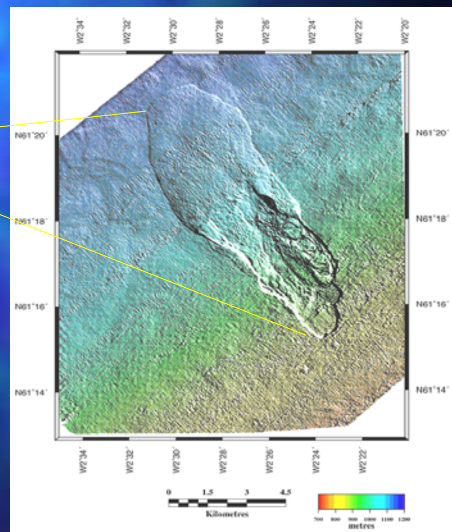
Presentation Summary

- Seafloor Stability Assessments
- Sediment Effects on Ground Acceleration
- Factor of Safety Modelling Capability
- Incorporate Models of Hydrate Bearing Sediments
- Applications of Hydrate Models – Instability Scenarios
- Information Gaps
- Current Projects and New Initiatives
- Suggested Additional Data / Research

Ground Models for Slope Instability

Are Slopes Stable ? - The Afen Landslide



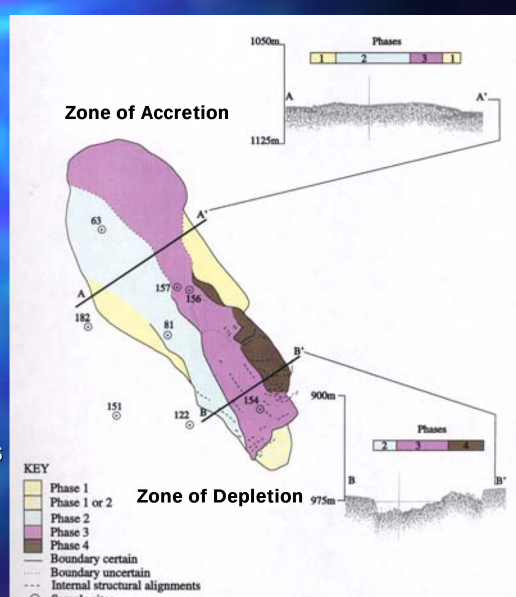


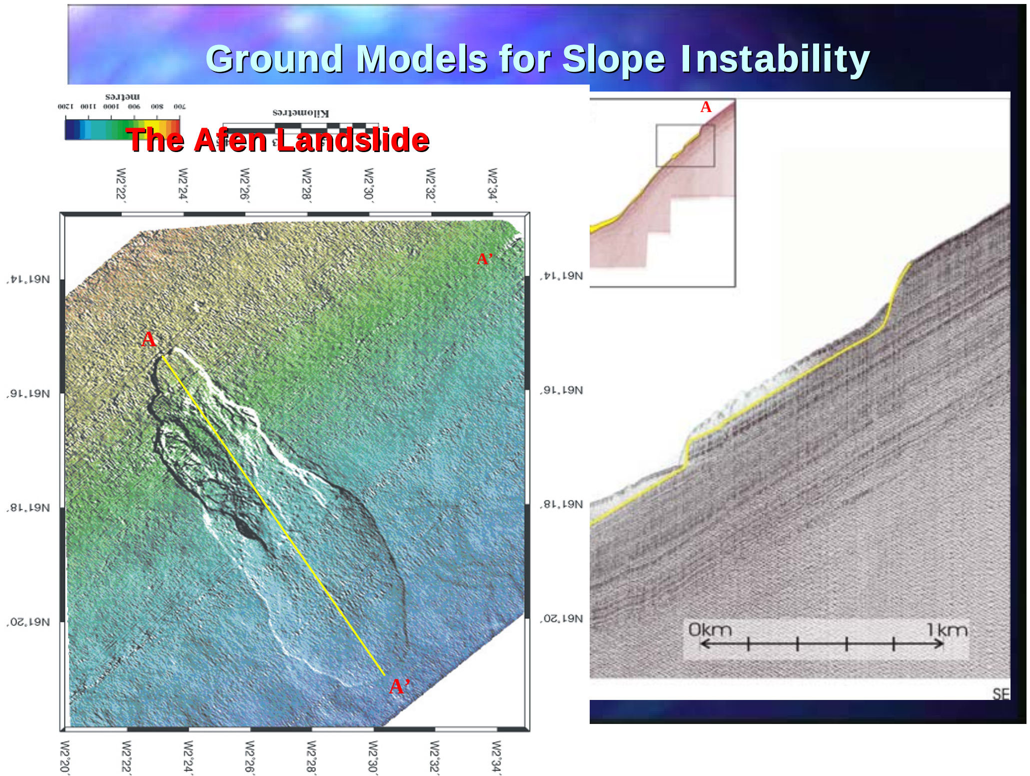
Initiated on a slope that was assumed stable !

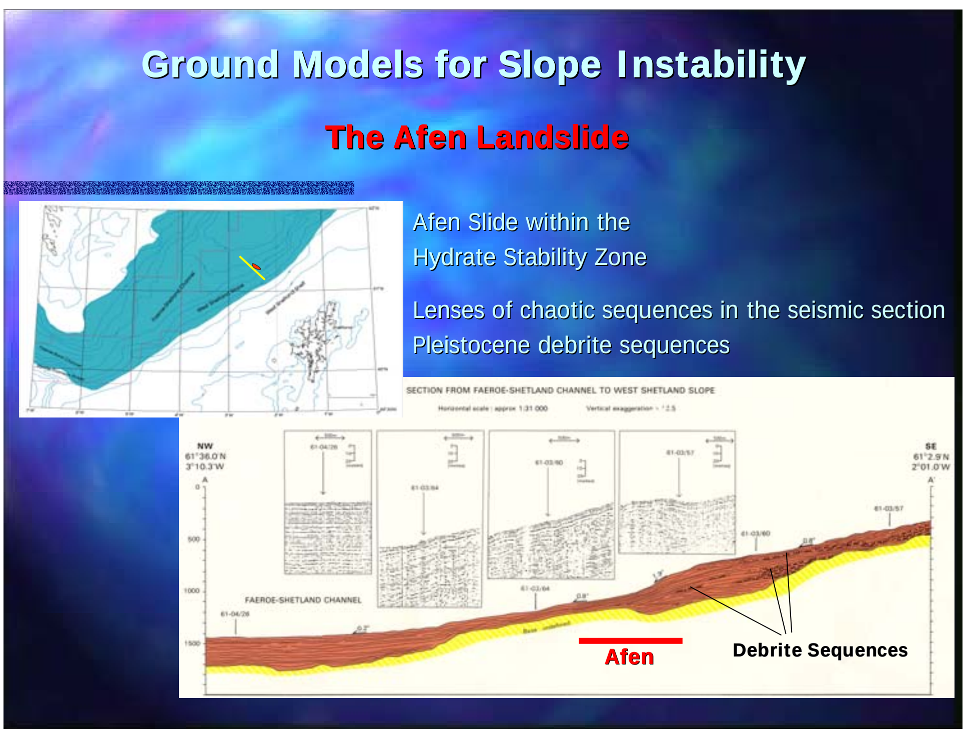
Ground Models for Slope Instability

The Afen Landslide

- Several phases
- 5, 800 year BP (C^{14})
- 12 km Long x 4 km Wide
- Water Depths 890 m - 1200m
- Slopes 1.5 – 2.5 degrees
- Current Headwall in contourites




Ground Models for Slope Instability
The Afen Landslide
A
A'
0km
1km
SE

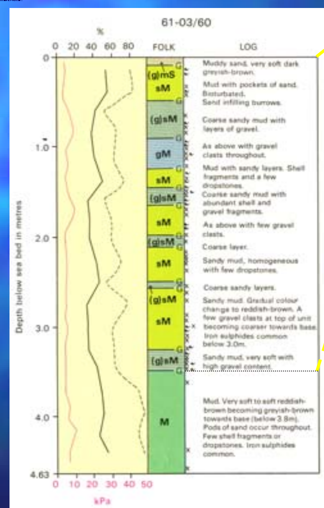

Ground Models for Slope Instability
The Afen Landslide
Afen Slide within the
Hydrate Stability Zone
Lenses of chaotic sequences in the seismic section
Pleistocene debrite sequences
SECTION FROM FAEROE-SHETLAND CHANNEL TO WEST SHETLAND SLOPE
NW
SE
FAEROE-SHETLAND CHANNEL
Afen
Debrite Sequences

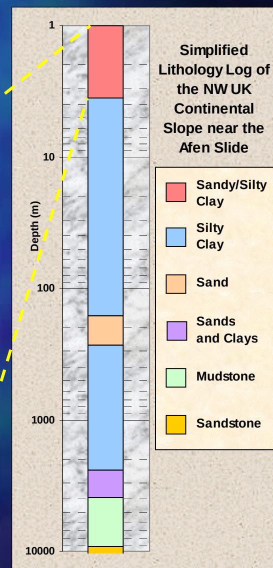
Ground Models for Slope Instability

The Afen Landslide

Seafloor Sediments

- Plio-Pleistocene:
- Faeroe Shetland Sequence
- Bio-turbated Muds, Sandy Muds with Dropstones, and thinner Muddy Sand Beds
- Contourite Deposit:
- Muddy Sand





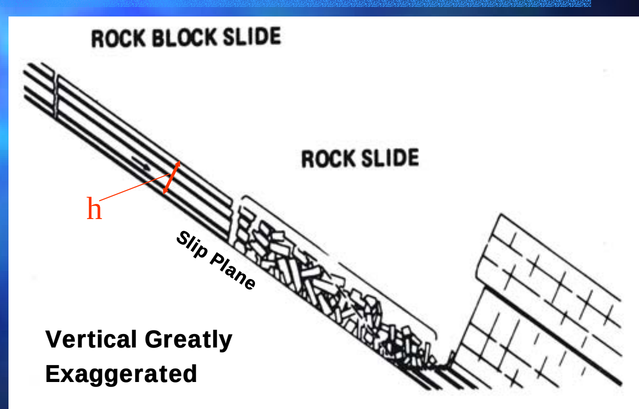
Ground Models for Slope Instability

Seafloor – Infinite Slope Approximation

$$Factor\ Of\ Safety \approx \frac{Undrained\ Shear\ Strength}{Height \times Density \times Seismic\ Acceleration}$$

- Low Slope Angles
- En Masse Movement
- Slip Plane Parallel to Seafloor

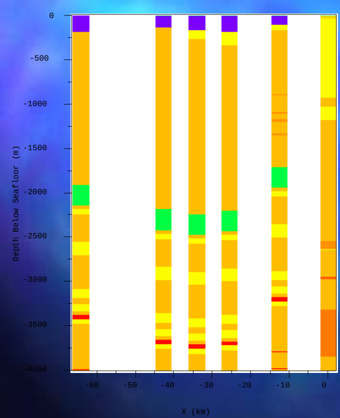
- FOS - Ratio:
- Slip Plane Strength
- Movement Forces

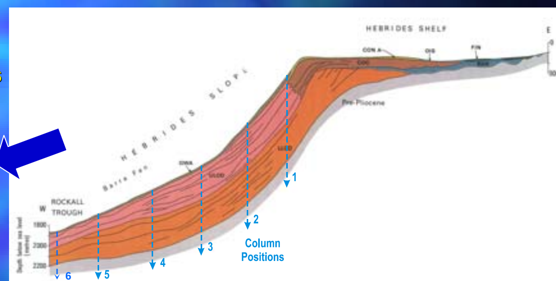


Ground Models for Slope Instability

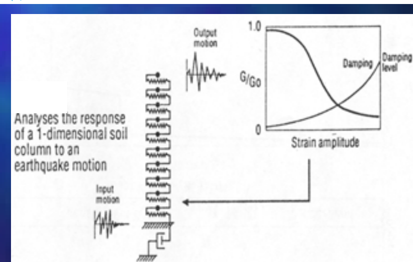
Earthquake Simulation - Acceleration Profile

Geology to Property Profiles





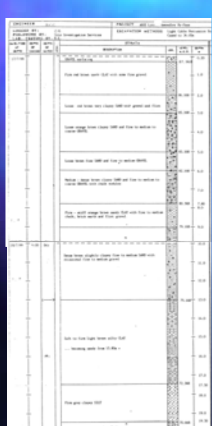
Property Profiles → Simulation

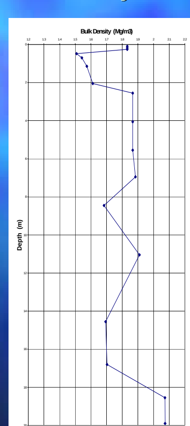


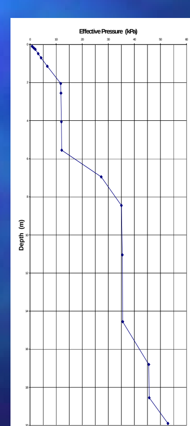
Ground Models for Slope Instability

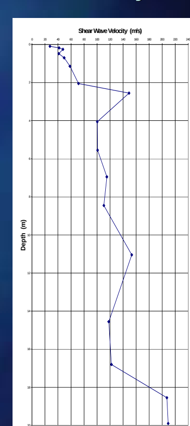
Lithology / Effective Stress Controlled Geophysical / Geotechnical Models

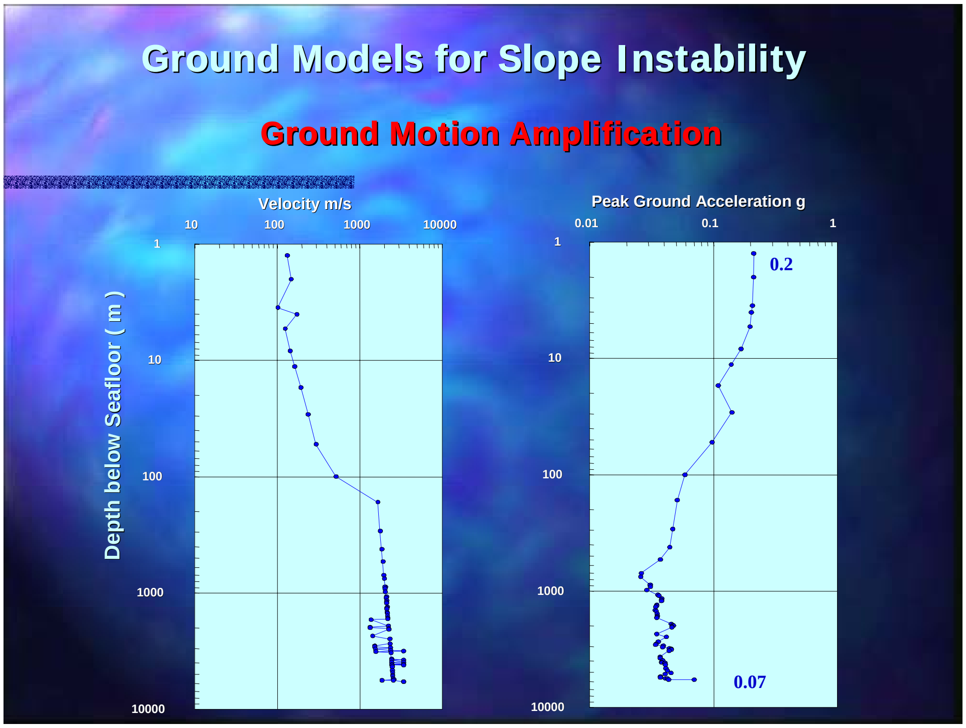
BH Log → Bulk Density → Effective Stress → Undrained Shear Strength Shear Wave Velocity

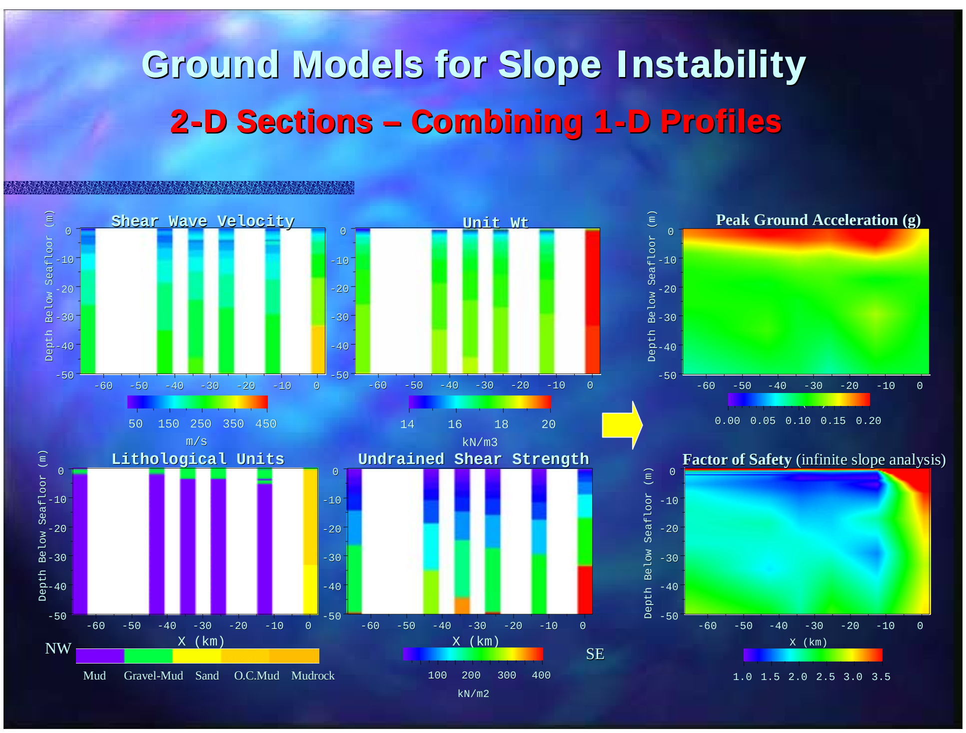









Ground Models for Slope Instability
Ground Motion Amplification
Velocity m/s
10
100
1000
10000
Depth below Seafloor (m)
1
10
100
1000
10000
Peak Ground Acceleration g
0.01
0.1
1
0.2
0.07


Ground Models for Slope Instability
2-D Sections – Combining 1-D Profiles
Shear Wave Velocity
Depth Below Seafloor (m)
50 150 250 350 450
m/s
Unit Wt
14 16 18 20
kN/m3
Peak Ground Acceleration (g)
0.00 0.05 0.10 0.15 0.20
Lithological Units
X (km)
NW
Mud
Gravel-Mud
Sand
O.C.Mud
Mudrock
Undrained Shear Strength
100 200 300 400
kN/m2
SE
Factor of Safety (infinite slope analysis)
1.0 1.5 2.0 2.5 3.0 3.5

Ground Models for Slope Instability

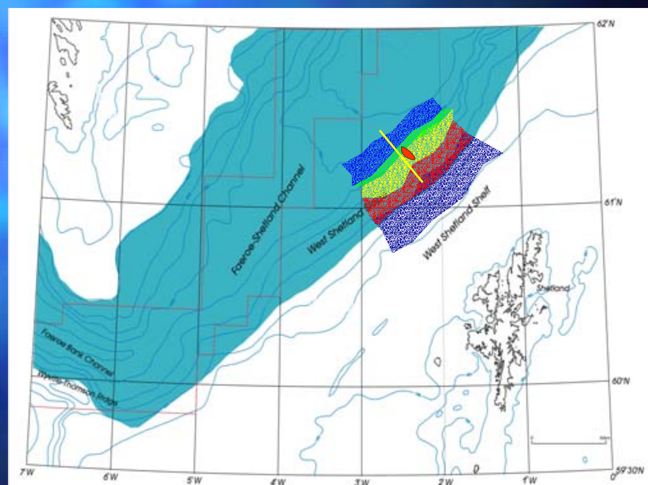
Slope Instability Susceptibility Maps

Scheme for a Simple Instability Susceptibility Map

Low High

10, 000 Year Earthquake

Ground Acceleration 0.07g



Ground Models for Slope Instability

Developing Hydrate Bearing Sediment Property Models

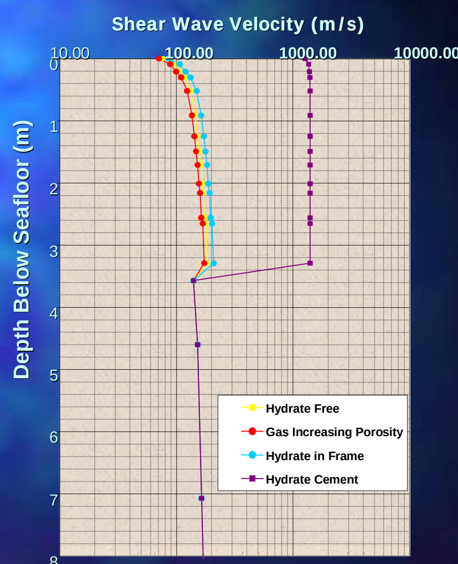
Seafloor of Afen

Basic Shear Wave Velocity Models

- Effective Medium Model (Effect of Density / Porosity) (not including pore pressure)
- Contact Cement Models

Knowledge Gaps

(after Dvorkin et al 2000)



Ground Models for Slope Instability

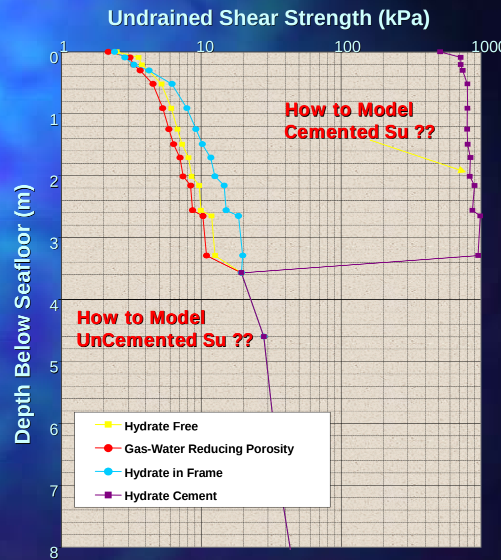
Developing Hydrate Bearing Sediment Property Models

Seafloor of Afen

Basic Shear Strength Models

- Uncemented Sediment Model
  - Changes in Frictional Component) (not including pore pressure)
- Cemented Models
  - Adjusted using Modulus of Shear

Big Knowledge Gaps !



Ground Models for Slope Instability

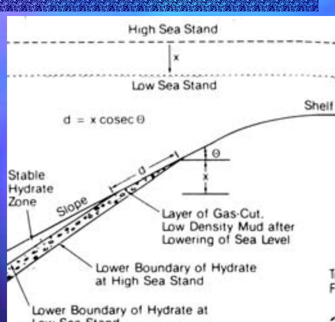
Impact of Dissociation - Sediment Properties: Base GHSZ meets Seafloor

Bottom Warming / Pressure Reduction Scenarios

Downslope Migration of the base of the GHSZ

Hydrate dissociates to water and gas

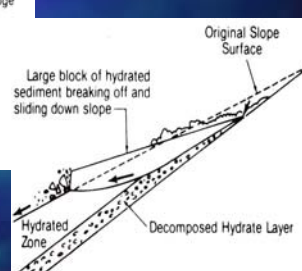
Large Effective Stress Reductions ?!



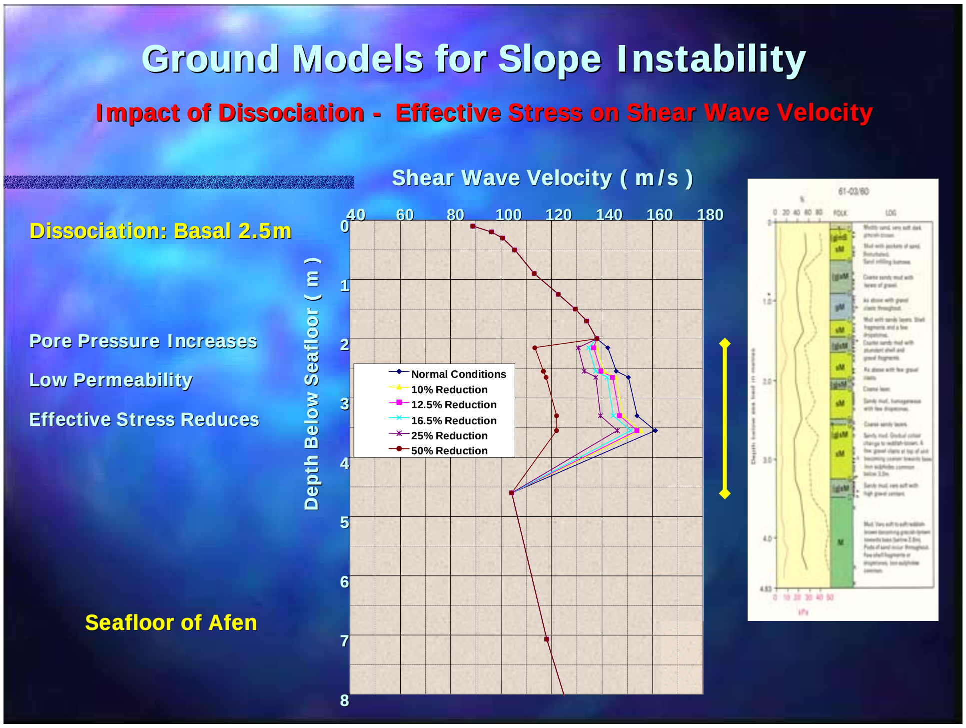
(after McIver, 1982)

Weak Sediments at Toe

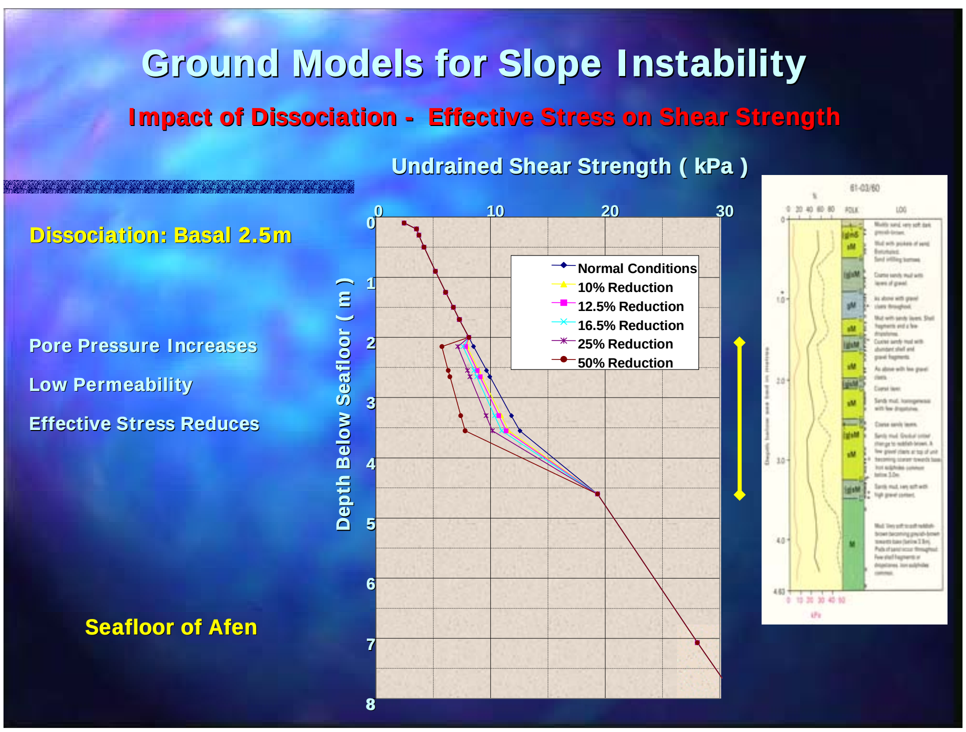
Unstable Hanging Wall



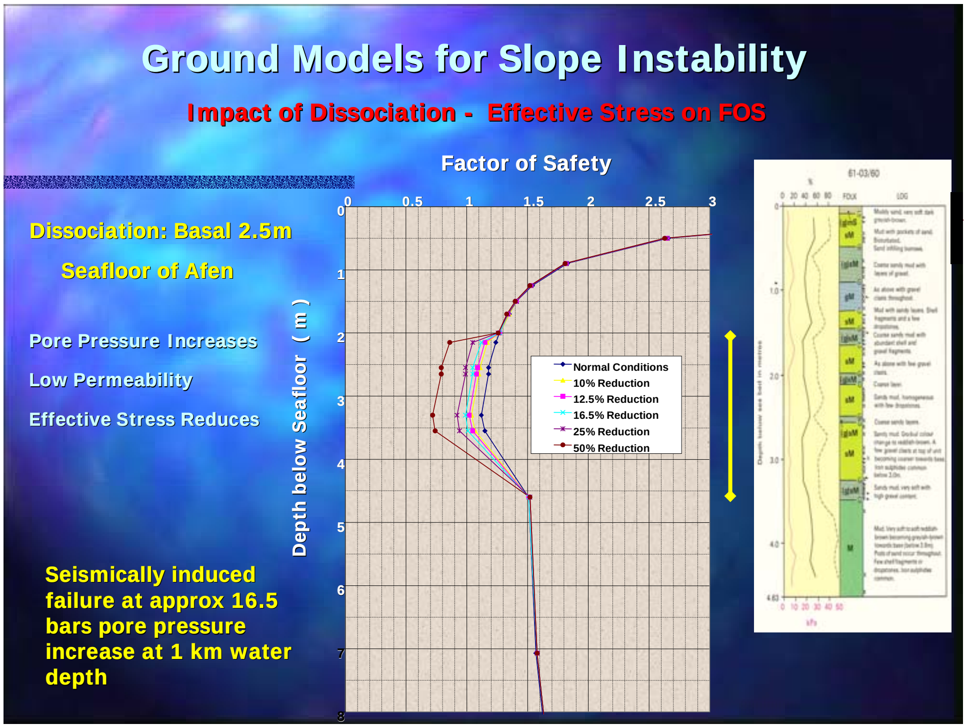
Could glide planes establish in low permeability layers due to low drainage ?

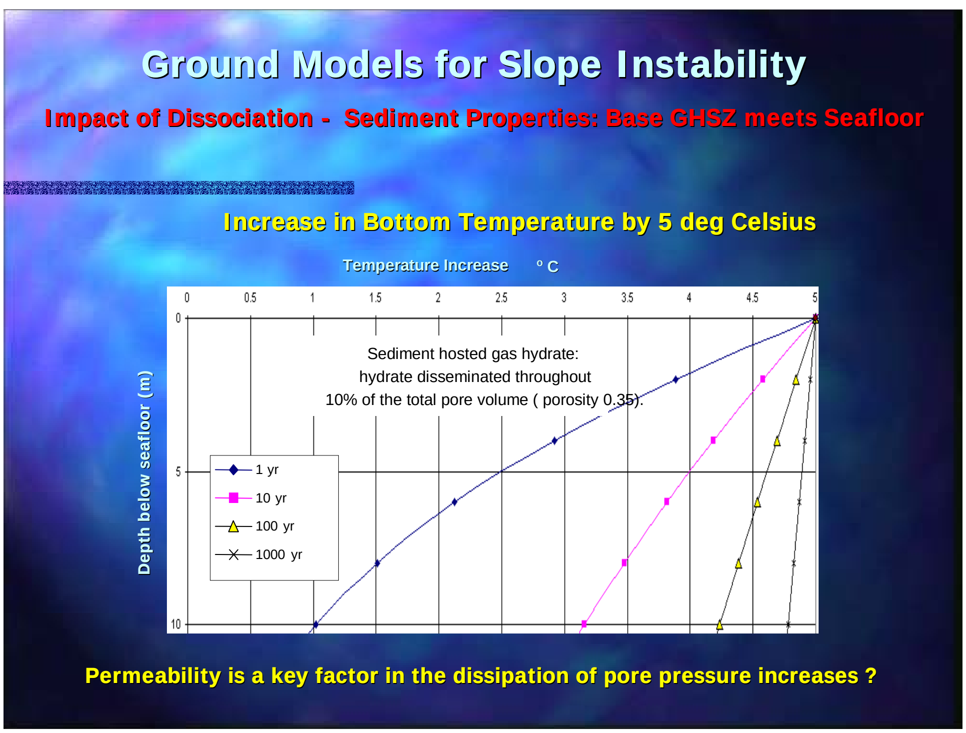


Ground Models for Slope Instability
Impact of Dissociation - Effective Stress on Shear Wave Velocity
Dissociation: Basal 2.5m
Pore Pressure Increases
Low Permeability
Effective Stress Reduces
Seafloor of Afen
Shear Wave Velocity (m/s)
Depth Below Seafloor (m)
Normal Conditions
10% Reduction
12.5% Reduction
16.5% Reduction
25% Reduction
50% Reduction



Ground Models for Slope Instability
Impact of Dissociation - Effective Stress on Shear Strength
Dissociation: Basal 2.5m
Pore Pressure Increases
Low Permeability
Effective Stress Reduces
Seafloor of Afen
Undrained Shear Strength (kPa)
Depth Below Seafloor (m)
Normal Conditions
10% Reduction
12.5% Reduction
16.5% Reduction
25% Reduction
50% Reduction


Ground Models for Slope Instability
Impact of Dissociation - Effective Stress on FOS
Factor of Safety
Dissociation: Basal 2.5m
Seafloor of Afen
Pore Pressure Increases
Low Permeability
Effective Stress Reduces
Depth below Seafloor (m)
0 0.5 1 1.5 2 2.5 3
0 1 2 3 4 5 6 7 8
Normal Conditions
10% Reduction
12.5% Reduction
16.5% Reduction
25% Reduction
50% Reduction
Seismically induced failure at approx 16.5 bars pore pressure increase at 1 km water depth


Ground Models for Slope Instability
Impact of Dissociation - Sediment Properties: Base GHSZ meets Seafloor
Increase in Bottom Temperature by 5 deg Celsius
Temperature Increase ° C
0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5
Depth below seafloor (m)
0 5 10
Sediment hosted gas hydrate:
hydrate disseminated throughout
10% of the total pore volume (porosity 0.35).
1 yr
10 yr
100 yr
1000 yr
Permeability is a key factor in the dissipation of pore pressure increases ?

Ground Models for Slope Instability

Impact of Dissociation - Effective Stress on FOS

Dissociation: Basal 2.5m

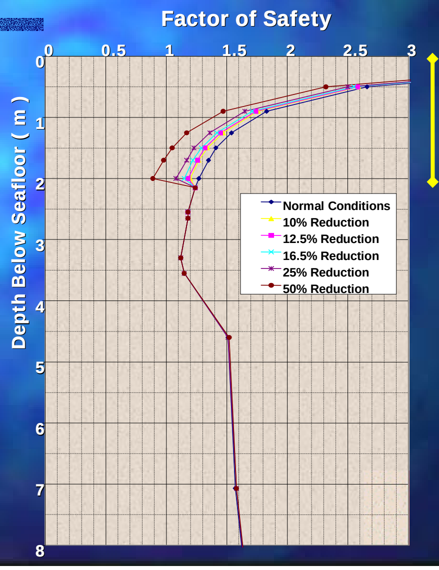
Seafloor of Afen

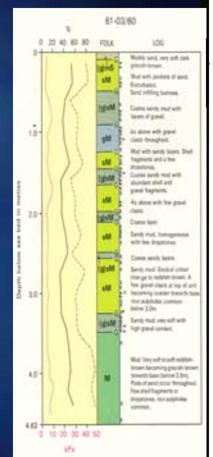
Pore Pressure Increases

Low Permeability

Effective Stress Reduces

Seismically induced failure at approx 30 bars pore pressure increase at 1 km water depth





Ground Models for Slope Instability

Geophysical / Geotechnical Property Models of Sediments affected by Dissociation

Base of the Gas Hydrate Stability Zone meets the seafloor.

What are the implications of bottom water warming ?

What are the implications of pressure reductions ?

What happens to pore / effective pressures ?

Could glide planes establish in low permeability layers due to low drainage ?

Effect on cohesive strength of fresh water?

Effect on cohesive strength of partially closed systems?


Future Research Needs
Laboratory Research / Modelling – Hydrate Sediment
Geophysical / Geotechnical Properties
Characterisation of Dissociation Process
Geophysical / Geotechnical Measurements
Pressure / Temperature Cycling
Salinity – Cohesion Relationship
Near In Situ Lithologies / Morphologies
Muddy Sand / Sandy Mud Sequences
Hydrate in Pores
Hydrate Around Grains
Hydrate Cementing Grains
Develop Hydrate Geo-Models
Pore Pressure / Eff. Stress Changes
Dissociation By-Products
Chemistry (Water Salinity)
Fabric Disruption: Fissures / Secondary Porosity

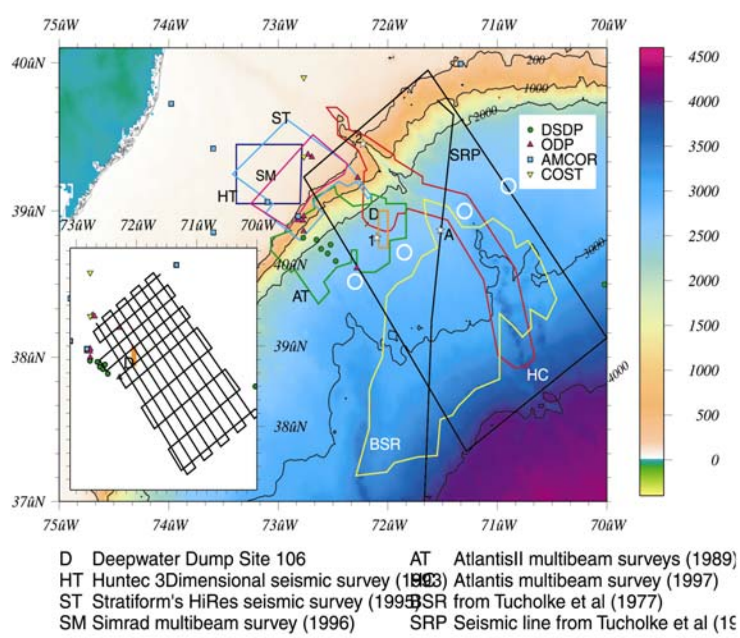
HUDSON CANYON REGION - A MAJOR GAS HYDRATE PROVINCE OFFSHORE NEW YORK, NEW JERSEY, AND DELAWARE

Jean Whelan, Brian Tucholke, Peter Rona, and Mary Scranton

Gas(methane)-hydrates on continental margins are the subject of intensive investigation for both scientific and societal reasons. Notably, hydrates and the gas that they release may be important in slope stability, climate change, support of chemosynthetic communities, and as an energy resource. An extensive gas-hydrate province (~20,000 sq. km) across the central and upper continental rise offshore New York, New Jersey, and Delaware offers significant potential for studying many of these issues. The province is marked by a well defined bottom-simulating reflection (BSR), and its up-dip edge is near the base of the continental slope which is a zone of extensive gravitational mass movements. Migration of free gas from beneath the hydrate seal to the slope may promote overpressures within the sedimentary column and reduce critical values of shear stress required to produce gravitational mass movements. Large mass movements in this area could have significant human impacts (e.g., generation of tsunamis and disruption of numerous seafloor communications cables). There is some evidence that methane is migrating through and being released from sediments in this area. From very limited sampling, methane anomalies have been detected in the water column, and submersible observations suggest that there is at least local venting of fluids from the seafloor. If there is indeed significant seafloor venting of methane here, it raises questions about the view that methane hydrates are frozen into sediments, to be released only on time scales of thousands of years, and it emphasizes the potential of methane as an important greenhouse gas. It also raises the possibility of finding chemosynthetic ecosystems at cold seeps for the first time in this region.

The features observed in the Hudson Canyon hydrate province make it ideal area to investigate the interplay between methane mobility in the sediment, gravitational mass movements, seafloor venting of gas, and possible development of associated chemosynthetic communities, through recent geologic time. A group of geologists, geophysicists, and geochemists from three institutions (Woods Hole Oceanographic Institution, Rutgers University, and Stony Brook University) have proposed a field program of high-resolution seismic-reflection and 3.5-kHz profiling, multibeam bathymetry, and water-column sampling for methane, together with laboratory data analysis, to study this province. The research objectives are: 1) to define in detail the distribution and seismic characteristics of the BSR at the base of the gas-hydrate zone, as well as reflectivity patterns that bear on hydrate distribution in the overlying sediments and gas distribution in the subjacent sediments, 2) to determine how BSR distribution and the seismic characteristics relate to, and may be controlled by, stratigraphy of the continental rise and lower continental slope, 3) from these features, to identify locations where venting of gas is likely and to examine possible relationships with bedding disruption and mass failure of the overlying sediments, 4) to constrain the source(s) of methane anomalies in the water column and determine their relation to possible venting zones interpreted from the seismic and morphology studies, and 5) from all available data, to identify sites with the highest probability of seafloor venting in preparation for future detailed, near-bottom studies.

Hudson Canyon slide

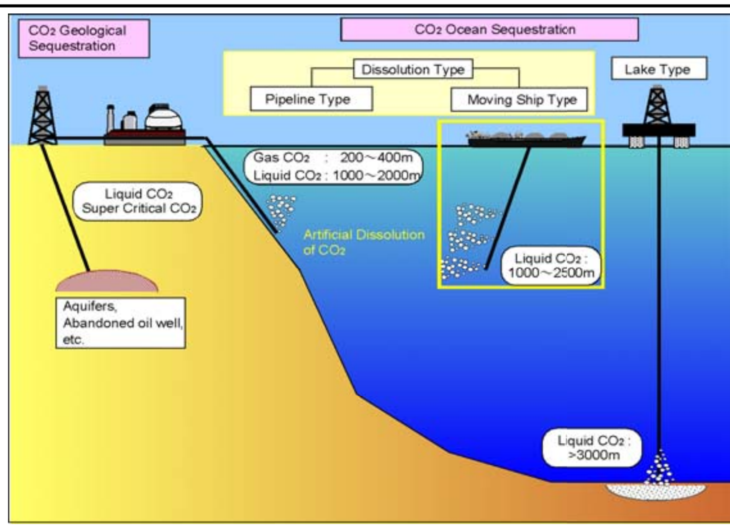


CO_2 Sequestration Technology in Consideration of CO_2 Hydrate

Masahiro Nishio
Thermal Engineering Research Group, Institute for Energy Utilization
National Institute of Advanced Industrial Science and Technology (AIST)

FIC02, 30 Oct. 2002

CO_2 Sequestration Technology



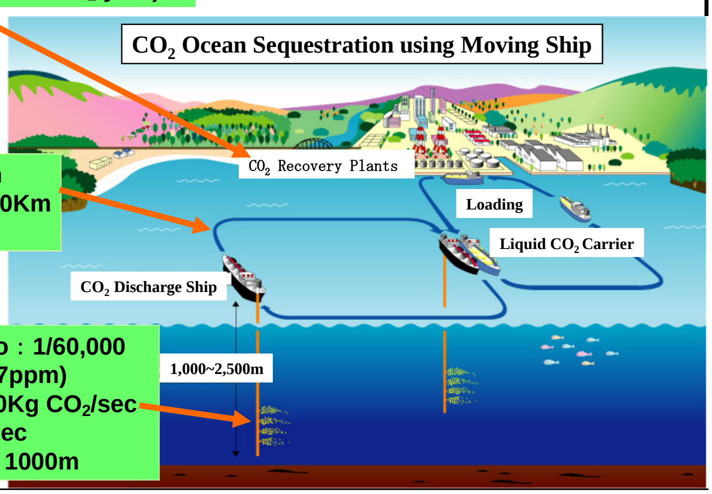
MITI/METI situation

- Preliminary examination in MITI (FY1995-96)
  - CO_2 Ocean Sequestration
    - Dissolution type
    - Lake type
  - CO_2 Geological Storage
    - Aquifer
    - EOR etc.
- **CO_2 Ocean sequestration project (Dissolution type) (phase 1:FY1997-2002, phase 2 FY2002-2006)**
- CO_2 Geological Storage project (FY2000-2004)
- Coal Bed Methane (FY2002-2006) etc.

Future Image

1000MW Coal Fired Plant
（Operation：70%、Recovery：85%）
CO_2 Emission：4MtCO_2/year/Plant
(Total in Japan：1.2GtCO_2/year)

Additional CO_2 is estimated to be 0.4ppm for the injection of 4Mt (0.004Gt) CO_2



Volume of Dilution
Area :100KmX100Km
Height :1000m

Initial dilution ratio：1/60,000 (17ppm)
Injection rate：100Kg CO_2/sec
Ship speed：3m/sec
Plume:2m width、1000m height

R&D Outcomes of Phase1

<RITE>
1. Behavior of liquid CO_2 in seawater
2. CO_2 transport and dilution technology
3. CO_2 Impact on Marine Organisms
4. Environmental Impact assessment Models
5. International joint research for field experiment

<KANSO>
1. Evaluation of the Ocean Circulation
2. Distribution of Carbon Compounds in Ocean
3. Biological Standing Stocks and Effects of CO_2
4. Development of Model for CO_2 Sequestration

Phase 2

Final objective: Modeling of Environmental Impact on Ocean and Marine Organisms

CO_2 Ocean Sequestration Technology and CO_2 Hydrate

- Behavior of liquid CO_2 droplet in seawater
  - Droplet shape deformation w/wo hydrate
  - Dissolution rate with/without hydrate
- Transport and Injection technology
  - Hydrate clogging in the pipeline and the release nozzle

RITE

CO_2 Hydrate

800m
Salt water
(276K)

4500m
Water
(281K)

RITE

High Pressure Vessel (50MPa)

Specification

- Materials: Stainless Steel
- Inner Diameter: 10cm
- Height: 30cm
- Pressure: < 55MPa

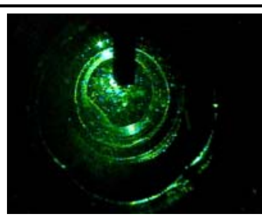
RITE

Small pressure vessel (AIST・RITE)

Specification

- Materials:
  Stainless Steel
- volume: 30ml
- Pressure: <15MPa

CO_2 hydrate precipitation (Case 1)



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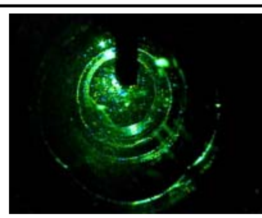

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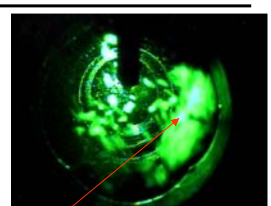

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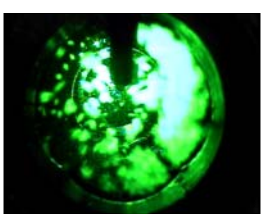

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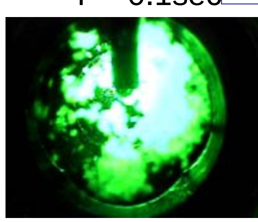

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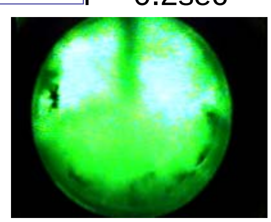
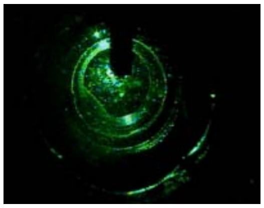


T = 2.0sec

CO_2 hydrate precipitation (Case 2)



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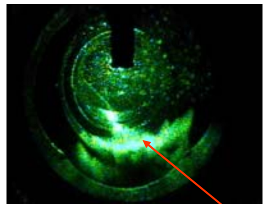

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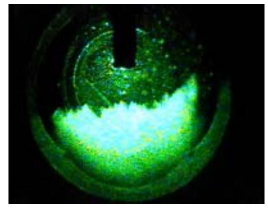

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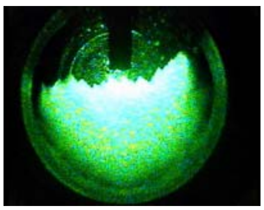

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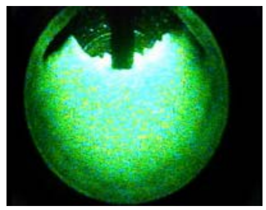

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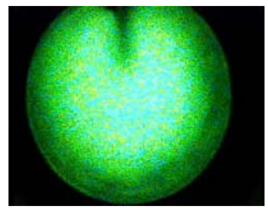


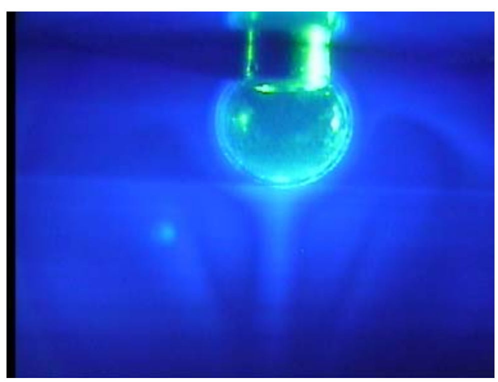
T = 24.0sec

RITE

Visualization of liquid CO_2 dissolution behavior

- Laser Induced Fluorescence (LIF) method
- PIV
- Interferometry

etc.



RITE

Feasibility Study Program of CO_2 Fixation and Utilization

- started FY2002 by METI
  - Managed by Research Institute of Innovative Technology for the Earth (RITE)
  - Number of theme: 8
  - Term: 2 – 3 years
  - Budget: 30 – 50 million yen /year/theme

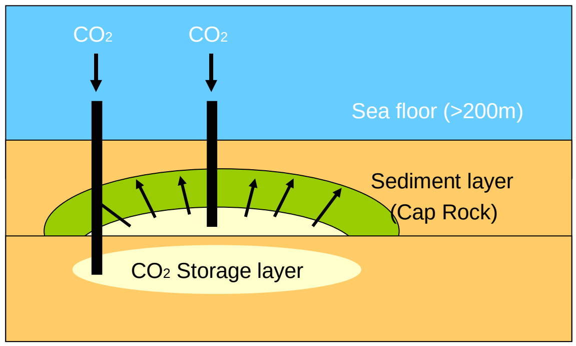
CO_2 Sequestration into sub-Seabed

•Deep ocean storage
Very large capacity
Environmental influence by
CO_2 dissolving in seawater.(?)
X Deeper than 3000m
…

•Geological storage
Large capacity
Long term storage
Low environmental impact
x Limited site
…

CO_2 sequestration into sub-seabed
Large capacity
Low environmental impact
Long term storage (?)
Not so deep
…

Conception diagram



Research Item

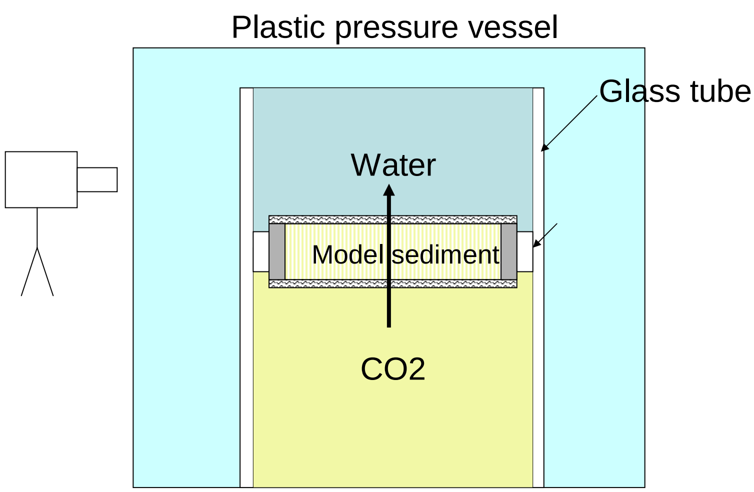
- Cap rock layer formation study by CO_2 hydrate
  - Hydrate formation in porous media
- Stability evaluation of CO_2 hydrate+sediment layer
  - Physico-Chemical stability (temperature, pressure)
  - *Mechanical strength*
- Evaluation of CO_2 gas/liquid enclosure performance
  - CO_2 leakage test (observation of CO_2 dissolution behavior)
- Modeling and Database development
  - CO_2 solution density, viscosity & solubility etc.

High pressure vessel (AIST・RITE)

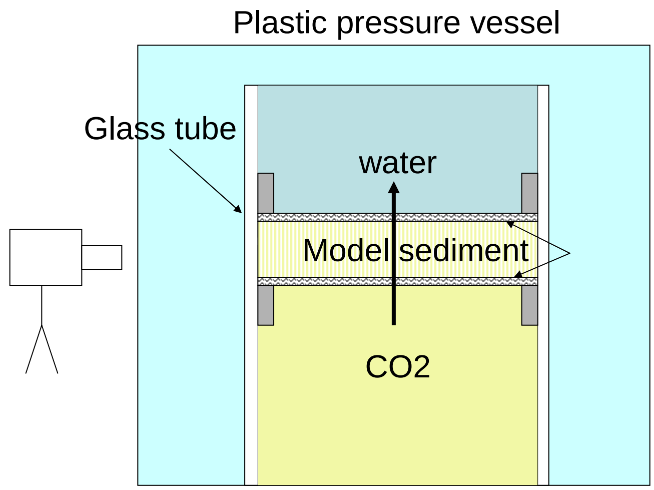
Specification

- Materials: Acrylic acid resin
- Inner Diameter: 5 - 10cm
- Height: 40cm
- Pressure: <15MPa

Observation of CO_2 dissolution behavior



Observation of CO_2 Hydrate formation into sediment layer



- Cap-rock layer formation study by CO_2 hydrate injection for CO_2 sequestration in seabed
- *CO_2 sequestration and Methane recovery*

Flow in Phase Separating Multi-component Fluid Mixtures: Application to Hydrate Dissociation

R.B. Pandey[1,2] and J.F. Gettrust[1]

[1] Naval Research Laboratory
[2] University of Southern Mississippi

ABSTRACT

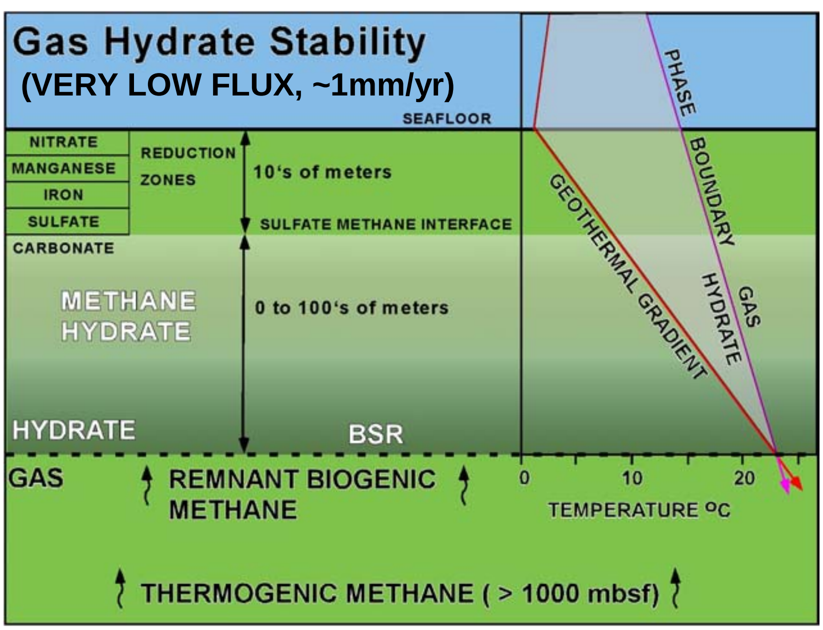
An interacting lattice gas model is used to study flow response in a multi-component system: a mixtures of fluid components A (methane) and B (water) in an effective medium host matrix. Fluid constituents emanate from a source at the bottom and flow into a box open at the opposite end. Molecular weight of the fluid is considered by its mass. The miscibility gap determines the strength of interactions. Apart from concentration gradient, a hydrostatic pressure bias drives the constituents against the rate of sedimentation. We examine the density profile, phase separation, and flow response as a function of pressure bias at steady-state. Response of mass flux density to bias shows interesting characteristics dependence on the molecular weight and miscibility gap at low bias to a universal linear response (Darcy Law) at high bias.

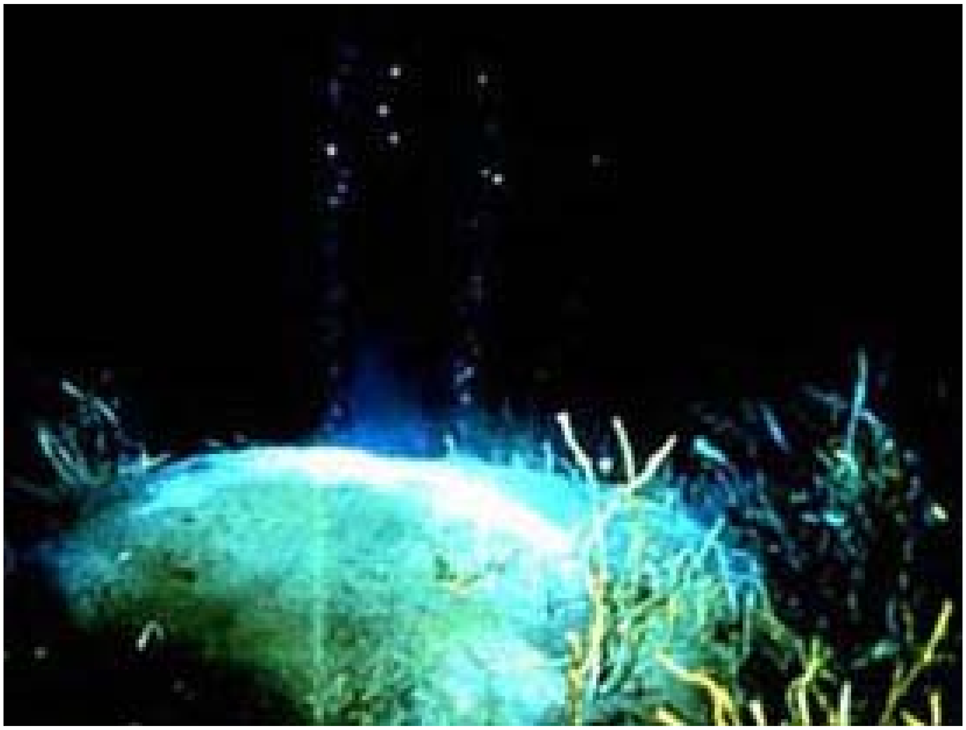
FLOW in PHASE SEPARATING MULT-COMPONENT FLUID MIXTURES

APPLICATION to HYDRATE DISSOCIATION

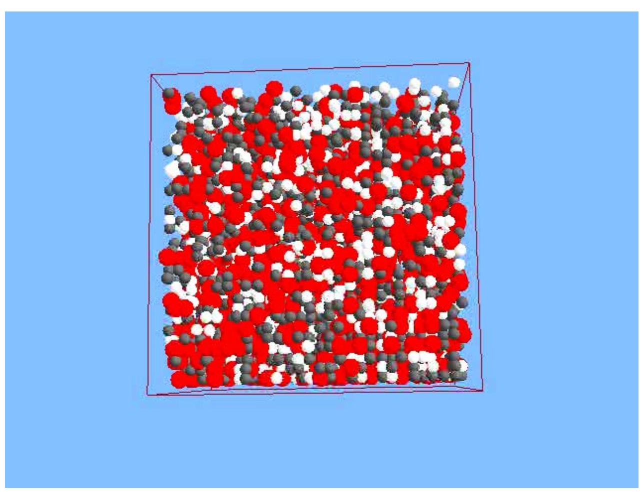
R.B. Pandey and J.F. Gettrust

NRL-Stennis Space Center





SYSTEM



Model

- Lattice: L×L×L
- Particles: A and B
  $m_B/m_A = 3$
- Fluid: x = 0 (source), x=L (open)
- Interaction energy: nearest neighbor, a < 0 (immisc), a >0 (miscible).

$$H = \sum_{ij} U(i, j),$$

$$U_{AA} = U_{BB} = -U_{AB} = a$$

PARAMETERS

- Pressure
- Temperature
- Porosity
- Miscibility
- Molecular weight
- …..

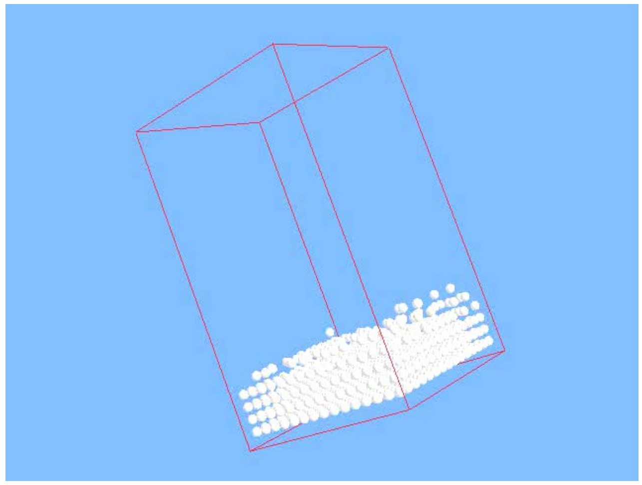
QUANTITIES

- RMS displacements
- Density Profiles
- Flux (Φ), current density (j)
- Response of j to H, pb

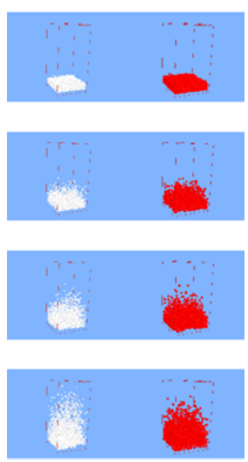
SYSTEMS

- Diffusion
- Porous Media
- Thermal-Driven
- Pressure Driven
- Fault Lines and Planes
- Multi-components: Miscibility, flow, phase separation, sedimentation …

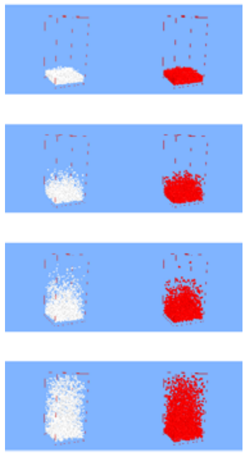
Diffusion: A ($H=1$, $p_b=0$)

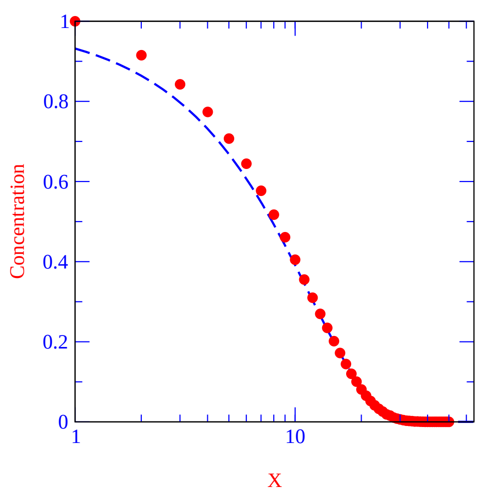


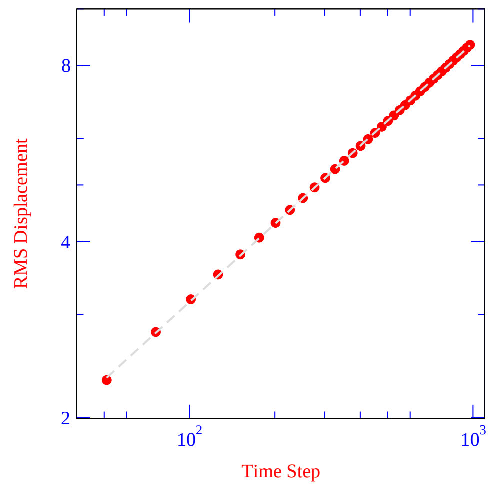
Diffusion Snaps: A,B ($p_b=0$, $H=0$)



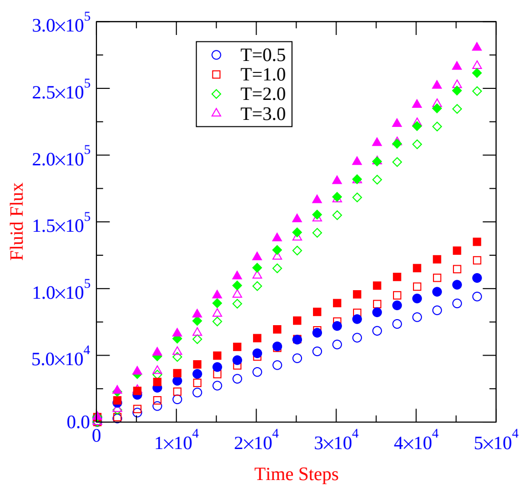
Diffusion Snaps: A, B (p_b=0,H=0.2)



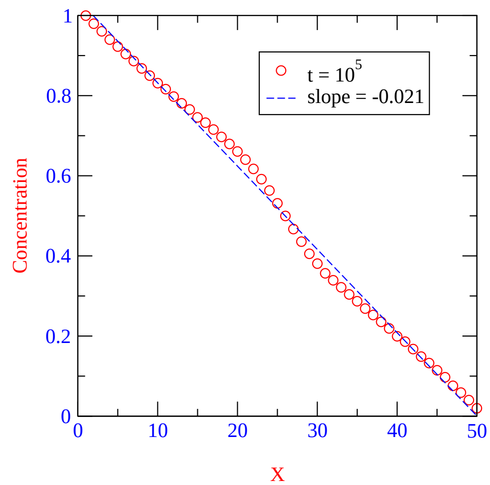


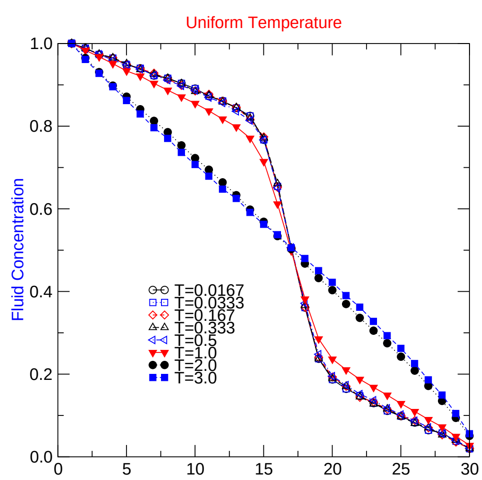


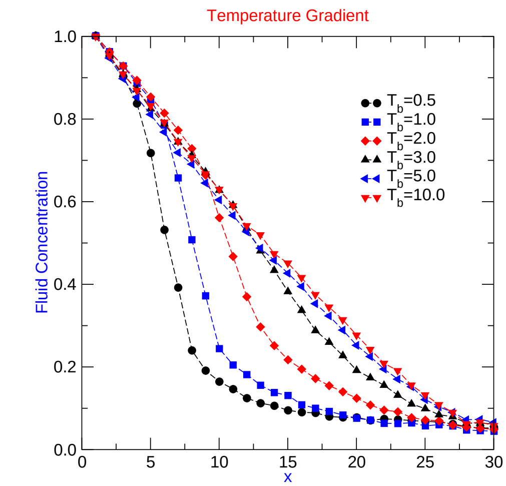
RMS Displacement
8
4
2
10^2
10^3
Time Step

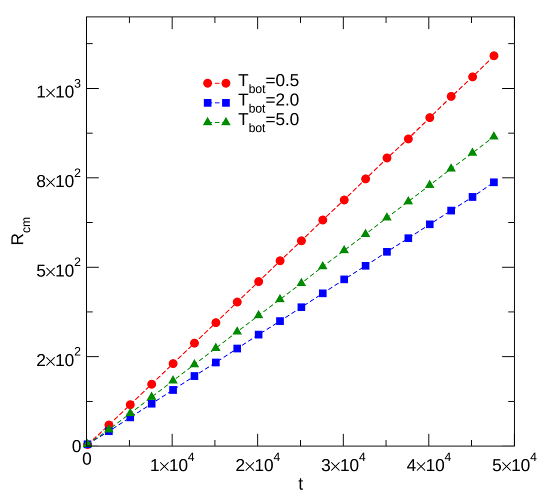


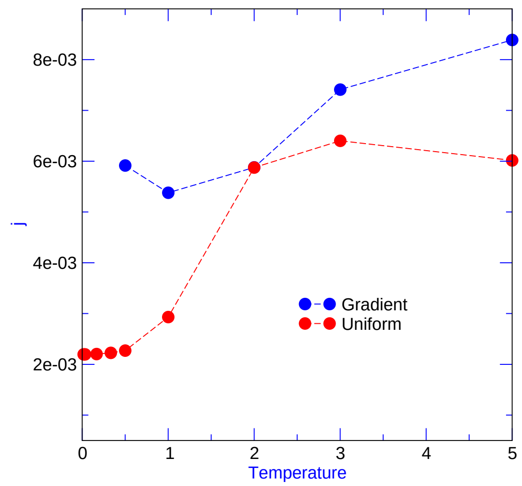
T=0.5
T=1.0
T=2.0
T=3.0
Fluid Flux
3.0×10^5
2.5×10^5
2.0×10^5
1.5×10^5
1.0×10^5
5.0×10^4
0.0
0
1×10^4
2×10^4
3×10^4
4×10^4
5×10^4
Time Steps


t = 10^5
slope = -0.021
Concentration
X
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50

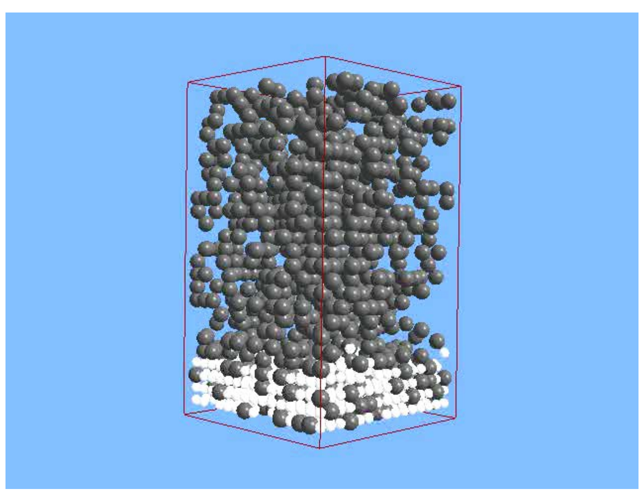

Uniform Temperature
Fluid Concentration
x
T=0.0167
T=0.0333
T=0.167
T=0.333
T=0.5
T=1.0
T=2.0
T=3.0
0.0
0.2
0.4
0.6
0.8
1.0
0
5
10
15
20
25
30


Temperature Gradient
Fluid Concentration
x
T_b=0.5
T_b=1.0
T_b=2.0
T_b=3.0
T_b=5.0
T_b=10.0
0.0
0.2
0.4
0.6
0.8
1.0
0
5
10
15
20
25
30

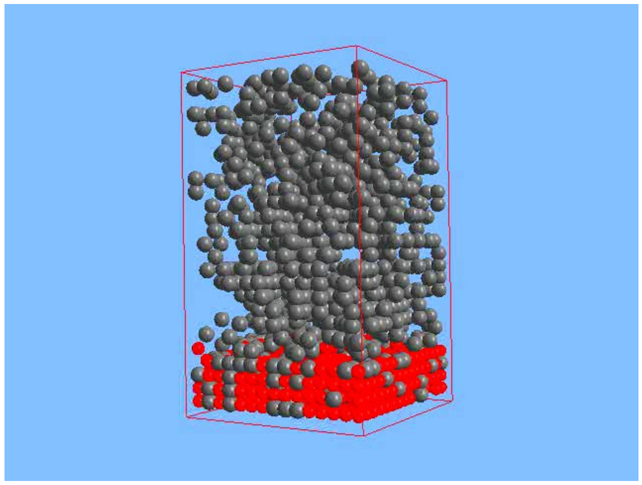

R_{cm}
t
T_{bot}=0.5
T_{bot}=2.0
T_{bot}=5.0
0
2×10^2
5×10^2
8×10^2
1×10^3
0
1×10^4
2×10^4
3×10^4
4×10^4
5×10^4



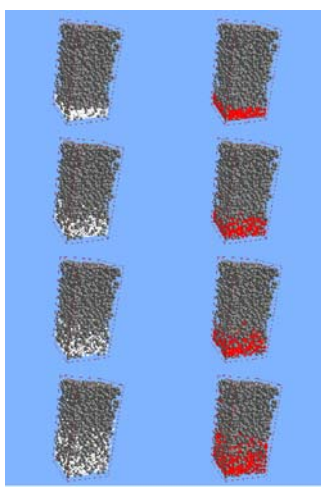
Porous: A (H=0, p_b=0.2)

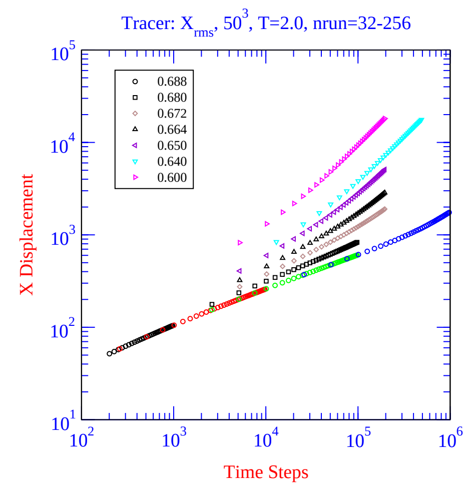


Porous: B (H=0, p=0.2)

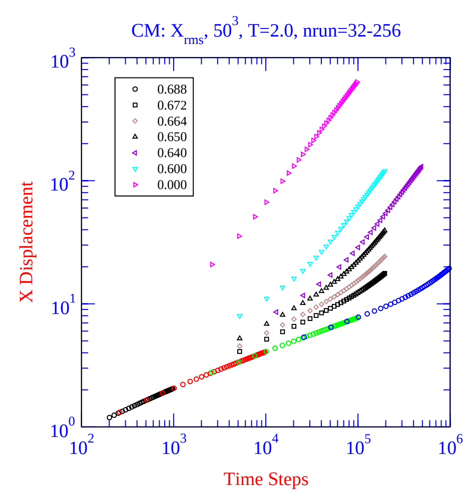


Porous Snaps: A, B (p_b=0.2, H=0)

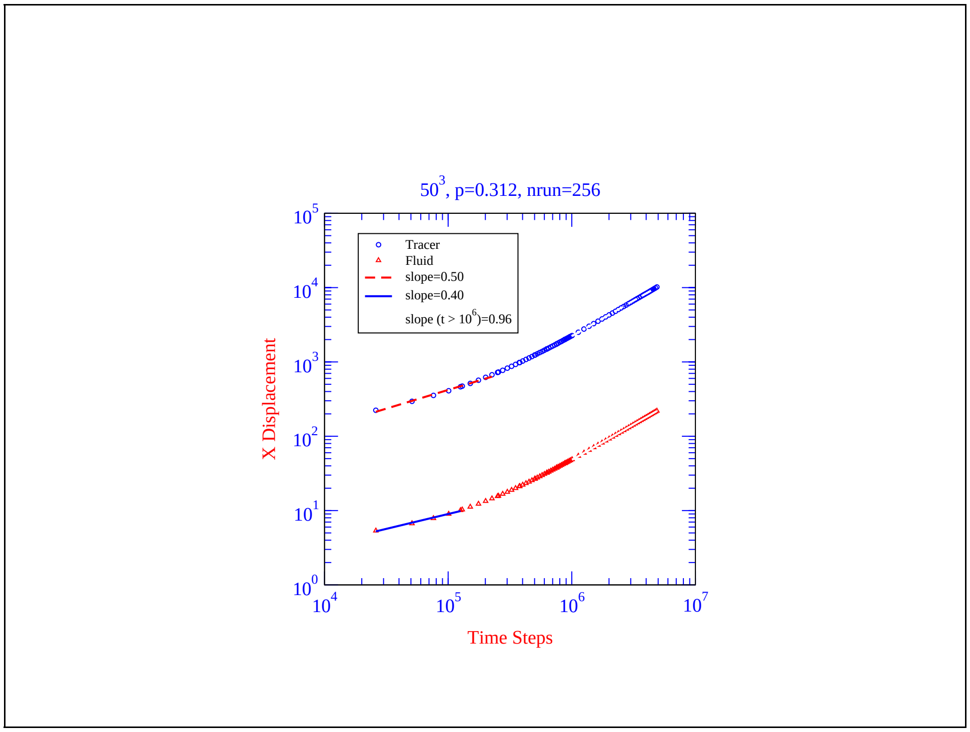


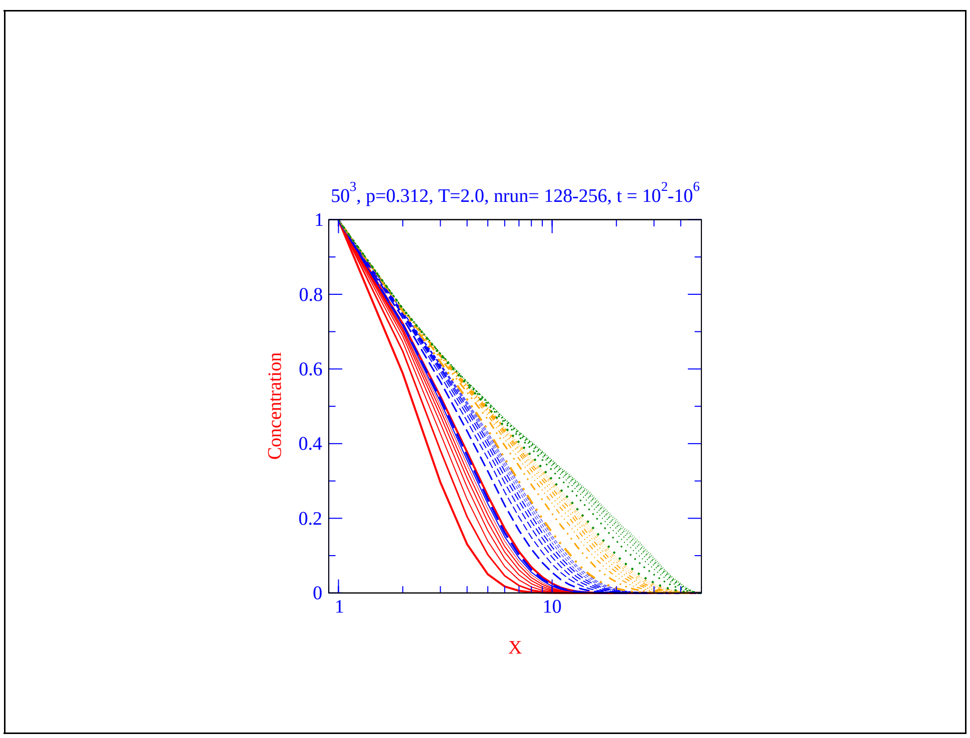


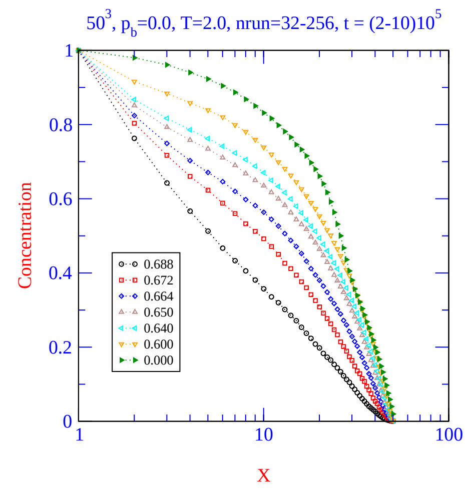
Tracer: X_{rms}, 50^3, T=2.0, nrun=32-256
0.688
0.680
0.672
0.664
0.650
0.640
0.600
X Displacement
Time Steps
10^1
10^2
10^3
10^4
10^5
10^6

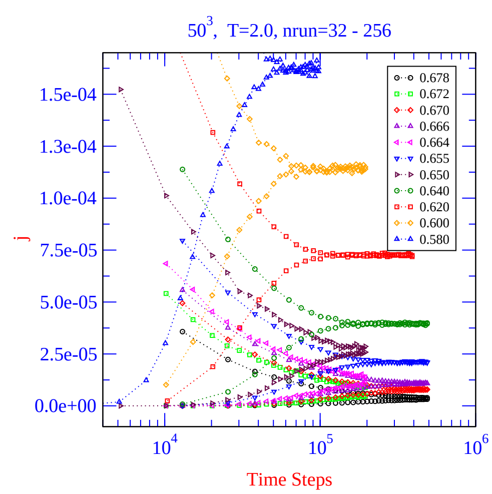


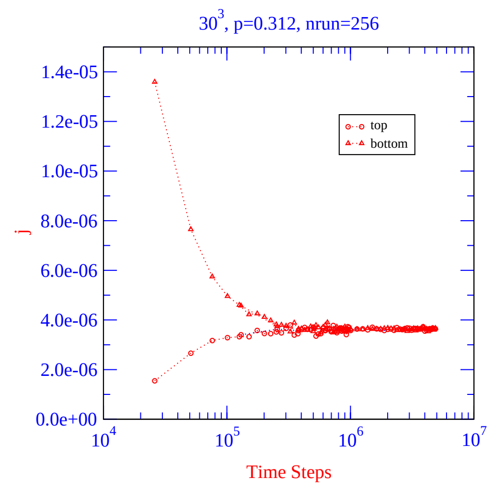
CM: X_{rms}, 50^3, T=2.0, nrun=32-256
0.688
0.672
0.664
0.650
0.640
0.600
0.000
X Displacement
Time Steps
10^0
10^1
10^2
10^3
10^4
10^5
10^6

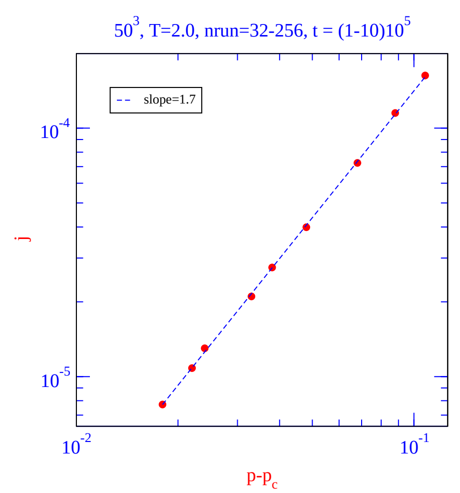

50^3, p=0.312, nrun=256
Tracer
Fluid
slope=0.50
slope=0.40
slope (t > 10^6)=0.96
X Displacement
Time Steps
10^0
10^1
10^2
10^3
10^4
10^5
10^4
10^5
10^6
10^7


50^3, p=0.312, T=2.0, nrun= 128-256, t = 10^2-10^6
Concentration
X
0
0.2
0.4
0.6
0.8
1
1
10

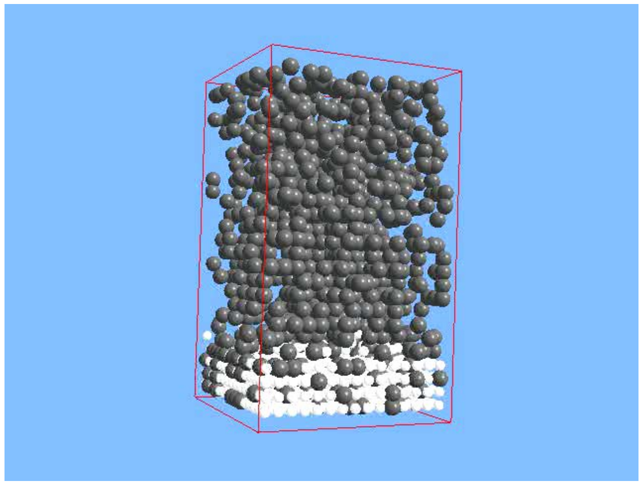

50^3, p_b=0.0, T=2.0, nrun=32-256, t = (2-10)10^5
Concentration
X
0.688
0.672
0.664
0.650
0.640
0.600
0.000


50^3, T=2.0, nrun=32 - 256
j
Time Steps
0.678
0.672
0.670
0.666
0.664
0.655
0.650
0.640
0.620
0.600
0.580

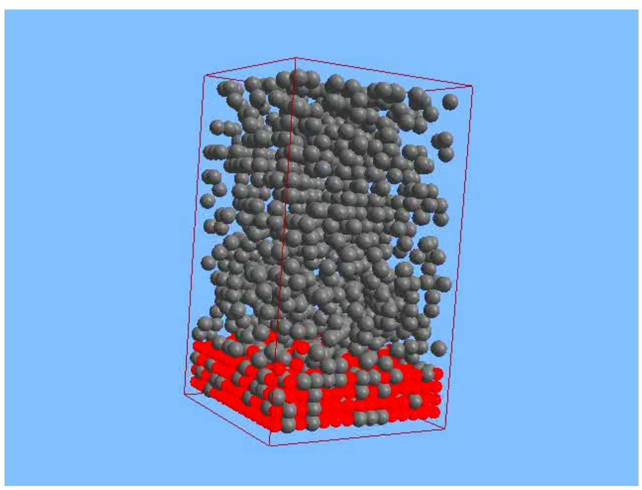

30^3, p=0.312, nrun=256
top
bottom
j
Time Steps
1.4e-05
1.2e-05
1.0e-05
8.0e-06
6.0e-06
4.0e-06
2.0e-06
0.0e+00
10^4
10^5
10^6
10^7


50^3, T=2.0, nrun=32-256, t = (1-10)10^5
slope=1.7
j
p-p_c
10^-4
10^-5
10^-2
10^-1

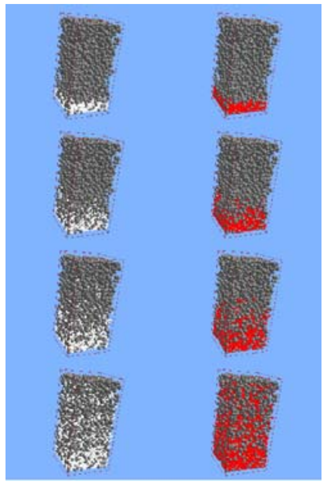
Porous Media (Bias): A

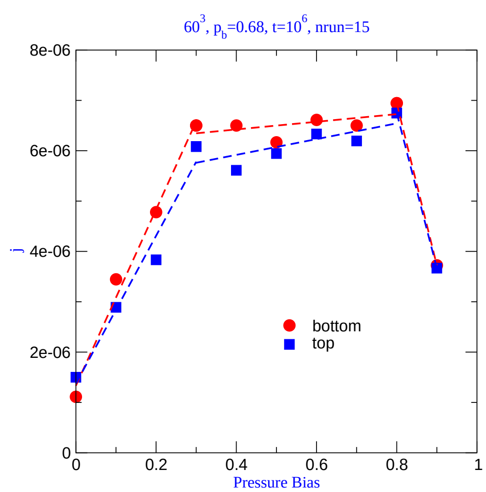


Porous Media (Bias): B

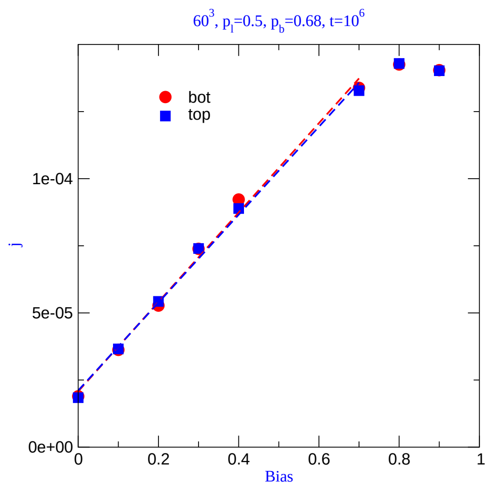


Porous Snaps: A,B (p_b=0.2, H=0.5)

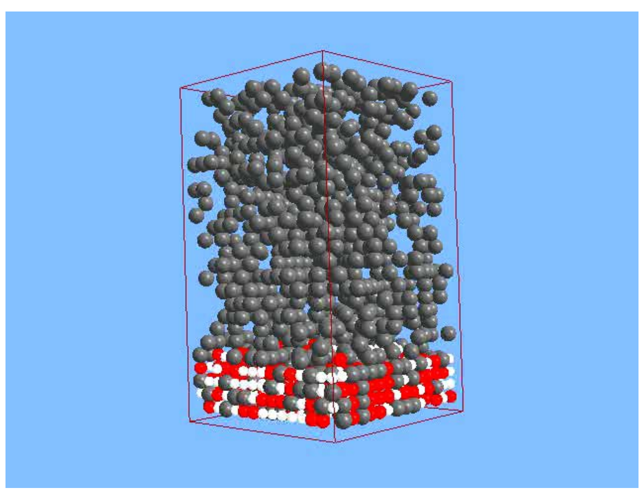




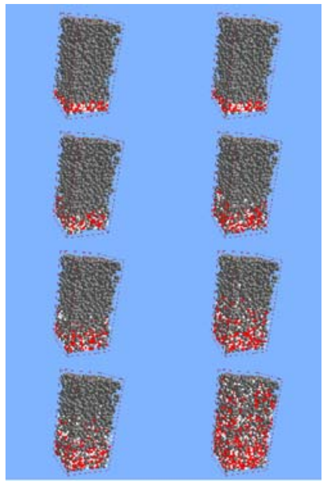
Laye 3)

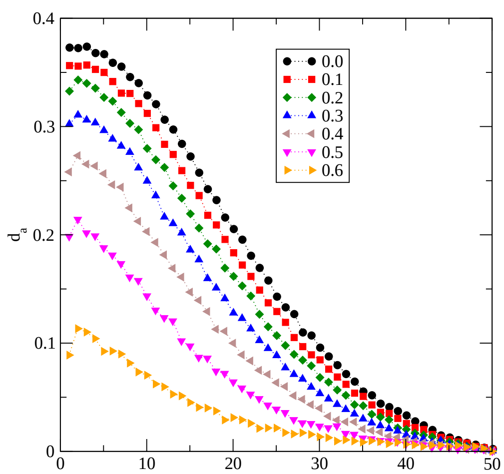


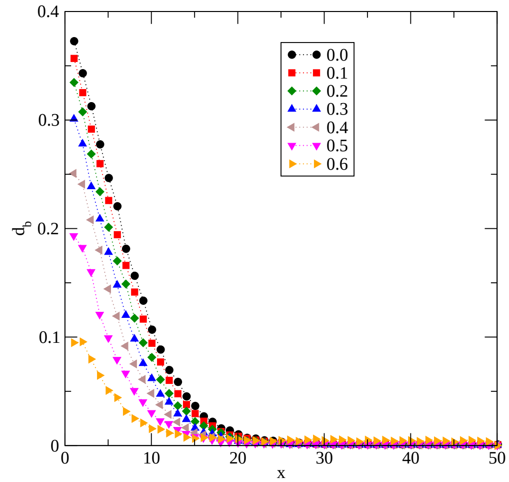
Porous Media: AB (H=0)

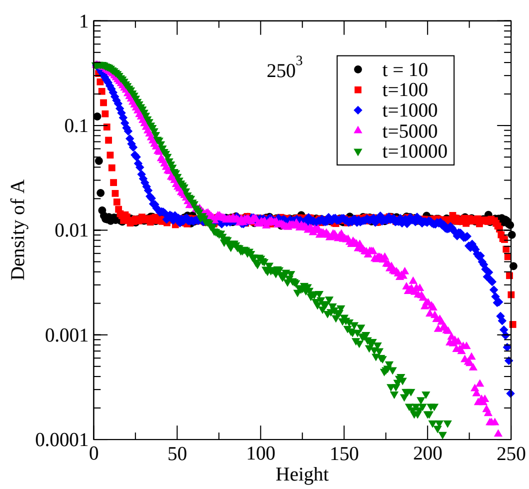


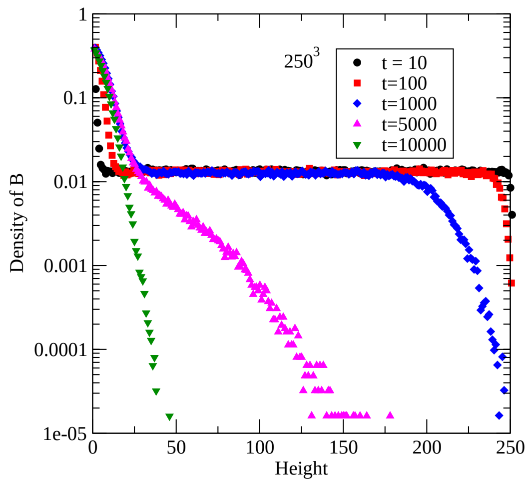
Porous Snaps: AB (H=0.0, 0.5)



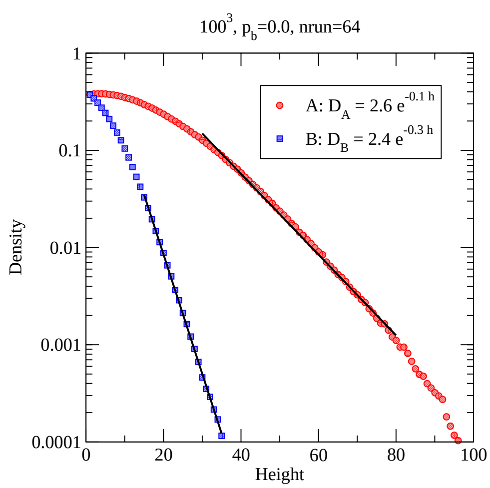



0.0
0.1
0.2
0.3
0.4
0.5
0.6
d_b
x
0
10
20
30
40
50
0
0.1
0.2
0.3
0.4

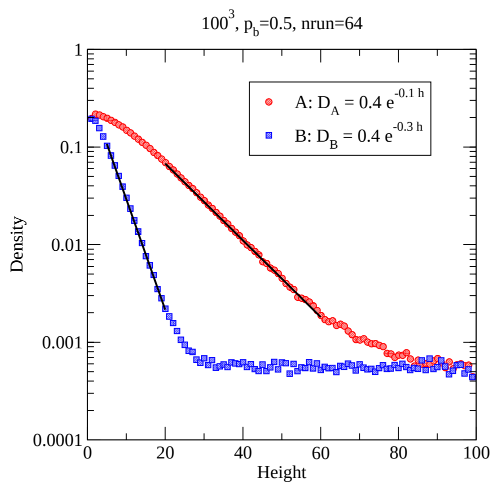

250^3
t = 10
t=100
t=1000
t=5000
t=10000
Density of A
Height
0
50
100
150
200
250
0.0001
0.001
0.01
0.1
1



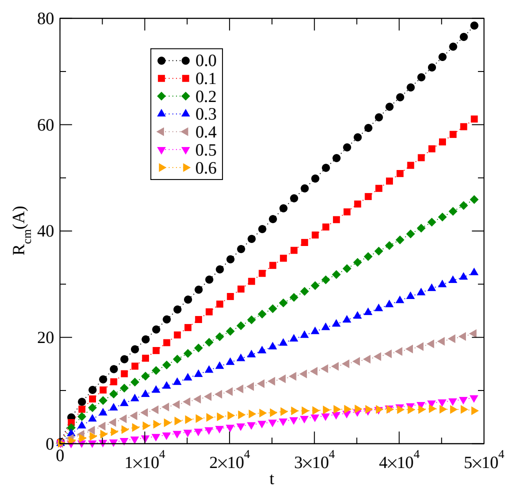
250^3
t = 10
t=100
t=1000
t=5000
t=10000
Density of B
Height
1
0.1
0.01
0.001
0.0001
1e-05
0
50
100
150
200
250



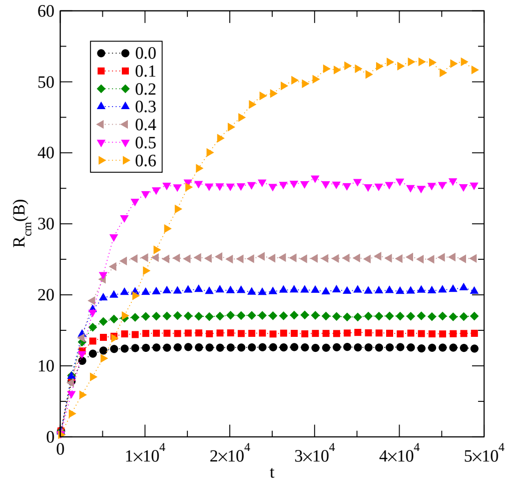
100^3, p_b=0.0, nrun=64
A: D_A = 2.6 e^-0.1 h
B: D_B = 2.4 e^-0.3 h
Density
Height
1
0.1
0.01
0.001
0.0001
0
20
40
60
80
100



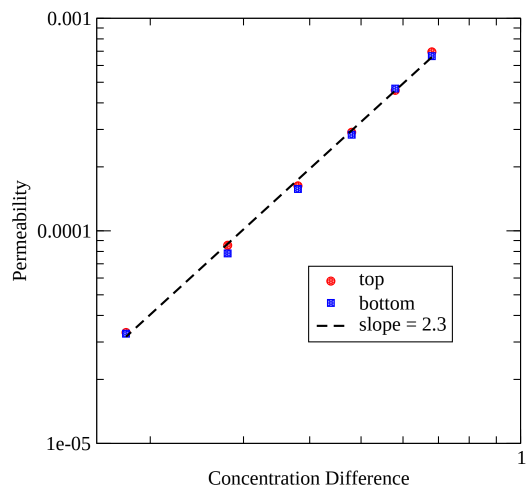
100^3, p_b=0.5, nrun=64
A: $D_A = 0.4\ e^{-0.1\ h}$
B: $D_B = 0.4\ e^{-0.3\ h}$
Density
Height
1
0.1
0.01
0.001
0.0001
0
20
40
60
80
100



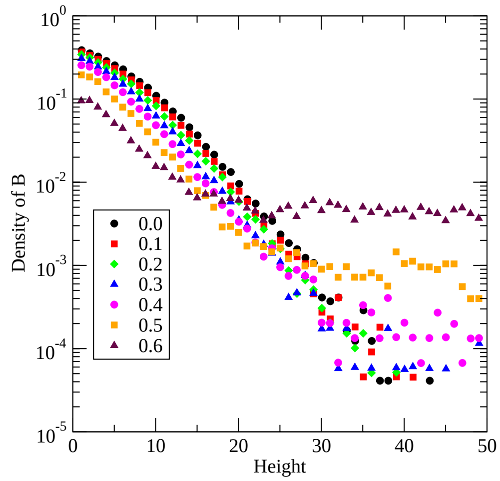
0.0
0.1
0.2
0.3
0.4
0.5
0.6
$R_{cm}(A)$
t
80
60
40
20
0
0
1×10^4
2×10^4
3×10^4
4×10^4
5×10^4



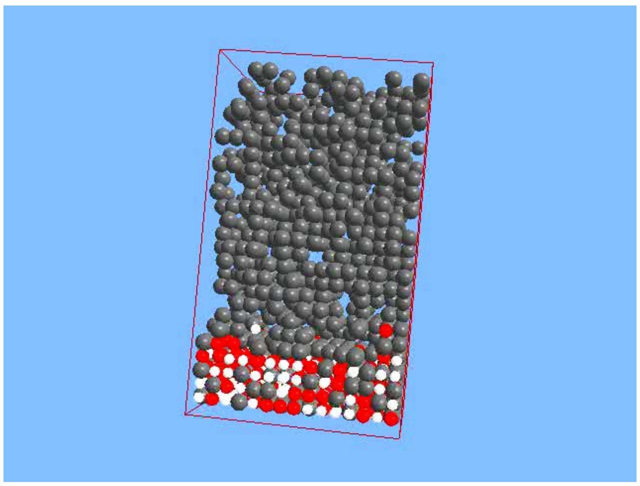
0.0
0.1
0.2
0.3
0.4
0.5
0.6
$R_{cm}(B)$
t
0
10
20
30
40
50
60
0
1×10^4
2×10^4
3×10^4
4×10^4
5×10^4



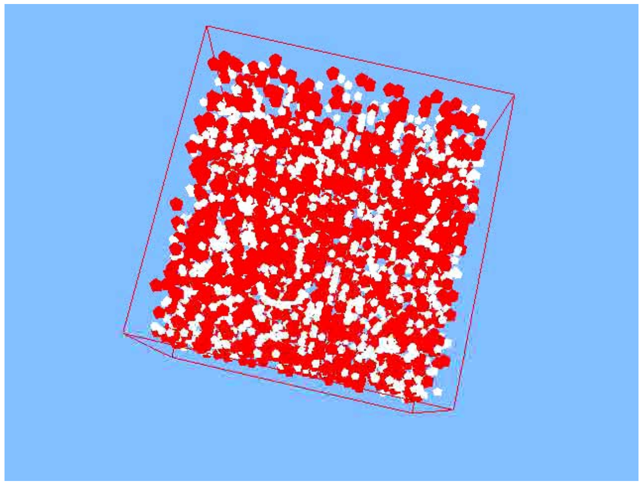
top
bottom
slope = 2.3
Permeability
Concentration Difference
0.001
0.0001
1e-05
1



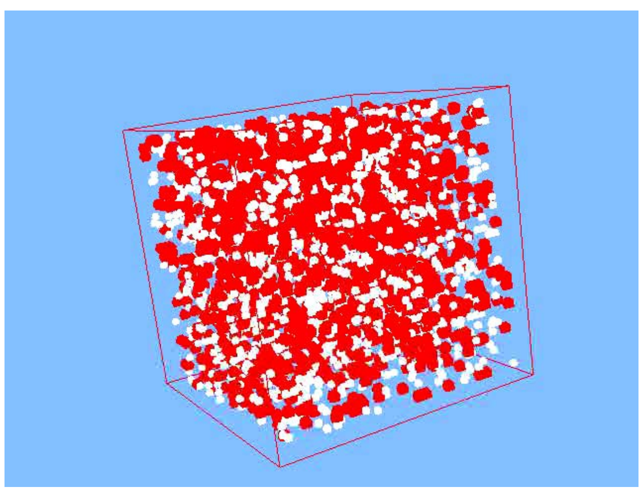
Porous Media (H=1)



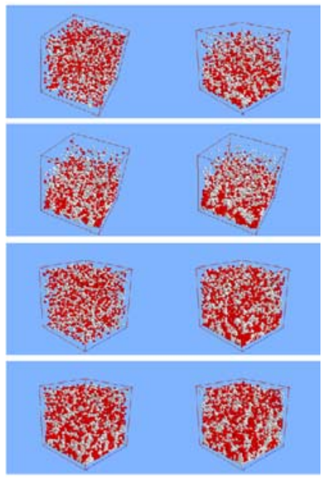
Immiscible (H=0.1)



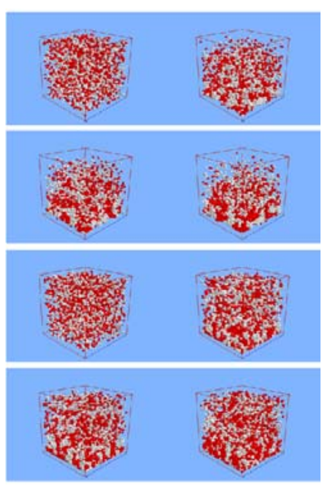
Immiscible (H=1.0)



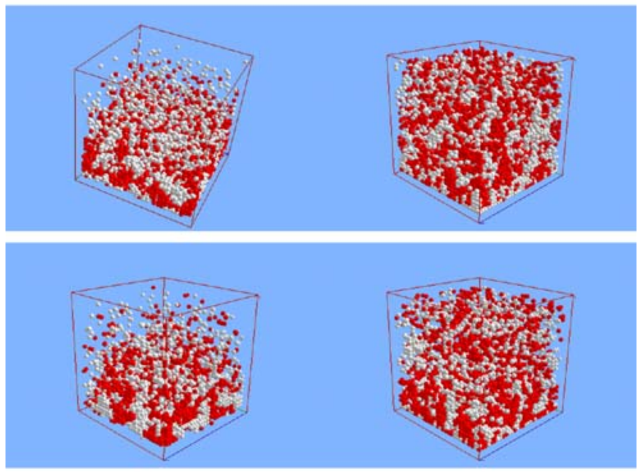
Immiscible Snaps (I=1,H=0, 1)

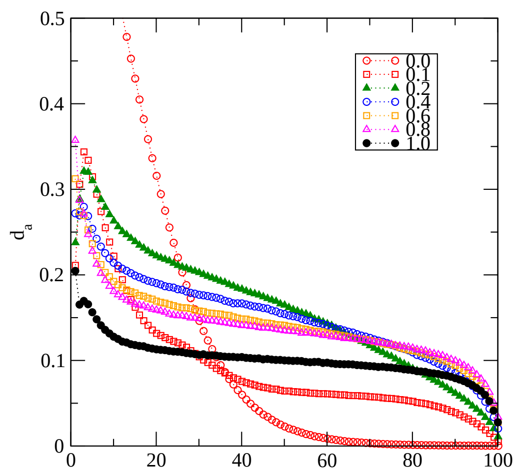


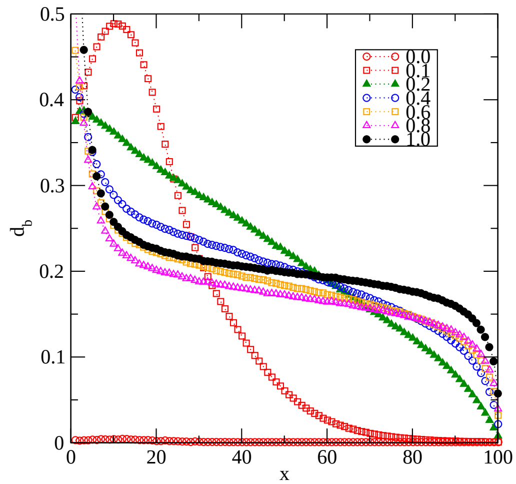
Immiscible Snaps (I=2, H=0, 1)



Immiscible Snaps (I=1,2, H=0,1)







0.0
0.1
0.2
0.4
0.6
0.8
1.0
d_b
x
0
20
40
60
80
100
0
0.1
0.2
0.3
0.4
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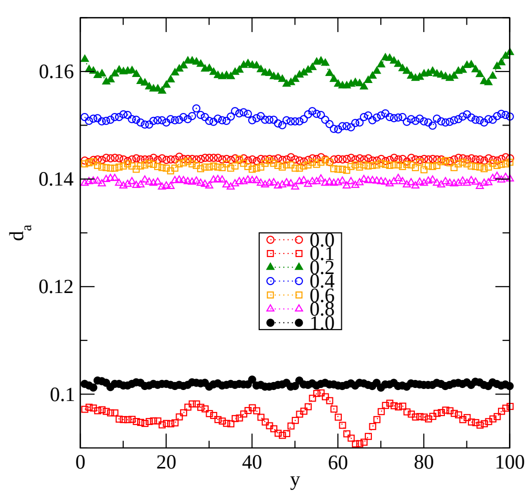

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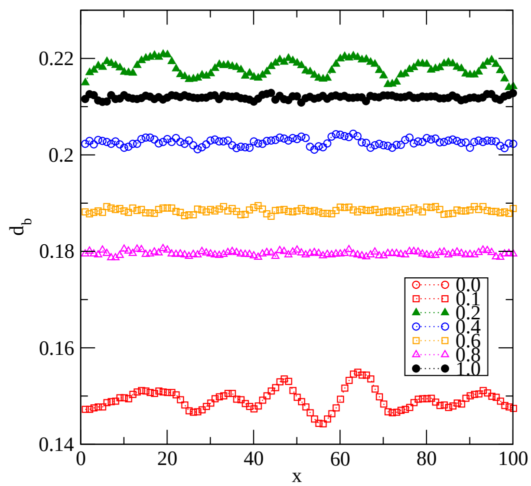
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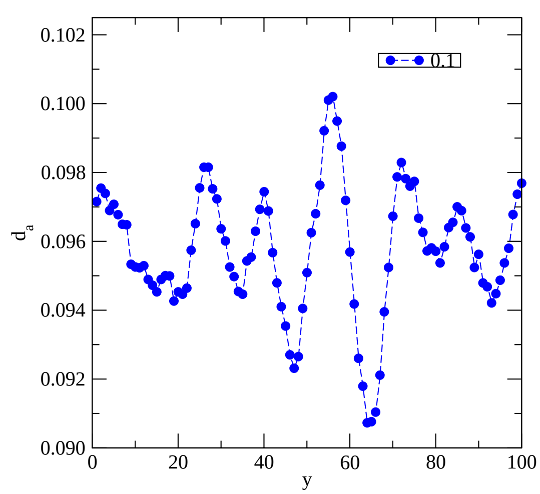
Der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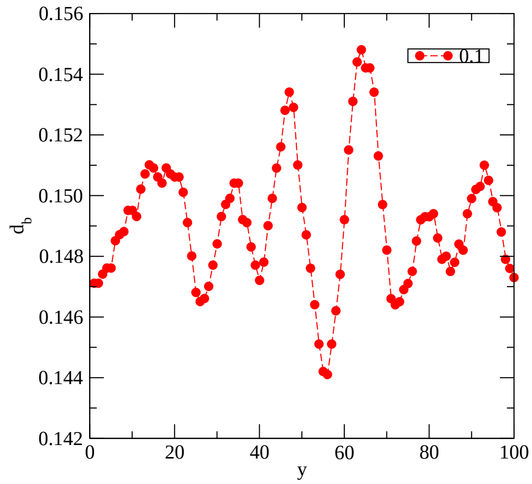

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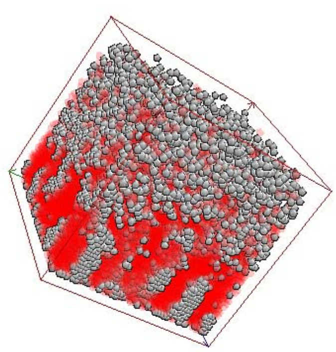

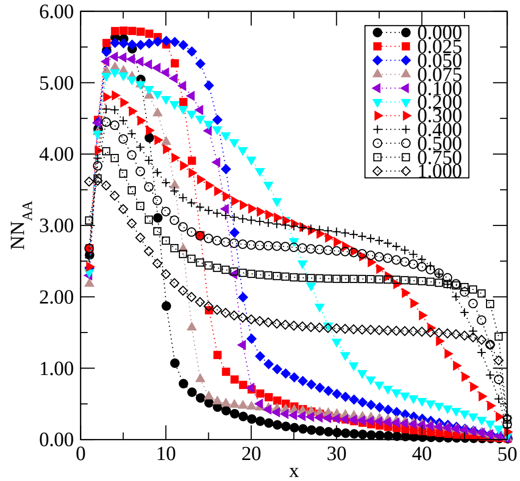
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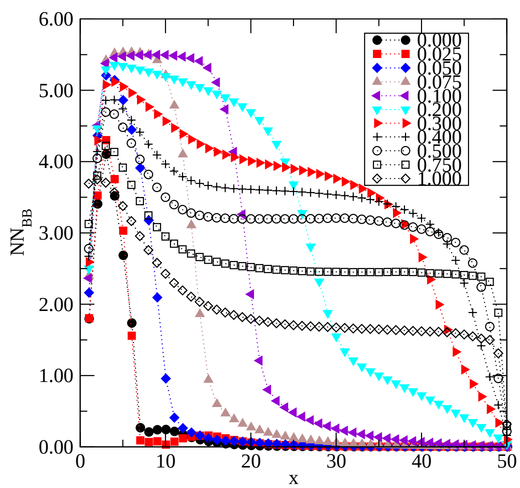
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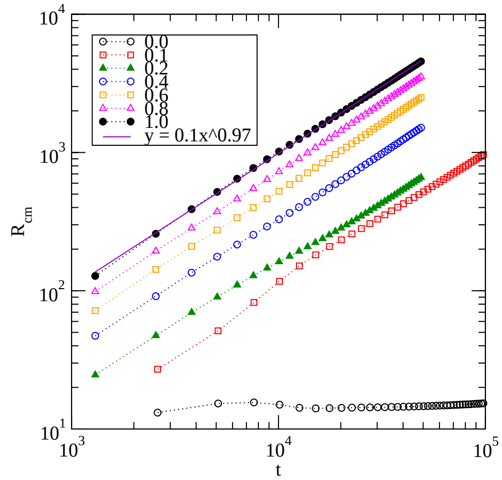

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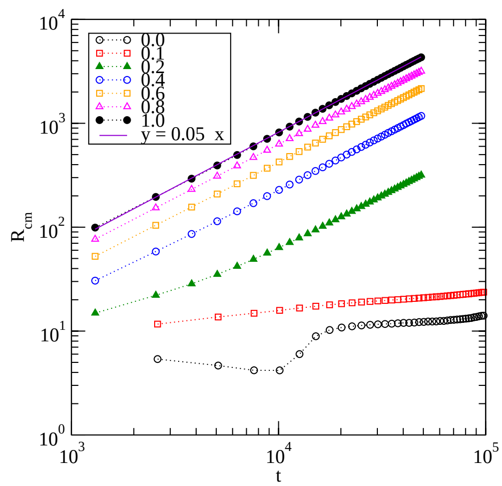

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R_{cm}
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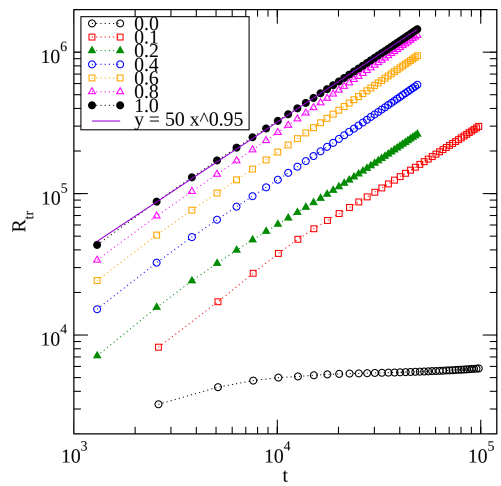

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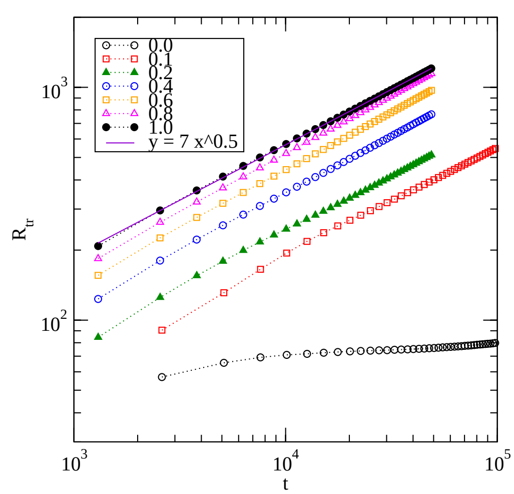
10^5
10^4
10^3
10^4
10^5
t



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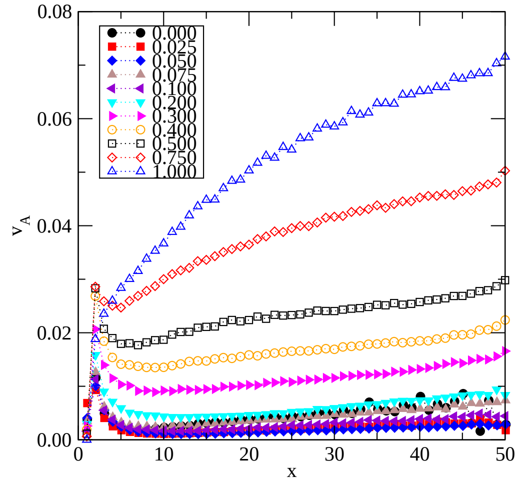
10^2
10^3
10^4
10^5
t



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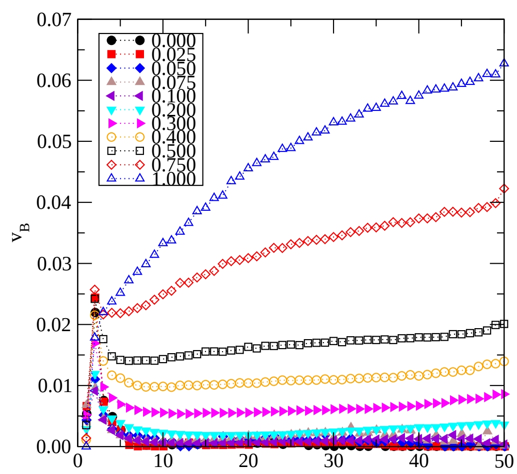

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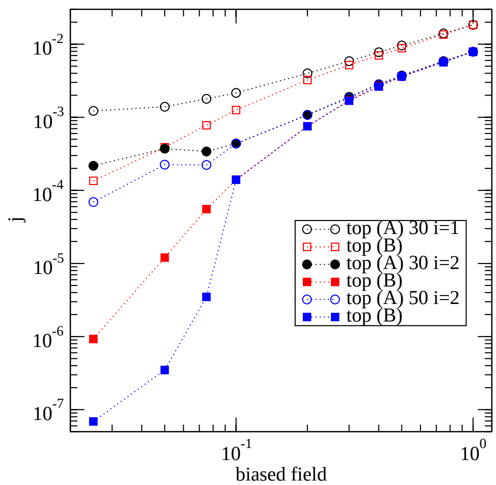
1.000
v_B
x

Cu



SUMMARY

- Sedimentation, density and velocity profiles, correlations, transport, flow rate, etc. and response
- Miscible - R.B. Pandey, D. Stauffer, R. Seyfarth, L. Cueva, J.F. Gettrust, and W. Wood, Physica A 310, 325 (2002)
- Immiscible – study

Miscible Systems

- Density decays $d_{A/B} \sim \exp(-m_A/m_B\ h)$
- d_A continue to decay up to top (lattice)
- $d_B \rightarrow d_{BC}$ at a certain height; d_{BC} increases with porosity.
- Steady-state: $j_{bot} = j_{top}$
- Drift – Sub-diffusion.
- Power-law scaling: $j_A \sim (p-p_c)^{\mu}$, $\mu \sim 2$.

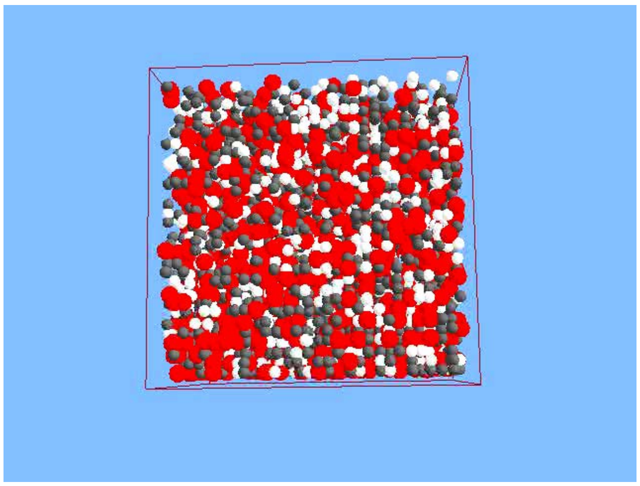
Immiscible System

- Longitudinal density profile depends on pressure bias, in-flux rate, and miscibility gap.
- Transverse density profiles show oscillation within a range of bias – a signal of phase separation, with possibly some layering.
- Transport – mostly drift-like except at high bias values.

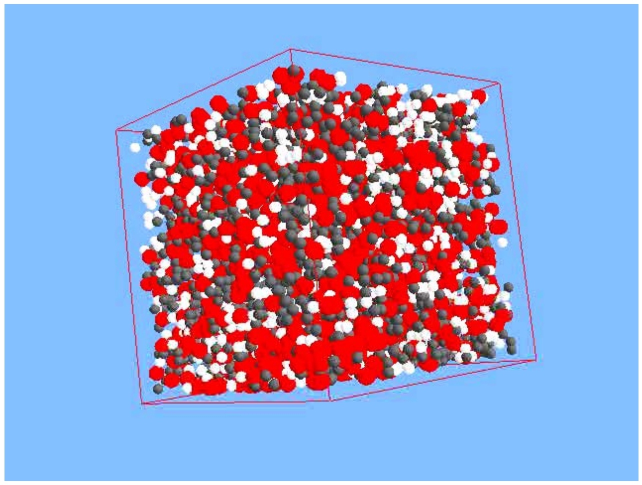
Immiscible - Flow

- Mass transport with time is linear, i.e., the current density remains constant (steady-state).
- Response of flux density to bias – linear with a crossover from low to high range of bias with different rates.
- Response depends on miscibility gap.

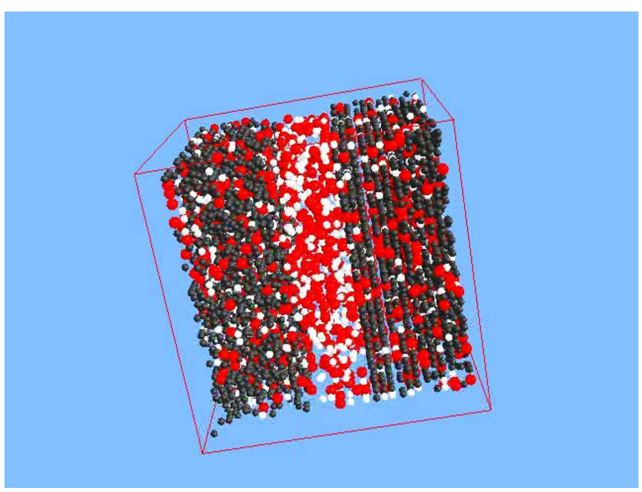
Immiscible (pb=0.1, H=0.1)



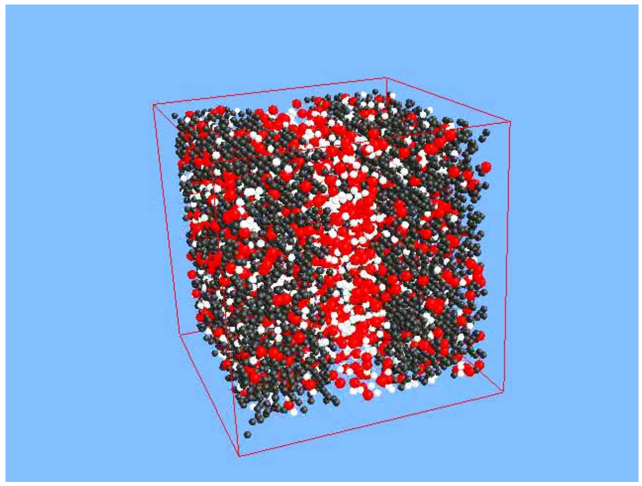
Immiscible (pb=0.1, H=0.5)



Fault (imm, pb=0.3, H=0.0)



Fault (imm, pb=0.3, H=0.1)



SESSION V

Methane Storage and Shipping

Chairman: Dr. Hitoshi Narita
Office of Naval Research
International Field Office
Tokyo, Japan

Rapporteur: Dr. Lewis Norman
Halliburton Energy Services
Duncan, OK, USA

THE DYNAMICS OF THE GLOBAL LNG INDUSTRY

Colleen Taylor Sen

Gas Technology Institute

ABSTRACT

One of the world's fastest growing fuels, liquefied natural gas (LNG) accounts for 21% of all internationally traded volumes and 5.6% of world gas demand. U.S. imports are approaching record levels, although still less than 2% of total supply. Power generation is a primary growth area. The emergence and expansion of a LNG spot market and the globalization of the gas industry are important market drivers.

The choice of sending gas to the market via pipeline or as LNG is based on economic and political considerations. Generally, LNG is economic when offshore piping would exceed 2000 km or onshore piping 3500 km, though there are tradeoffs between project size and distance.

The LNG chain consists of four components: production, processing and liquefaction, shipping, and receiving/regasification. An 8-million tonne/year (mta) LNG grassroots project costs between $3.7 and $6.8 billion, which translates to $2.10-$3.80/million Btu. Of this, 40-50% is liquefaction and processing costs; 20-30% receiving and vaporization facilities; 10-15% shipping; and 15-20% production. The expansion of existing projects costs considerably less.

Worldwide, liquefaction plants with a combined production capacity of 125 mta (1 mta ≈ 1.38 million cubic meters or 48.7 billion CF of natural gas) are operating at 15 sites in 12 countries, with approximately half in the Asia Pacific. Another 40 mta of capacity (mainly expansions) is under construction while more than 200 mta of new capacity has been announced. The Middle East and West Africa are emerging as potentially important exporters.

Forty-one receiving terminals are operating in ten countries (half of them in Japan), seven are under construction, and more than forty have been proposed in the U.S., Mexico, the Caribbean, Europe, and elsewhere. In the past the focus of imports was Asia but the Atlantic Basin is becoming an increasingly important market.

Over the past 10-15 years the costs of all links of the LNG chain have been steadily declining. The past decade has seen a 35-50% reduction in liquefaction costs because of greater economies of scale (train size has increased from 1.2 mta to more than 4 mta); smaller purpose-built plants; improved technology and engineering techniques; reduced over-design; the integration of terminals with powerplants; and competition. The costs of regasification terminals and storage tanks have also fallen substantially for similar reasons.

A critical element in the economics of LNG is shipping, which costs several times more than crude oil on an energy basis. Today's LNG fleet consists of 132 ships; a record 61 ships are on order at the 9 shipyards that are actively building LNG tankers.

The price of an LNG tanker has declined from more than $250 million in 1991 to around $150 million today. This reflects economies of scale (tankers are getting bigger subject to port and terminal constraints), competition, and more realistic pricing. But the industry is conservative and slow to change. The LNG fleet is one of the last in the world to use steam boilers and shipowners have been reluctant to introduce diesel/electric engines and other "new" propulsion technologies. Still, the increase in the number of ships and participants, the purchase of several ships "on speculation," and the emergence and growth of an LNG spot market are leading to greater flexibility in the entire LNG industry.

The Dynamics of the Global LNG Industry

Colleen Taylor Sen
Gas Technology Institute

The Second Workshop of the International Committee on Gas Hydrates
29-31 October 2002
Washington DC

Outline of Presentation

- Definition
- Global Trends
- The LNG Chain
  - LNG Export Facilities
  - LNG Import Facilities
    - Economics
  - LNG Shipping
- Prospects for LNG

What is Liquefied Natural Gas?

A colorless odorless liquid

Natural Gas Treated and Cooled to -161^{O}C
Pressure: 1 Bar
Volume reduction: 1:600

Composition (Typical)		low	high
Methane	C1	80	99%
Ethane	C2	1	17%
Propane	C3	.1	5%
Butane	C4	.1	2%
	C5+	<1%	
Nitrogen	N2	0	1%

Calorific Value 1000 - 1160 btu/scf
Density 0.45 - 0.47 g/cc

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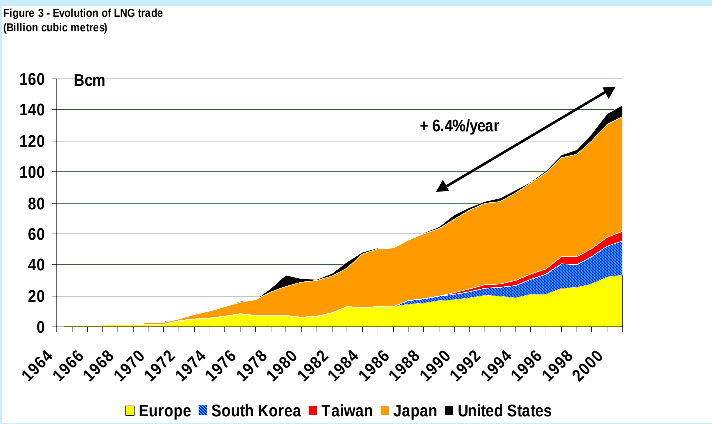
World LNG Trade 1964-2001



Source: Cedigaz

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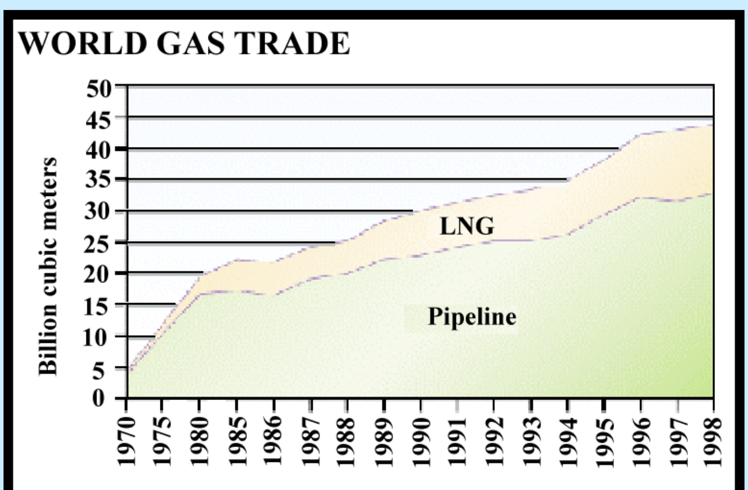
Snapshot of World LNG Demand

- 1995-2001, LNG demand grew 6-7%/yr
- In 2001,LNG use rose 4.2% to 143 bcm vs. 1.5% for world gas consumption and 3.3% for pipelines
- LNG = 21% of world gas flows and 5.6% of gas demand
- U.S. imports at record levels, but still less than 1% of supply
- Dramatic growth of spot trade: now 8% of total sales
- Will LNG become a commodity like oil or LPG?

LNG/Pipeline Competition Expanding



Proved Gas Reserves, 2000

Country	Proven Reserves (TCF)	Country	Proven Reserves (TCF)
1. Russia *	1,700	14. Uzbekistan	66
2. Iran *	812	15. Kazakhstan	65
3. Qatar LNG	394	16. Netherlands	63
4. Saudi Arabia	213	17. Canada	61
5. Abu Dhabi LNG	196	18. Kuwait	52
6. United States LNG	167	19. Libya LNG	46
7. Venezuela *	147	20. China	48
8. Algeria LNG	130	21. Australia LNG	45
9. Nigeria LNG	124	22. Norway*	44
10. Iraq	110	23. Ukraine	40
11. Turkmenistan	101	24. Egypt*	35
12. Malaysia LNG	82	25. Mexico	30
13. Indonesia LNG	72	26. Oman LNG	29
TOTAL WORLD			5528

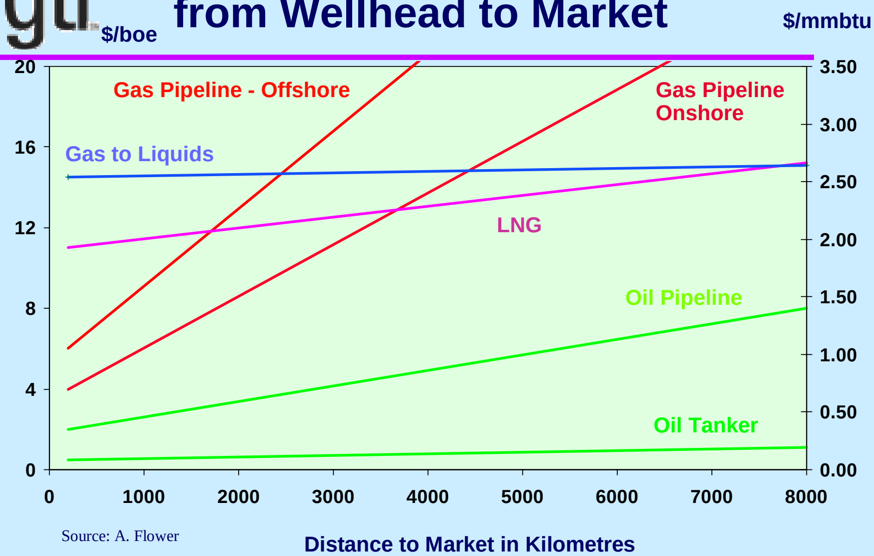
Requirements for an LNG Export Project

- Sufficient reserves: Reservoir should be 125% larger than plant size
  - E.g., a 1.5 TCF reservoir will support a 1.2 mta plant for 20 years
- Quality of gas: + and -
- Political and company will and commitment
  - e.g., Trinidad vs Iran,
- Patience: Nigeria, Trinidad projects began in 1970s
- Distance

LNG vs. Pipeline

- Location: LNG is most economical when –
  - Offshore piping would exceed 2000km
  - Onshore piping would exceed 3500 km
- LNG has the benefits of modular buildup
- Pipelines can serve a multiplicity of markets en route and provide more flexibility of supplies
- Other factors include:
  - the cost of purchasing pipeline rights of way
  - the maximum flow required to meet peak demand
  - the depth of the water and nature of the seabed
  - security and political concerns (e.g., India)
  - economic benefits to the importing/exporting country (e.g., shipbuilding)

Indicative Cost of Moving Gas from Wellhead to Market



Source: A. Flower

LNG Exports, 2001
(billion cubic meters)

Country	Exports
Indonesia	31.80
Algeria	25.54
Malaysia	20.91
Qatar	16.54
Australia	10.20
Brunei	9.00
Nigeria	7.83
Oman	7.43
Abu Dhabi	7.08
Trinidad	3.65
U.S.	1.79
Libya	0.77
Taiwan (re-export)	0.41
Total	142.95

Source: Cedigaz

Liquefaction Export Plants

- Plants at 15 sites in 12 countries
- Total 65 trains
- Annual production capacity 125 million tonnes
- Actual average utilization around 85%
- Capacity under construction: 34 mta
- Surplus is fueling ‘spot’ trade
- Note growing role for Middle East, Africa

Liquefaction Capacity by Region

Middle East	mta
Abu Dhabi	5.7
Oman	6.6
Qatargas	7.7
RasGas	6.4
Subtotal	**26.4**

Atlantic Basin	
Algeria – Arzew	17.3
Algeria -- Skikda	5.1
Libya	1.8
Trinidad, 1&2	6.3
Nigeria, 1&2	6.6
Subtotal	**37.1**

Asia/Pacific	mta
Alaska	1.8
Australia	7.5
Brunei	7.2
Indonesia-Bontang	22.9
Indonesia – Arun	6.8
Malaysia I & II	15.4
Subtotal	**61.6**

Total **125.1**

Liquefaction Capacity under Construction

Atlantic LNG, Train 3	3.2 mta
Nigeria LNG,Trains 3,4,&5	11.2
Northwest Shelf, Train 4	4.2
Malaysia Tiga	7.6
Ras Laffan, Train 3	4.7
Egypt, Damietta	5.0
Norway, Snohvit	4.0
Total	39.9

Announced Liquefaction Plants

Middle East	mta
Yemen	6.1
Oman, Train 3	3.5
Qatargas, Trains 4, 5&6	19
RasGas, Train 4,5 &6	15
Iran, Pars	8-16
	52-58

Western Hemisphere	
Trinidad 4 & 5	9.6
Bolivia	7.0
Alaska N. Slope	14.0
Venezuela	4
Peru	4
	39

Asia	mta
Bontang Train I	3.6
Tangguh	3.5-7.0
NWS Train 5	4.2
Gorgon	5.0
Timor Sea	7.0-7.5
Sakhalin II	9.6
	33-37

Africa	
Nigeria, Train 6	4.1
Angola	3.4-6.8
Equit. Guinea	4
Nigeria, Brass River	8
Egypt (Idku)	7-10
Egypt (Damietta)	5
	31-35

LNG Imports, 2001
(billion cubic meters/year)

Country	Imports
Japan	74.07
Korea	21.83
France	10.45
Spain	9.84
U.S. (incl. P.R.)	7.22
Taiwan	6.30
Italy	5.25
Turkey	4.83
Belgium	2.40
Greece	0.50
Portugal (via Spain)	0.26
Total	142.95

Source: Cedigaz

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LNG Receiving Terminals

- 41 terminals operating in 10 countries:
  - 24 in Japan 3 Spain, 3 in U.S. plus 1 in Puerto Rico, 2 in Korea, 2 in France, 1 each in Italy, Belgium, Turkey, Taiwan, Dominican Republic & Greece
- Total sendout capacity: 950 bcm/day
- Total storage capacity: 17.5 bcm of LNG
- New terminals under construction in Korea (1), India (2), Spain (2), Portugal (1), Turkey (1), Cove Point will reopen
- Many terminals are being expanded
- Nearly forty terminals announced or proposed in 16+ countries, incl. Canada, the U.S., Mexico, Bahamas, Honduras, Brazil, Jamaica, Spain, Portugal, Italy, Turkey, Poland, Taiwan, China, Japan, India, Philippines.

Why Does a Country Import LNG?

- Domestic supplies are insufficient to meet baseload demand or remote from markets: Japan, Korea, Taiwan, China, India, Spain
- Need to diversify energy supplies by source and fuel: Spain, France, Turkey, Japan
- Power generation primary growth area:Taiwan, Caribbean, Mexico, Brazil
  - Use of natural gas for power production forecast to double by 2010
  - Progress in combined cycle gas power plants
- Mounting environmental pressures toward cleaner burning fuels: Japan, China, India
- Resistance to nuclear power: Italy, U.S.

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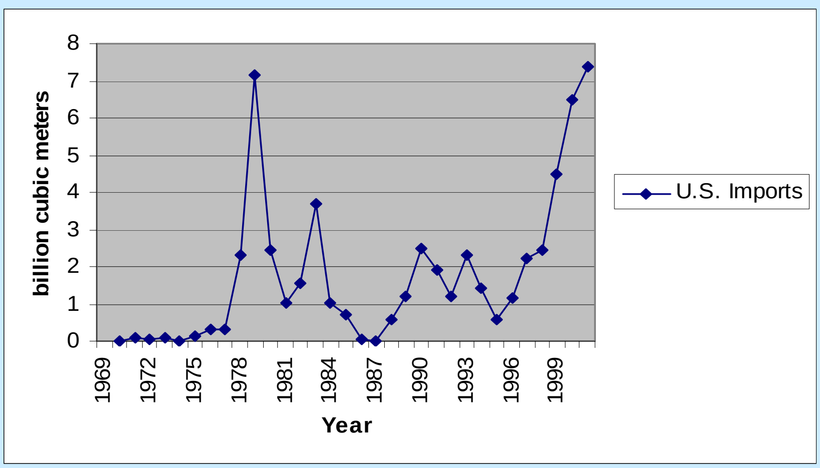
Why Does a Country Import LNG?

- **Spot sales to meet temporary shortfalls due to seasonal needs, stronger than expected demand:** Spain, Korea, U.S.
- **Spot trade soared 42% to a record 10.8 bcm in 2001**
  - Growth = 80% of the increase in the world LNG trade
  - Spot trade = 7.8% of the world LNG trade
  - Driven by surplus production capacity, but constrained by availability of uncommittedshipping
- **Competitive pricing: U.S.**

U.S. LNG Imports, 1970-2001

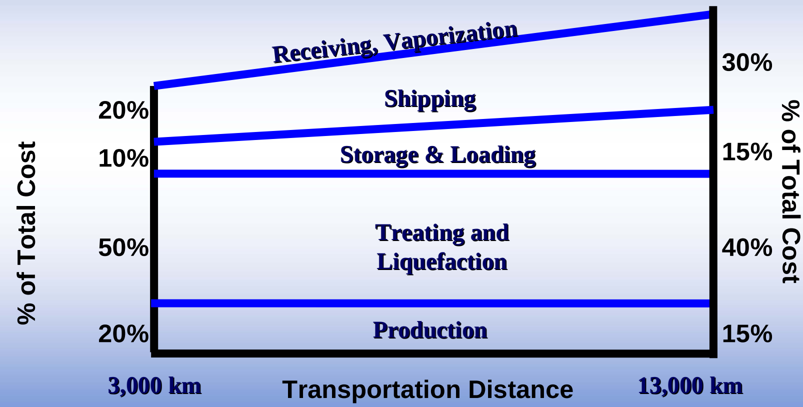


Why Does the U.S. Import LNG?

- Price competitiveness
  - Deep, liquid, and transparent gas market gives producers opportunity to market their LNG, provided they are prepared to be ‘price-takers
  - Availability of instruments to hedge price risk
- Surplus production capacity in export projects
  - U.S. has been the ‘Federal Reserve’ of LNG: Buyer of last resort
- Growth in demand, including summer peaking
- Capacity availability at 3 terminals, expansions planned
- In medium-term, domestic & Canadian supplies not expected to keep pace with growing demand
- EIA forecasts LNG imports could reach 700 BCF in 2005, 900-1600 BCF in 2010

New Terminals Announced in US, Canada, Mexico and the Bahamas

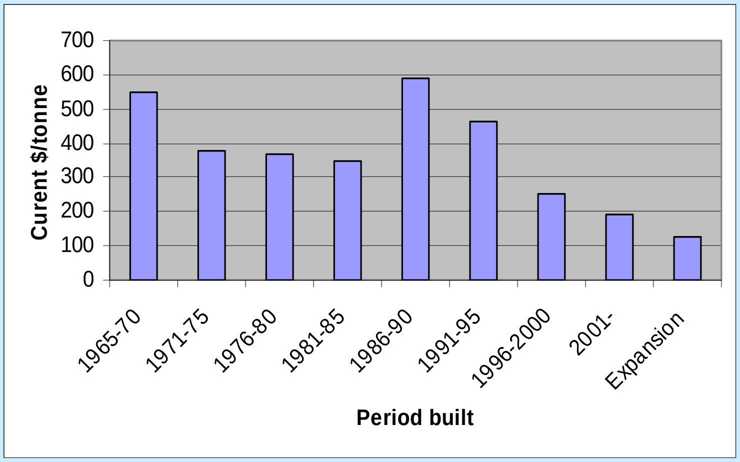
Relative Capital Costs of a LNG Project



Illustrative Costs for an 8 Mta Greenfield Project

	US$ (2001)	$/mmbtu
Gas Production	$1.0 - $2.0bn	0.50-1.00
Liquefaction	$1.2 - $1.8bn	0.80-1.20
Shipping	$1.0 - $2.0bn	0.50-1.00
Regasification	$0.5 - $1.0bn	0.30-0.60
Total	**$3.7 - $6.8bn**	**2.10-3.80**

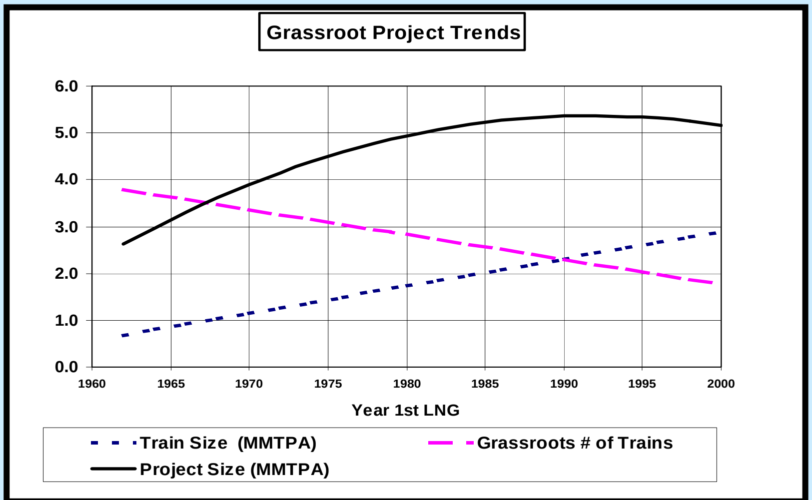
Estimated Capacity Costs of LNG Plants



Why Are Production Costs Lower?

- 35-50% reduction in production costs in past ten years because of:
  - Economies of scale: new trains in Qatar will be 7.5mta
  - Larger and fewer storage tanks
  - Improved technology, e.g., gas turbines,larger axial compressors, multiple compressors, turbines on single shaft
  - Improved engineering techniques
  - Smaller plants for specific projects
  - Integration of terminals with power plants
  - Competition (e.g., Trinidad)
  - Expansion projects
- Similar trends in receiving terminals and storage

Change in LNG Plant Nameplate Capacity



Source: KBR

LNG is Very Distance Sensitive

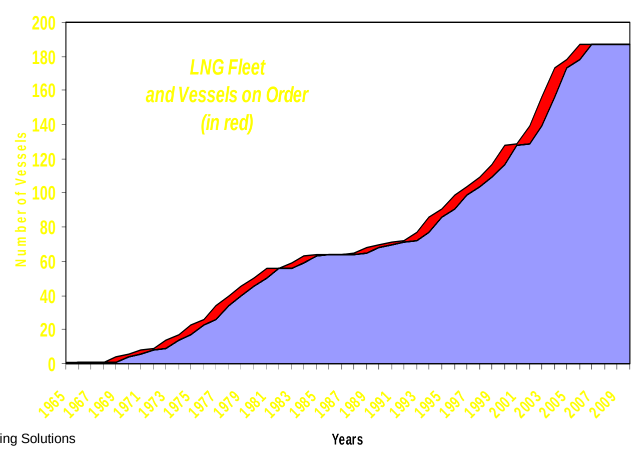
Transportation Costs to U.S., 2001

Source	$/Million Btu
Trinidad	0.47
Algeria	0.54
Nigeria	1.03
Oman	1.41
Australia	1.71
Qatar	1.88
Indonesia	2.21
Abu Dhabi	2.62

LNG Shipping

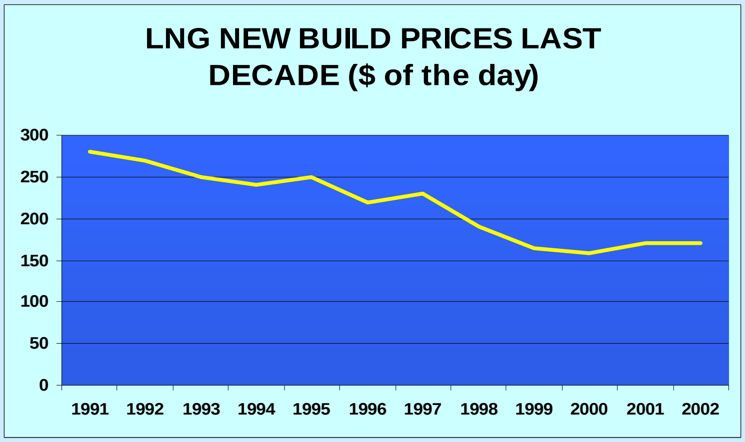
- Purpose-built, mature technology
- 132 ships in current fleet, record 61 ships on order
- Most ships dedicated to projects
- Very conservative industry:
  - Still use steam turbine
  - 50%-90% of fuel comes from boil-off gas
  - No fleet sharing, tram-line route
  - Ageing fleet
  - Slow increase in size
  - Reluctant to adopt new technology

Fleet Growth



LNG Shipping Solutions

LNG Ship Pricing



Changes in Shipping

- More ships being built at more shipyards
- At last, a little technical innovation (diesel engine)
- Larger ships (138,000 to 150,000 cu m)
- More players: BP, Shell, Japanese utilities, LPG operators
- First speculative ships
- Slow emergence of more flexible arrangements, including freedom of destination
- May result in changes to organization of shipping

Potential Constraints on LNG

- Sustained period of low oil prices could postpone development of high-cost sources of gas supply
- Economic downturn in gas-using countries
- Competition with pipelines
- Asia: Deregulation causing confusion about demand, intensifying gas-on-gas and interfuel competition
- New markets (India): political economic, regulatory risks,
- U.S.: Potential obstacles: public opposition, concerns over safety/security, regulatory and siting issues
  - Thus, companies look at offshore terminals, terminals in Mexico, El Paso's "Energy Bridge

Structural Changes in the LNG Industry

Old Model:

- LNG has been very conservative industry: developed slowly over 40 years, reluctant to change
- Exclusive "club" of few players
- 20-year contract with rigid take-or-pay provisions, oil-based pricing, little flexibility

New Model:

- More participants means diminution of "club" mentality
- Around 200 mta of new capacity announced or planned
- Competition for markets intense
- Buyers demanding and receiving more flexibility in contract terms

- Prospects for continued growth of global LNG industry are good

ADVANCES IN EXXONMOBIL's AGC-21 GAS-TO-LIQUIDS TECHNOLOGY

J. W. Johnson, R. A. Fiato,
L. L. Ansell and C. W. Quinlan

ExxonMobil Research and Engineering Company
Annandale, New Jersey USA 08801

ABSTRACT.

Conversion of natural gas to liquids (GTL) utilizing Fischer-Tropsch (FT) hydrocarbon synthesis technology is an attractive option to bring static gas resources to market. Since 1981, ExxonMobil has played a leading role in this area, with $450M invested in research and development of its proprietary process, Advanced Gas Conversion for the 21st Century (AGC-21). ExxonMobil has pioneered the development of new high performance catalysts and reactor technology for synthesis gas generation and conversion, and recently introduced industry leading upgrading technololgy to produce various fuel, lubricant and specialty products that can be tailored to specific business needs. This state-of-the-art GTL technology provides an important commercial option for utilization of stranded natural gas located around the world. Continuing research at ExxonMobil is leading to additional technology improvements that will further reduce the cost of producing liquids from natural gas. This article discusses recent advances in ExxonMobil's AGC-21 technology achieved as a result of an ongoing, comprehensive research, development and engineering program.

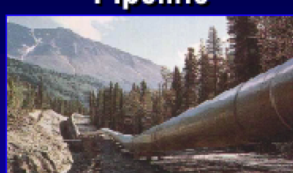
ADVANCES IN AGC-21 GAS-TO-LIQUIDS TECHNOLOGY

J. W. Johnson, L. L. Ansell, R. A. Fiato, and C. W. Quinlan
ExxonMobil Research & Engineering Company
October 30, 2002

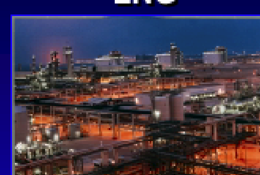
ExxonMobil

OPTIONS FOR TAKING GAS-TO-MARKET

Pipeline



LNG



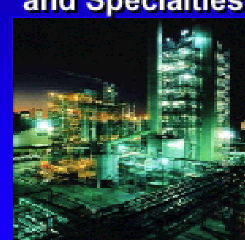
Gas Production

Commercialize Gas Through Chemical Technology

Gas to Gasoline

Ultra-Clean Gasoline/Petrochemicals
- High Octane, Zero Sulfur & Nitrogen

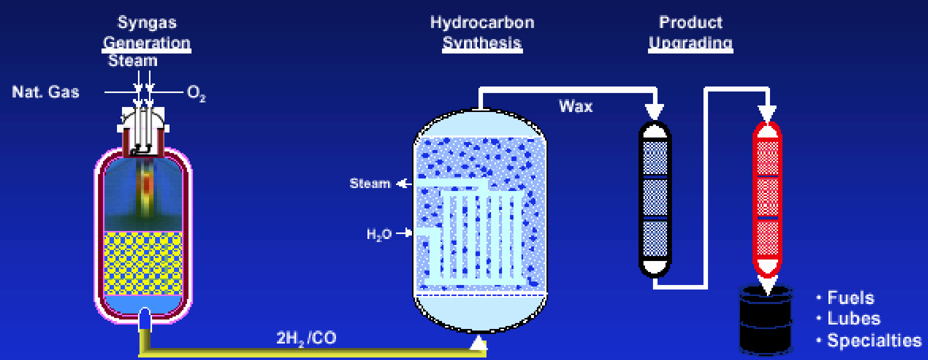
Gas to Fuels, Lubes and Specialties



Ultra-Clean, High-Cetane Diesel
- Zero Sulfur, nitrogen, and aromatics

ADVANCED GAS CONVERSION TECHNOLOGY AGC-21

- Industry-Leading Technology For Converting Natural Gas To High Value Liquids

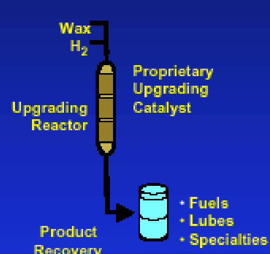


- Unique Hydrocarbon Synthesis and Product Upgrading At Heart Of Process
- Strong IP Position Covering Catalyst, Process, And Product Compositions
- Discussions Now Underway For A World Class GTL Plant in Qatar

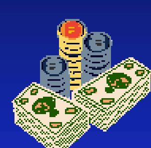
GAS-TO-LIQUIDS

- Given the right conditions GTL can provide an economic means of commercializing remote gas
- A viable world-scale GTL projects needs :

A Premier Resource



High Added Value Technology



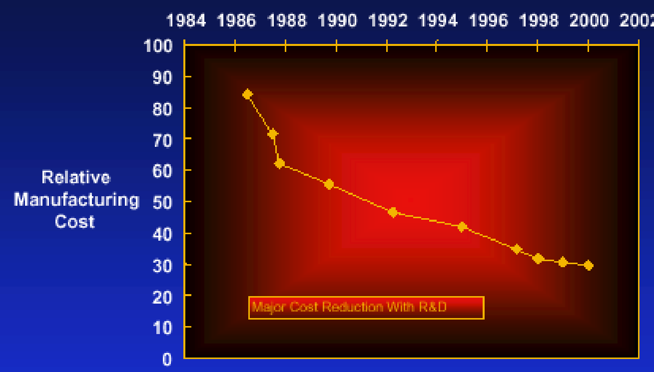
Financial Strength

Large Project Execution Capability

Marketing Capabilities

STEADY PROGRESS IN AGC-21

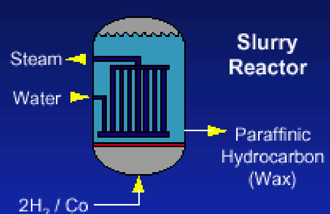
- Technology Has Reduced GTL Production Costs Significantly
- GTL Utilizes Low Value Feedstock
  - Large volumes of natural gas remote to pipeline markets
  - Remote gas valued below crude parity

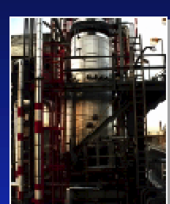


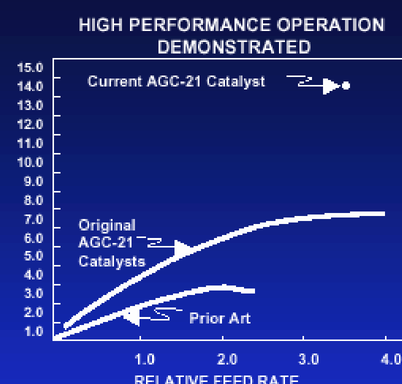
- Nature Of GTL Products Provide Opportunity For Improved Margins

CONVERT SYNGAS TO WAXY HYDROCARBONS

Proprietary Reactor Design



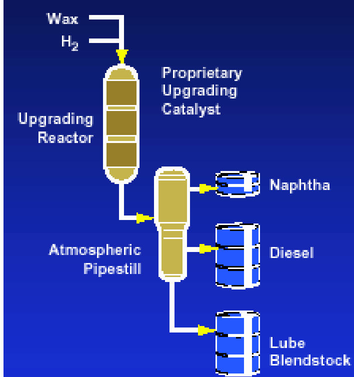




- Converts synthesis gas into long straight-chain hydrocarbons (wax)
- Proprietary slurry reactor is an enabling technology for large economies of scale
- Isothermal reactor enables high selectivity
- Integrates heat removal with HCS reaction

- Slurry Productivity Over Four Times Higher Than Prior Art
- Major Improvement Achieved by Controlling Interplay of –
  - →Three Phase Hydrodynamics
  - →Process Conditions
  - →Catalyst Properties

UPGRADE WAX TO HIGH-VALUE ULTRA-CLEAN PRODUCTS



Wax Upgrading Reactor
- Converts wax to high quality naphtha, diesel, and lubestock
- Utilizes ExxonMobil industry leading MSDW upgrading catalysts
- Builds on extensive ExxonMobil refining experience

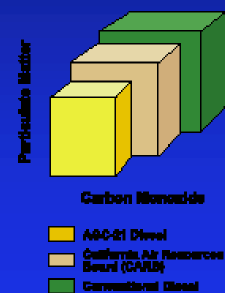
AGC-21 Naphtha
- Increases steam cracker olefin yield by 17%
- Potential fuel for advanced power systems

AGC-21 Diesel
- Zero sulfur, nitrogen and heavy metals
- Meets / exceeds all existing environmental specifications

AGC-21 Lubes
- High quality synthetic lube basestock
- Zero sulfur, highly biodegradable
- Well suited for next generation motor oils
- Based on extensive dewaxing process and catalyst development experience

Fuel/Engine Testing Facility

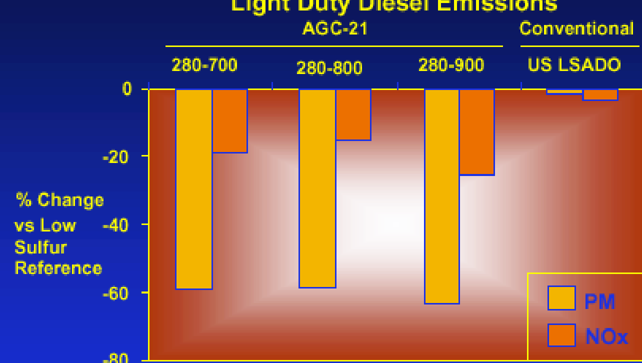
Relative Engine Emission



AGC-21 DIESEL CLEANER IN ENGINE TESTS

Fuel/Engine Testing Facility

Light Duty Diesel Emissions

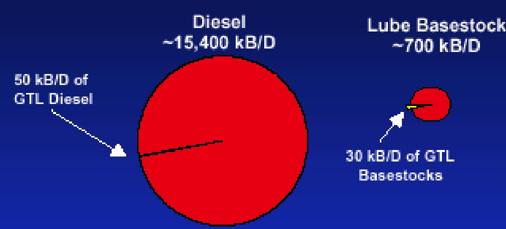


AGC-21 Diesel
- Zero sulfur, nitrogen and heavy metals
- Meets or exceeds all existing environmental specifications

GTL FUELS AND LUBES MARKETING CONSIDERATIONS

- GTL products have unique characteristics -- especially in the form of high quality Lubes Basestocks
- Market premiums for fuels and lubes may be possible in short term or in small niche markets but unlikely to be sustainable
- GTL plants will have the capability of producing large volumes of high quality products
- Significant presence and extensive marketing capabilities are critical to successful product disposition

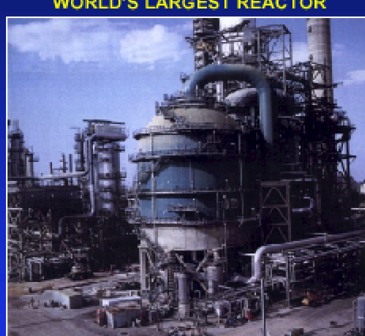
RELATIVE MARKET SIZE



LARGE PROJECT EXECUTION

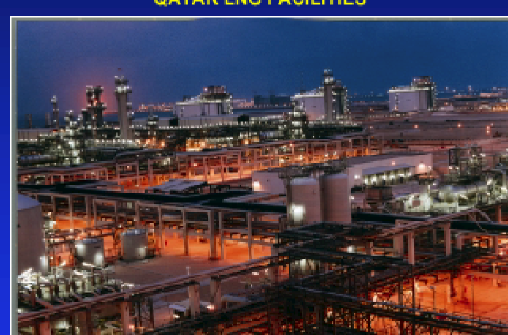
- By any measure world-scale GTL developments are very large projects
- Ability to meet budget and schedule will be critical to host governments

AMUAY FLEXICOKER
WORLD'S LARGEST REACTOR



70 Ft Diameter Gasifier
Unique Fluid Solids Processing

QATAR LNG FACILITIES



4.7 Million Ton Per Year Trains
Planned for Future Expansion

SUMMARY

- ExxonMobil AGC-21 – A Proprietary State-of-the-Art Process for High Quality Diesel and Lube Basestock Production from Natural Gas
- Key Features Include Patented Slurry Phase FT Synthesis Coupled with Industry Leading MSDW Family of Upgrading Catalysts and Process Technologies
- Integrated Process Provides Efficient Route for World Scale Production of Group III Basestocks
- Now Ready for Commercial Implementation

Gas Hydrate Transportation Technology Development in the UK

Dr. Mark Taylor

Advantica Technologies, Ltd.

ABSTRACT

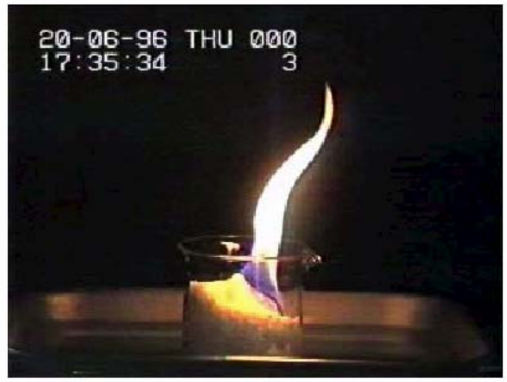
Disposal of, or monetizing associated gas and government requirements to eliminate flaring has received increased interest in response to environmental requirements for technological solutions. Hydrate technology development by Advantica has focused on using gas hydrates as a low CAPEX solution to managing associated gas in regions lacking in gas infrastructure and/or market. It can be small-scale, modular and particularly appropriate for associated-gas applications.

A comprehensive understanding of hydrate behaviour is necessary to understand the technology for transoceanic gas transportation. This paper discusses the results of laboratory and pilot scale studies on the stability and composition of hydrates produced in a continuous stirred tank reactor and the implications of these results on the process design and overall economics. The paper describes the 'BG hydrates dry and slurry production processes' and their integration into systems for delivering gas for small to medium scale power projects in regions of the world that lack gas pipeline infrastructure. The challenges to be met before the technology can be commercialised are described and an outline for a way forward presented.

ADVANTICA

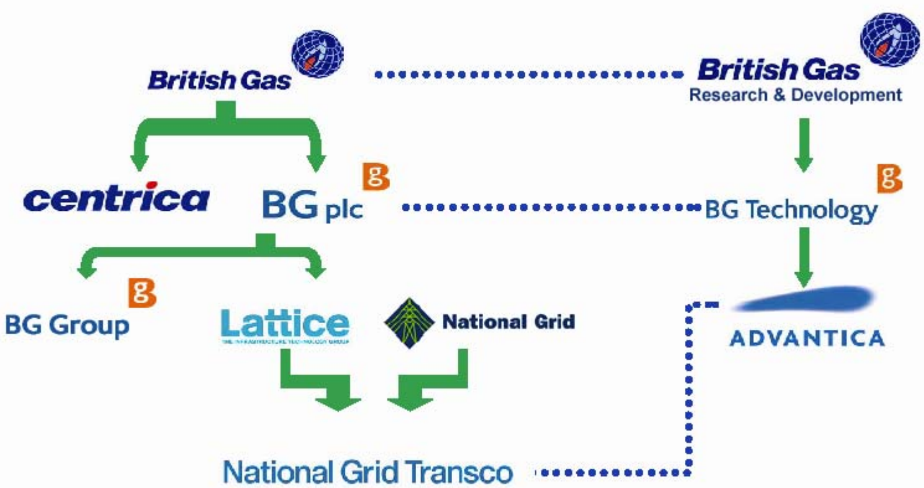
The BG Hydrate Project Technology Development

Mark Taylor
30th October 2002
Washington DC



The British Gas Heritage

ADVANTICA



Content

ADVANTICA

- BG Hydrate transportation processes
- Dewatering Technologies
- Hydrate Properties
- Shipping
- Economics
- Commercialisation

Hydrate Equilibrium Curves

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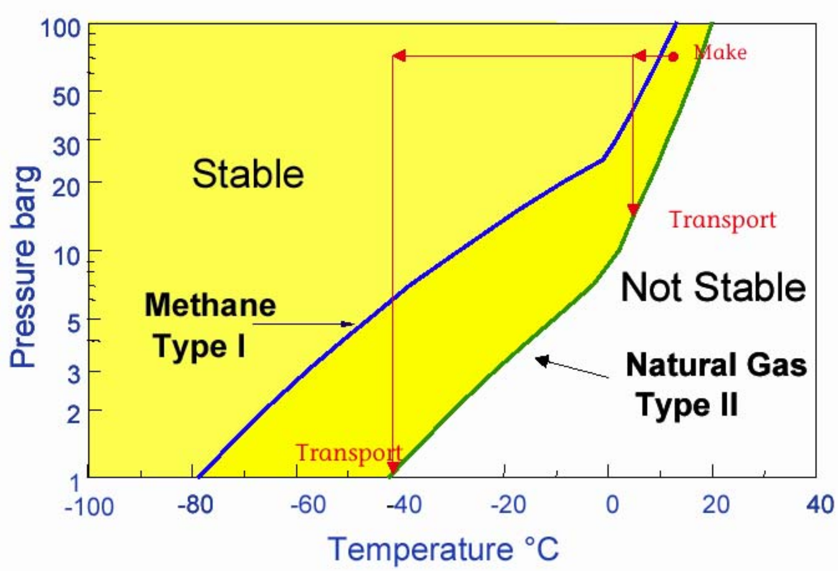
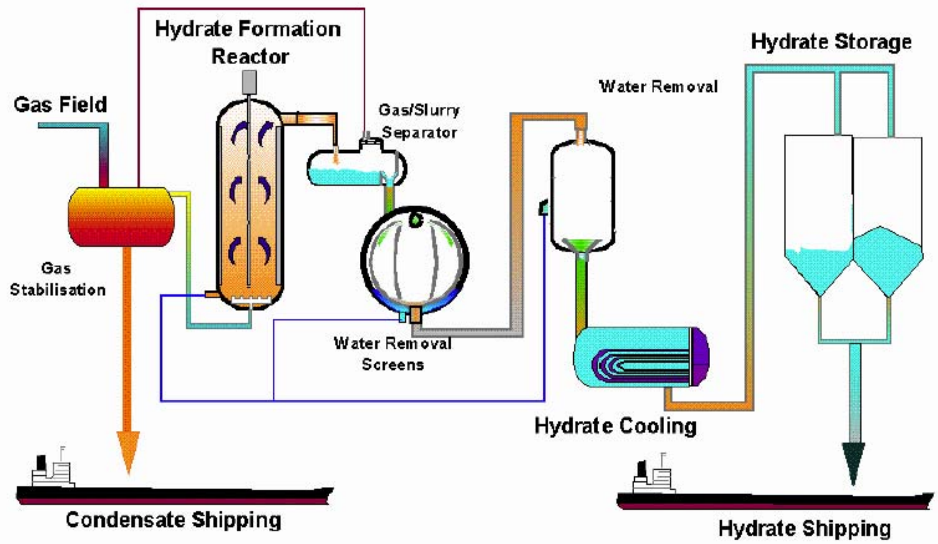


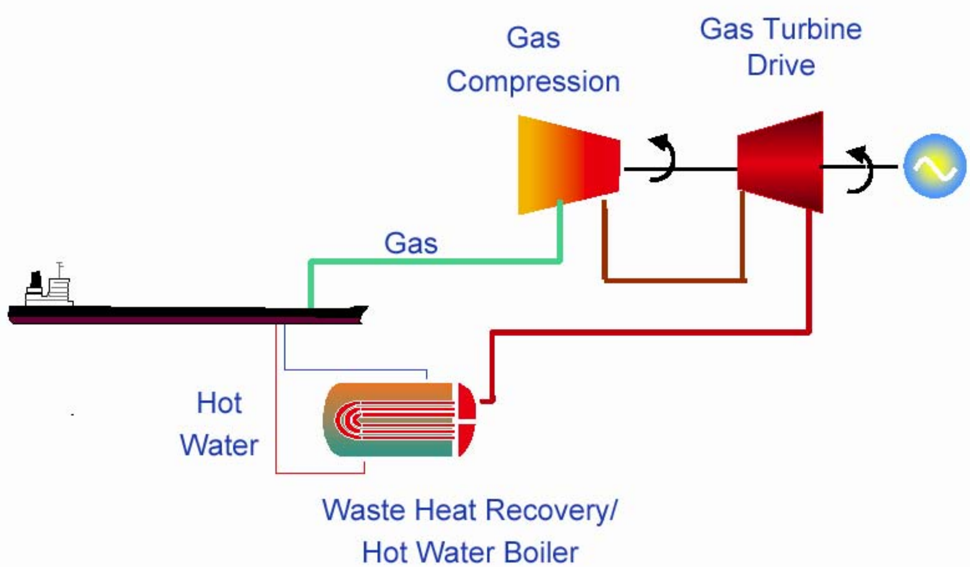
The BG Gas Hydrate Transportation Process

ADVANTICA



The BG Gas Hydrate Transportation Process

ADVANTICA



Slurry hydrate gas transportation system

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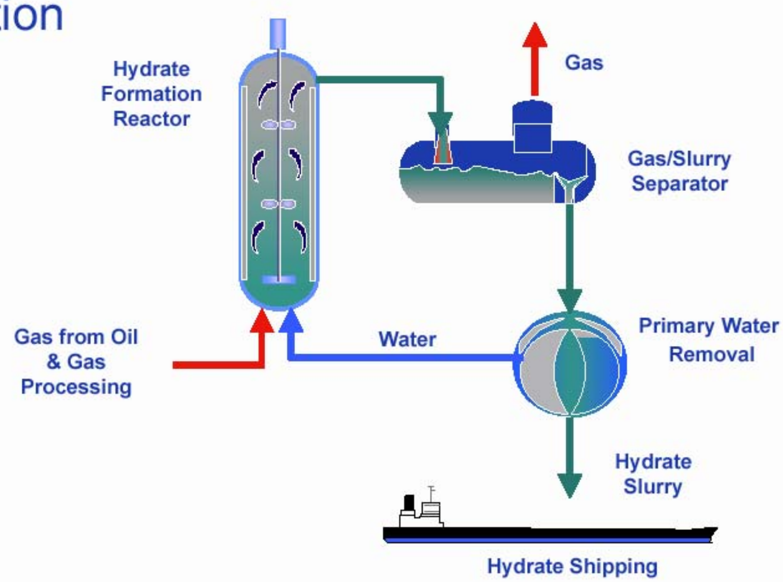
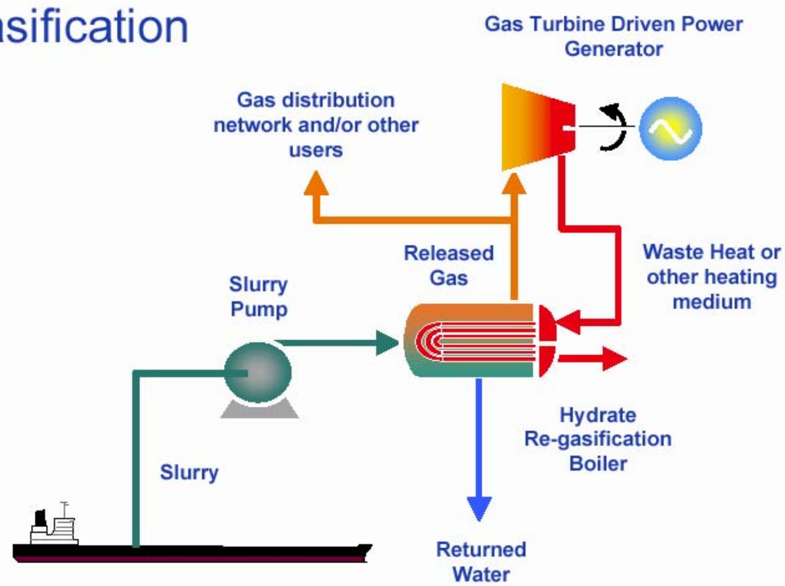
Production



Slurry hydrate gas transportation system

ADVANTICA

Gasification



Advantica's Hydrate laboratory

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Laboratory Hydrate Production

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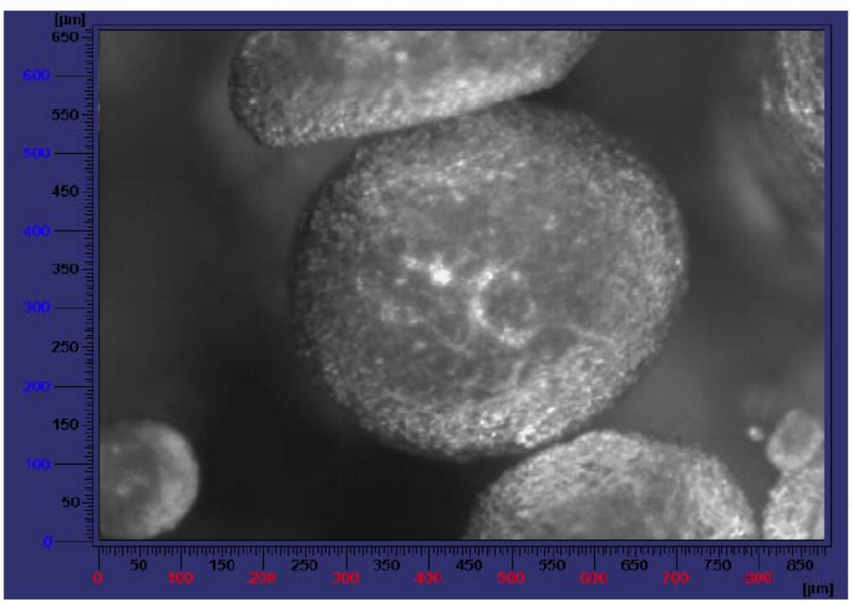

Hydrate dewatering technologies

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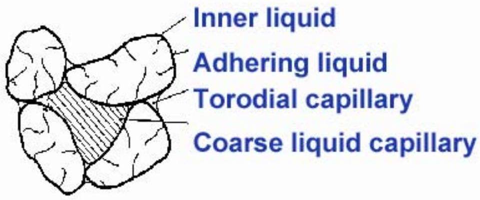

- Screens
- Hydrocyclones
- Sedimentation
- Centrifuges

Screens

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Simulated hydrate dewatering

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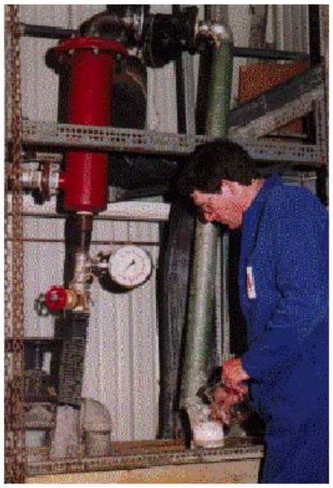

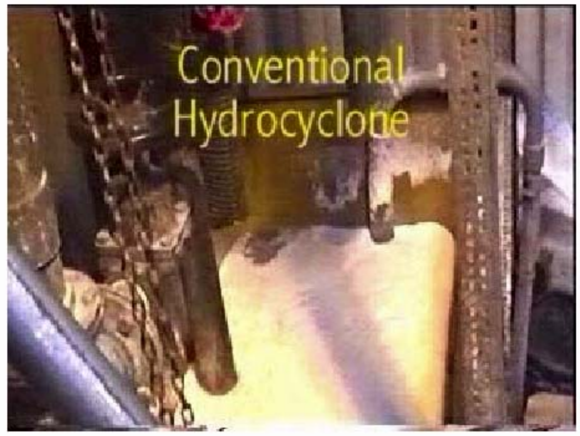

Ice Silo

ADVANTICA

Centrifuge Development

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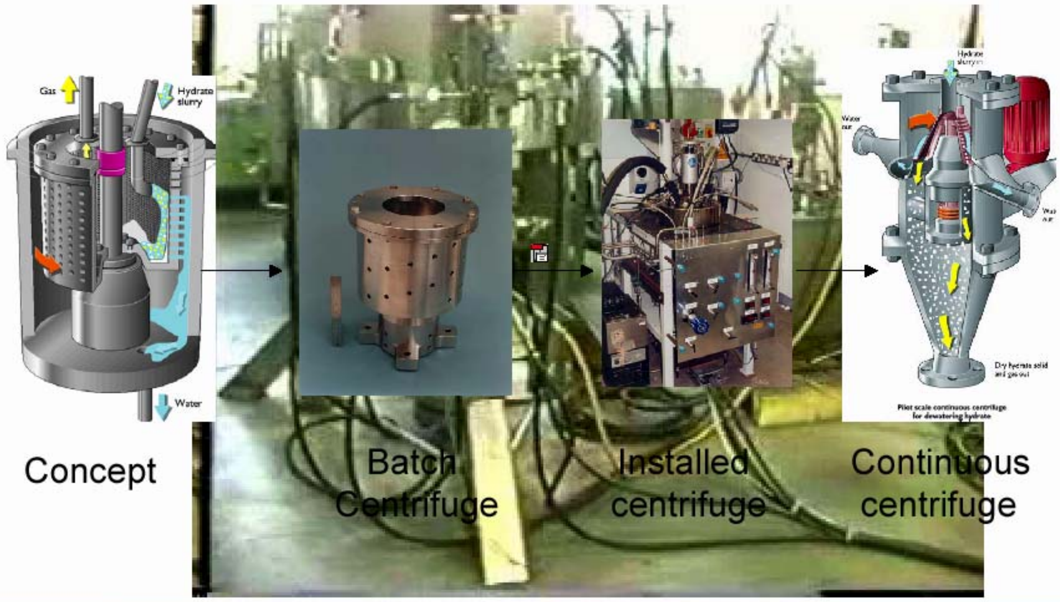
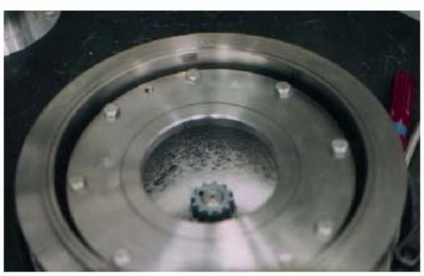


Hydrate production

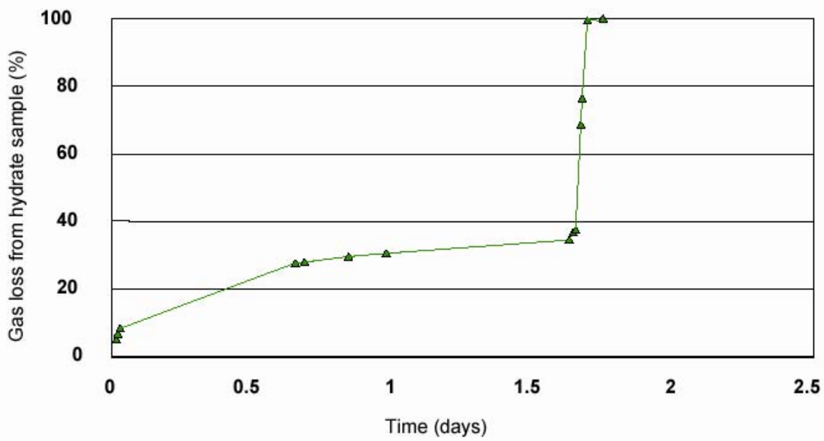
ADVANTICA



Blue dye permeability test

Methane hydrate storage

ADVANTICA



Final volume factor 113 m³/tonne
sample stored at -18°C

Hydrate decomposition trials

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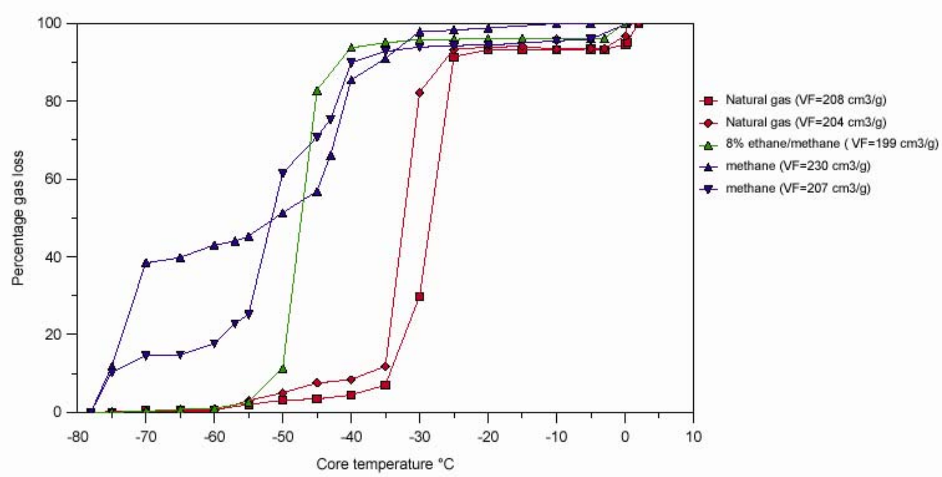

natural gas composition
91.6% methane 6.6% Ethane and 2.3% propane

Electron micrographs of methane hydrate

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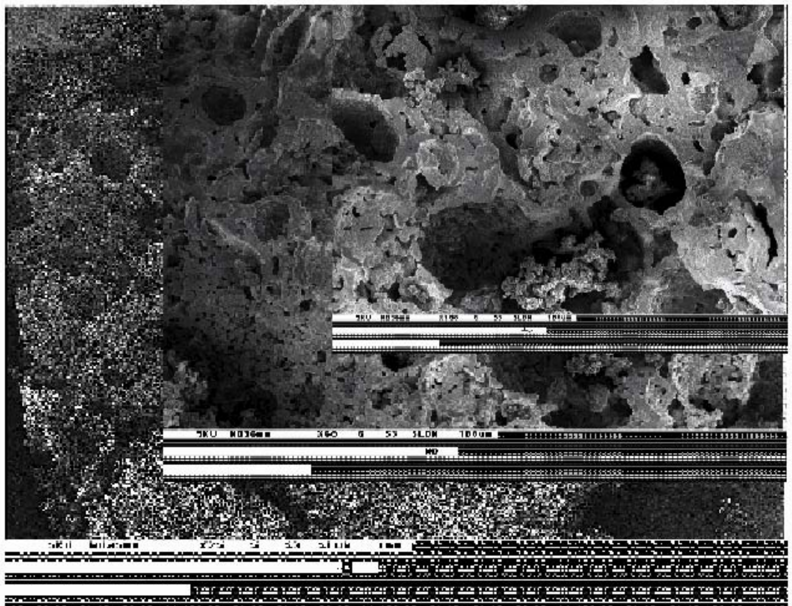

Hydrate Reactor Modelling

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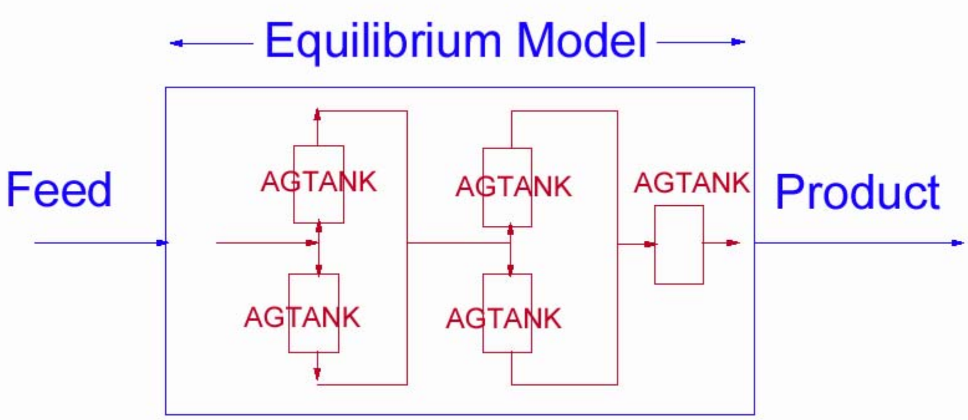

Hydrate pilot plant

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Lab Synthesis experiments

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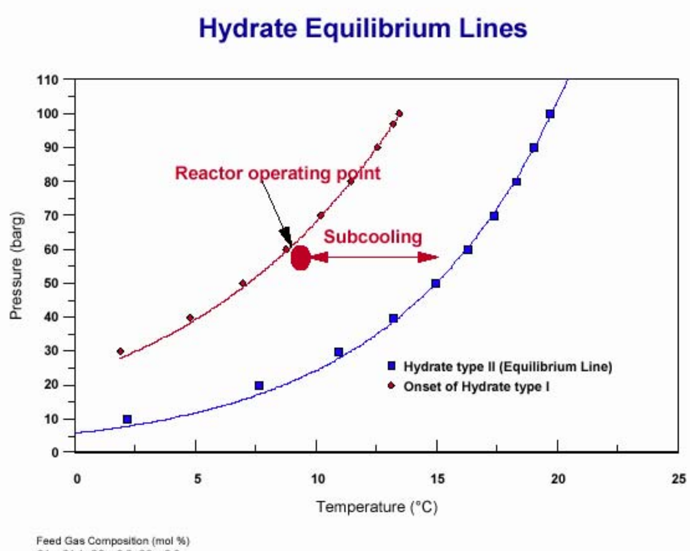

Model Predictions

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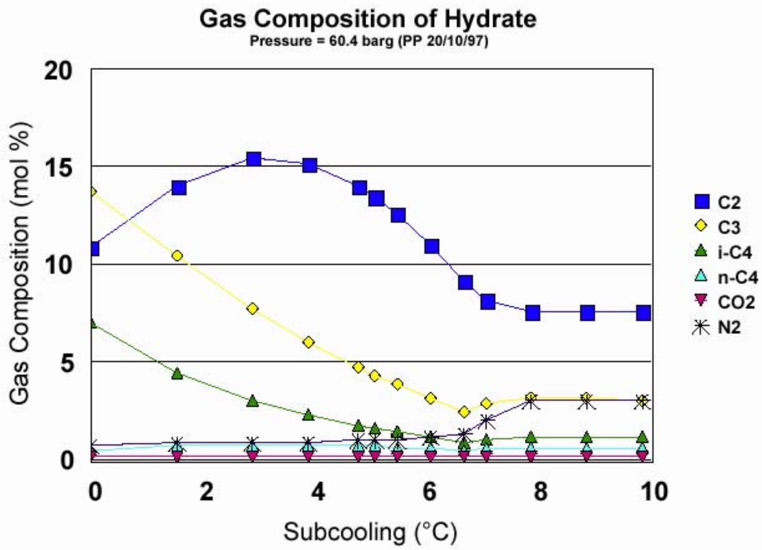
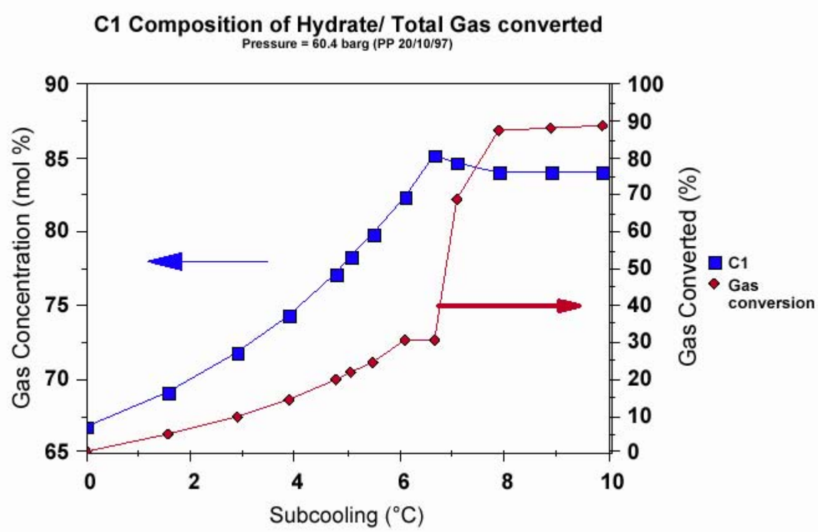


Model Predictions

ADVANTICA



Pilot Plant Results

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	Predicted at equilibrium	Predict at outlet condition	Predicted at inlet condition	Measured from pilot plant
Temp (°C)	14.89	9.4	8.2	9.4
Subcooling (°C)	0	5.49	6.69	
C1	66.83	79.89	85.22	79.13
C2	10.88	12.67	9.22	11.72
C3	13.71	3.92	2.57	4.26
iC4	7.02	1.49	0.97	0.41
nC4	0.57	0.71	0.52	1.2
iC5	0.00	0.00	0.00	0.03
nC5	0.00	0.00	0.00	0.01
C6+	0.00	0.00	0.00	0.03
CO2	0.16	0.24	0.27	0.89
N2	0.82	1.08	1.31	2.33
% gas converted	0	24.56	30.43	

	Equilibrium	Predicted for reactor exit	measured from pilot plant
Temp (°C)	18.01	14.4	14.4
Subcooling (°C)	0	3.61	
C1	66.00	72.28	74.11
C2	11.52	15.18	14.58
C3	14.09	6.40	5.36
iC4	5.14	1.90	1.25
nC4	1.06	1.67	1.17
iC5	0.00	0.00	0.033
nC5	0.00	0.00	0.002
C6+	0.00	0.00	0.032
CO2	0.16	0.20	1.45
N2	2.02	2.38	2.02
% gas converted	0	18.87	
C2:C1	0.1745	0.2100	0.1967
C3:C1	0.2135	0.0885	0.0723
C2:C1 (hydrate/feed)	2.972	3.577	3.351
C3:C1 (hydrate/feed)	12.782	5.299	4.329

Shipping Concepts

ADVANTICA

PickUpCat barge concept

Conventional tug/barge system

Panamax Type Bulker

LASH Barge Carriers

Heat Transfer in Ship hold

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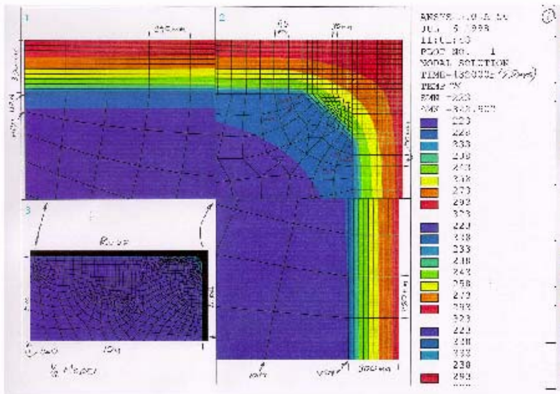
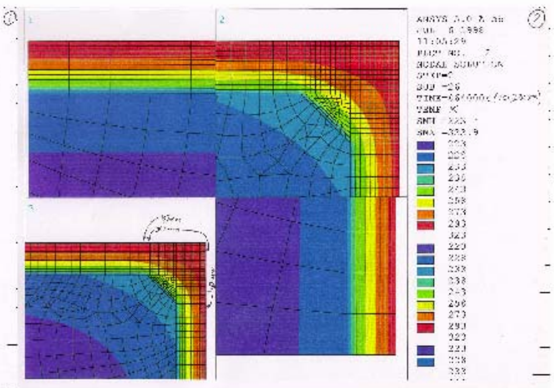


5 Days



10 Days

Hydrate Cost Model

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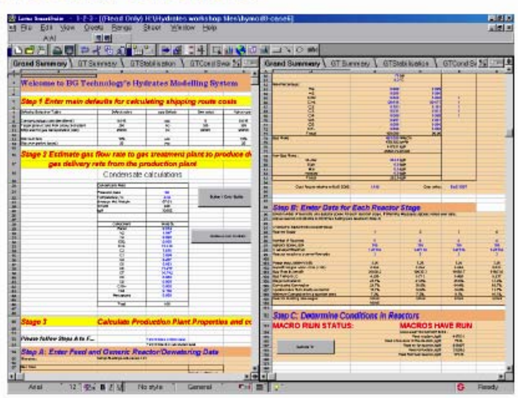
Cost Model calculates costs for

- Dry Process – Onshore (and Offshore)
- Slurry Process – Onshore and Offshore

Key Variables

- Plant Capacity
- Shipping Distance
- Process Design
- Operating Cost



Transportation cost dry process 1997-8

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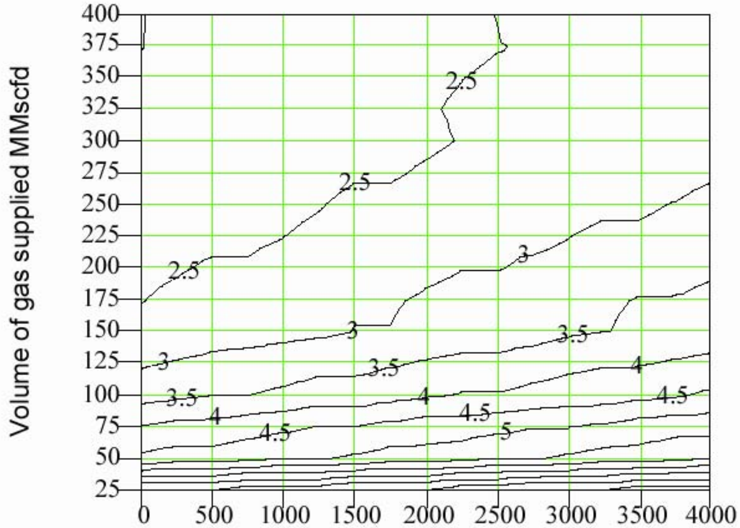


Voyage distance km one way

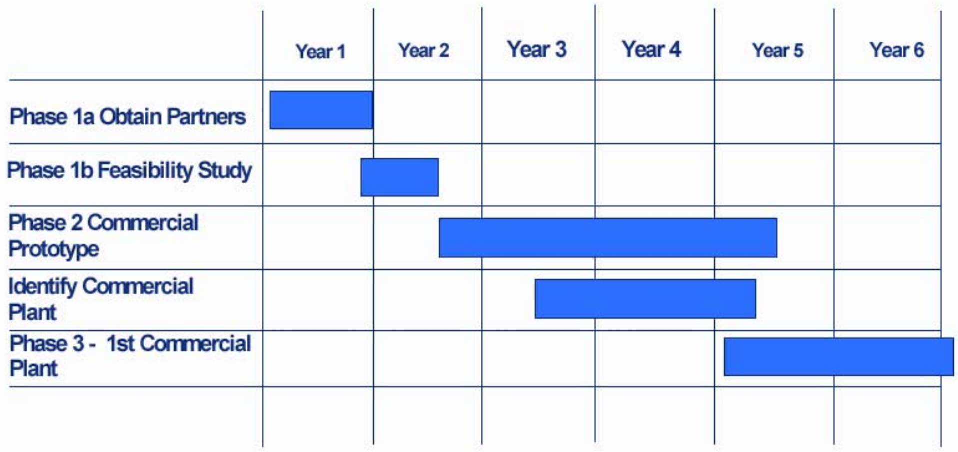
IP - Patents

ADVANTICA

Subject Country	Multi reactors Patent	 Status	Hydrate Storage Patent	 Status	Slurry Transportation Patent	 Status
United Kingdom	9626665.5	granted	0006113.5	to be granted	0028455.4	to be granted
Argentina	970100170	to be granted	101335	to be granted	000106176	to be granted
Algeria	8/97	to be granted	000045	to be granted		
Egypt	44/97	granted	352/2000	applied for		
Indonesia	970129	granted	W00200102062	to be granted		
India	2320/mas/96	to be granted	2001/01304	to be granted		
Libya	441/97	to be granted	3009/2000	to be granted	3079/2001	to be granted
Malaysia	PI97000189	to be granted	20001132	to be granted	PI20005495	to be granted
Nambia	97/0002	granted	0018/2000	granted	2000/0061	granted
Philippines	55220	granted	2000-00691	to be granted	1-2000-03244	to be granted
Pakistan	32/97	to be granted	257/2000	to be granted	1076/2000	applied for
Thailand	35088	to be granted	056346	to be granted	061747	to be granted
Tunisia	97013	to be granted	00059	to be granted	00.224	to be granted
Taiwan	86100557	granted	89107356	to be granted		
Hong Kong			02100270.9	to be granted	1106388.6	to be granted
South Africa	0078/97	granted	2001/7672	applied for		
Australia	13865/97	granted	31806/00	to be granted		
Canada	2214373	granted	2368020	to be granted		
China	97190182.1	to be granted	00805477.9	to be granted		
Denmark	1007/97	applied for				
Japan	525764/1997	granted	606549/2000	to be granted	540298/2001	to be granted
Sri Lanka	11266	to be granted				
Mexico	977070	to be granted	009597	to be granted		
New Zealand	325367	granted				
African Intellectual Property Org	PV70080	granted	1200100241	to be granted		
Poland	322305	to be granted	P-3505689	to be granted		
Turkey	57385/97	to be granted	2798/21	applied for		
Trinidad	970112	granted		applied for		
United States	08/913412	granted	09/937338	to be granted		applied for
Vietnam	S19970896	granted				
European Patent Convention	97900274.8	granted	00909523.3	to be granted	00977677.4	to be granted
Angola	98109477.6	to be granted			1209	to be granted
Nigeria					477/2000	granted
West Bank					58	to be granted
GAZA					54	granted
Patent Coorporation Treaty	GB97/00021	dormant	GB00/00942	to be granted	GB00/04432	Query

Development Schedule

ADVANTICA

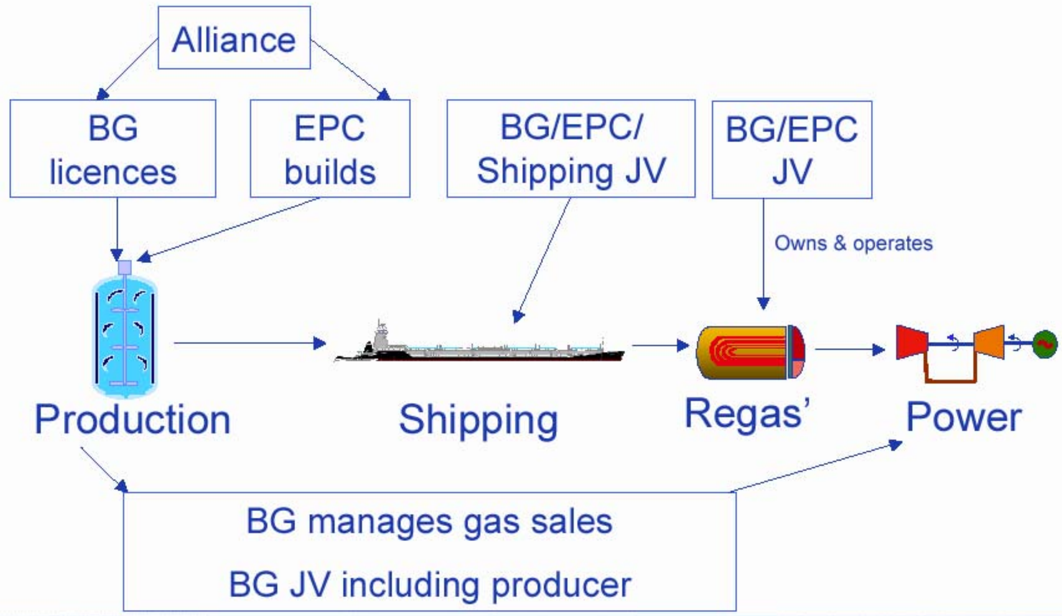


Business Model

ADVANTICA

- **BG not fixed on any single business model**
- **Several potential business models**
- **Whole chain**
  - JV builds, owns, operates plant; takes the gas; ships; builds & owns regasification plant, sells gas.
- **Licences & build**
  - JV licences and builds plant or;
  - BG licences & EPC builds
- **Hybrids in between**

The Proposed Model

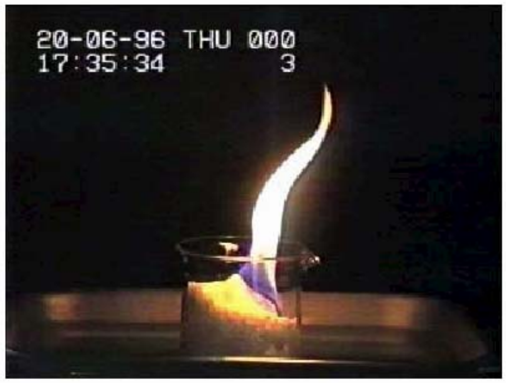


Next Steps

- **Technology proof**
- **Cost/shipping study**
- **Plan commercialisation route (approach to producers)**
- **Market studies**
- **Funding for commercial prototype**

ADVANTICA

Thank You for Listening



A Challenge to High-rate Industrial Formation of Methane Hydrate and Continuous Dehydration of Gas Hydrate Slurry for Transportation and Storage System with Gas Hydrates

K. Yoshikawa[1], H. Nagayasu[1], S. Iwasaki[2], T. Kimura[2], T. Kawasaki[3], K. Yamada[3], K. Kikuchi[3], D. Terasaki[3], H. Narita[4], T. Ebinuma[4], T. Uchida[4], S. Takeya[4], T. Hondo[5], Y. Suehiro[6], K. Bando[6], M. Ihara[6], T. Okui[6]

[1]Takasago R&D Center, Mitsubishi Heavy Industries Ltd.;
[2]Kobe Shipyard and machinery works, Mitsubishi Heavy Industries Ltd.;
[3]Tokyo Gas Co. Ltd.; [4]National Institute of Advanced Industrial Science and Technology; [5]Hokkaido University; [6]Technology Research Center, Japan National Oil Corporation

ABSTRACT

The natural gas has been focused as a countermeasure of the global warming. In order to develop marginal natural gas field in South East Asia, the technologies which supply with natural gas at low cost are trying to be developed in these days.

As necessities of natural gas transportation with gas hydrates (GH), we are investigating various technologies, such as basic properties, optimization of formation conditions, dehydration of GH slurries, and behavior of GH loaded. In this paper, we introduce experimental results of synthetic GH formation and dehydration of GH slurry for industrial use.

The GH formation is supposed to be a considerable part in the total cost of GH transportation chain. It is necessary to minimize the GH producing reactor by enlarging the contacting area between water and gas in order to reduce the capital cost of the GH production process. In this study we examined the water spray method for effective GH formation. Temperature, pressure and water droplet size were selected as parameters.

Formation rate was strongly accelerated by cooling. The rate was also accelerated pressurization. From these experimental results, it was suggested that formation rate simply depended on temperature difference from the corresponding equilibrium point.It was also suggested that kinetic effect of salts was stronger than thermodynamic one. Hydrate formation was apparently decelerated by synthetic standard seawater whereas equilibrium lines were not obviously affected under the conditions.

The water content in GH has an effect on the cost of GH transportation process. It is necessary to dehydrate GH slurry effectively in order to reduce the capital and running cost of the GH production process. In this study we employed the centrifugal filtration and screw press methods to continuous dehydration of GH slurry. We used GH slurry of alternative freon gas because it is easy to be produced and handled.

The main results of formation rate and dehydration are briefly summarized below,

1) Temperature difference between the equilibrium point and operation condition is one of the obvious driving forces to promote the GH production rates.
2) Production rate also depends on the contacting area between water and natural gas.
3) Optimization of the droplet size and water flow rate is required for acceleration of GH production.
4) Salts decelerate formation, more than thermodynamic inhibition.
5) Both centrifugal filtration and screw press methods are able to apply to the dehydration of GH slurry.
6) The water content of GH after dehydration used by centrifugal filtration method becomes 30～40wt% from initial 90wt%.

7) The water content of GH after dehydration used by screw press method becomes 20～30wt% from initial 90wt%.
8) The screw press method is superior to the centrifugal filtration method for the dehydration of GH slurry.
9) To contact with natural gas to the dehydrated GH, we got 10wt% water content GH.

Reference

(1) S. Iwasaki, T. Kimura, K. Yoshikawa, H. Nagayasu: Proc. of 4^{th} Int. Conf. on Gas Hydrates, Yokohama, May 19-23, Japan, 978-981, (2002)

(2) T. kimura, S. Iwasaki, K. Yoshikawa, H. Nagayasu: Proc. of 4^{th} Int. Conf. on Gas Hydrates, Yokohama, May 19-23, Japan, 19-23, 1003-1006, (2002)

(3) K. Miyata, T. Okui, H. Hirayama, M. Ihara, K. Yoshikawa, H. Nagayasu, S. Iwasaki, T. Kimura, T. Kawasaki, K. Kikuchi and D. Terasaki: Proc. of 4^{th} Int. Conf. on Gas Hydrates, Yokohama, May 19-23, Japan, 19-23, 1031-1035, (2002)

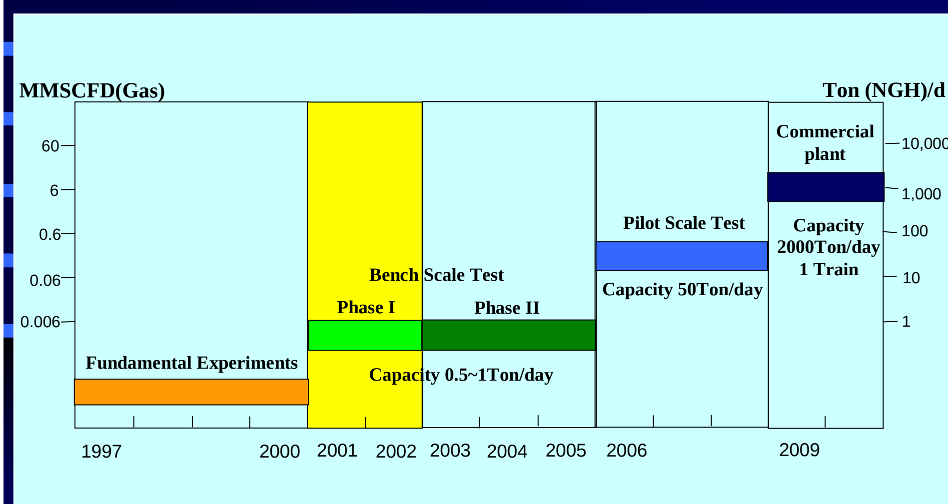
A Challenge to High-rate Industrial Formation of Methane Hydrate and Continuous Dehydration of Gas Hydrate Slurry for Gas Transportation and Storage System with Gas Hydrates

Oct. 30, 2002

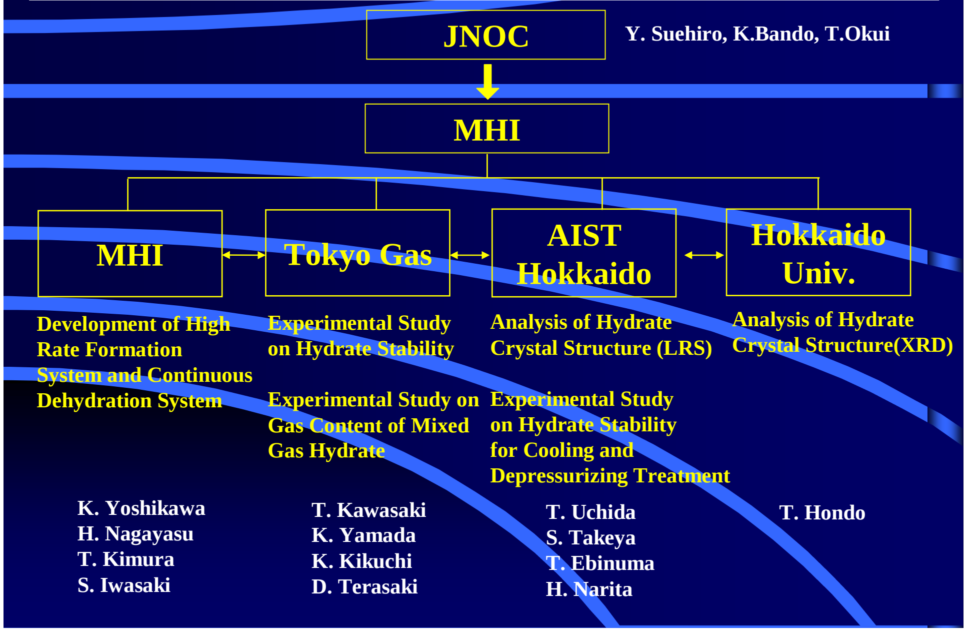
Mitsubishi Heavy Industries, Ltd.
Takasago R&D Center
Kozo Yoshikawa

Research & Development Schedule

MITSUBISHI HEAVY INDUSTRIES, LTD.



Organization (2001~)

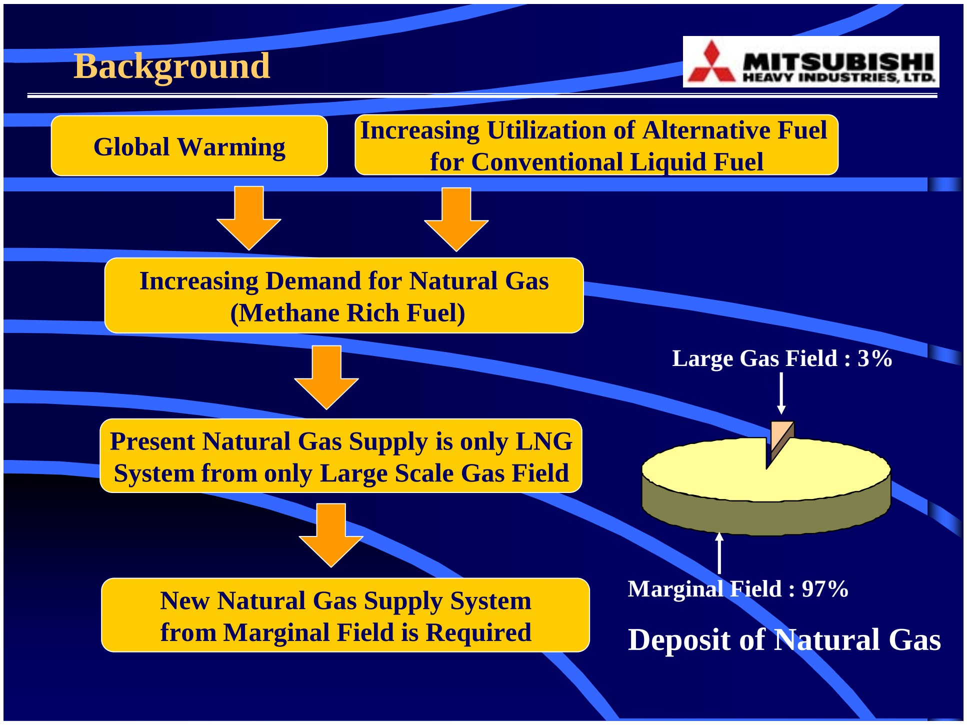


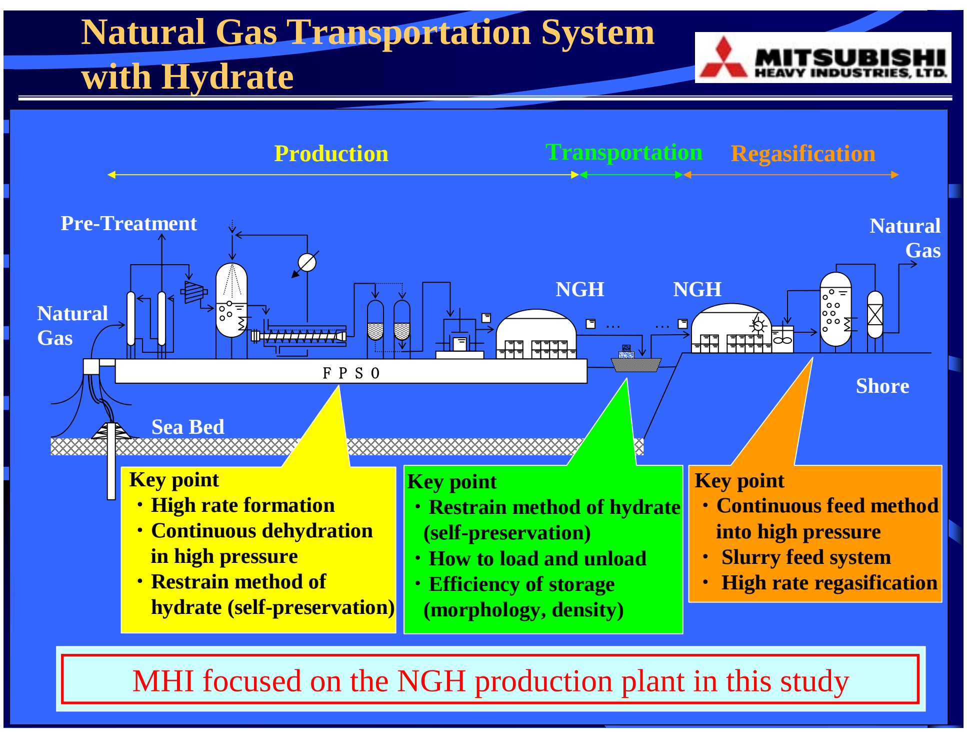
Outline

1. Concept of natural gas transportation and storage system using natural gas hydrate

2. Laboratory scale experiments by methane gas(~2000)

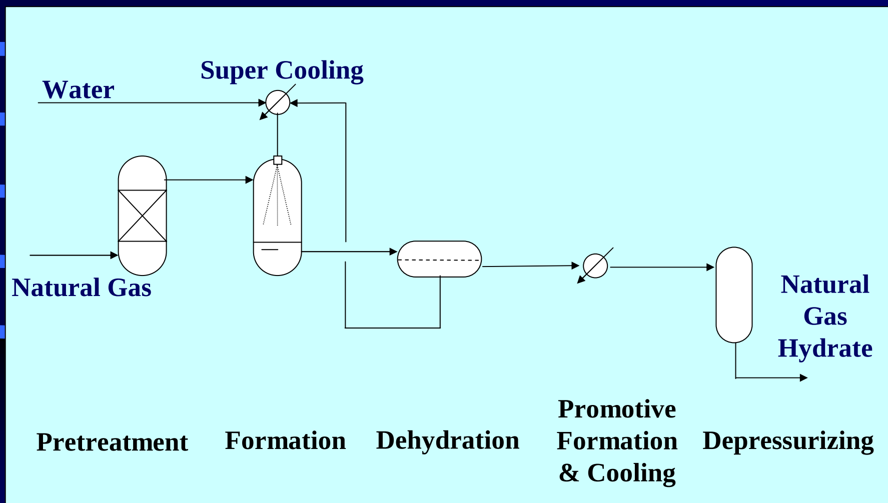
3. Bench scale test (1Ton/day) by R143a hydrate (2001~)


Background
MITSUBISHI HEAVY INDUSTRIES, LTD.
Global Warming
Increasing Utilization of Alternative Fuel for Conventional Liquid Fuel
Increasing Demand for Natural Gas (Methane Rich Fuel)
Present Natural Gas Supply is only LNG System from only Large Scale Gas Field
New Natural Gas Supply System from Marginal Field is Required
Large Gas Field : 3%
Marginal Field : 97%
Deposit of Natural Gas


Natural Gas Transportation System with Hydrate
MITSUBISHI HEAVY INDUSTRIES, LTD.
Production
Transportation
Regasification
Pre-Treatment
Natural Gas
NGH
NGH
Natural Gas
F P S O
Sea Bed
Shore
Key point
・High rate formation
・Continuous dehydration in high pressure
・Restrain method of hydrate (self-preservation)
Key point
・Restrain method of hydrate (self-preservation)
・How to load and unload
・Efficiency of storage (morphology, density)
Key point
・Continuous feed method into high pressure
・Slurry feed system
・High rate regasification
MHI focused on the NGH production plant in this study

Conceptual Flow of Production Process

MITSUBISHI HEAVY INDUSTRIES, LTD.



Outline

MITSUBISHI HEAVY INDUSTRIES, LTD.

1. Concept of natural gas transportation and storage system using natural gas hydrate

2. Laboratory scale experiments by methane gas (~2000)

3. Bench scale test (1Ton/day) by R143a hydrate (2001~)

4. Video-show ?

Fundamental Experiment on Lab. Scale

MITSUBISHI HEAVY INDUSTRIES, LTD.

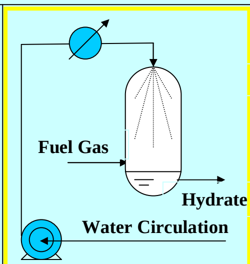
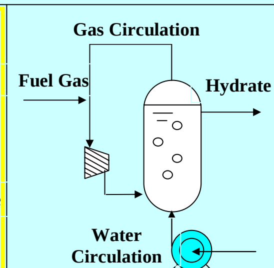
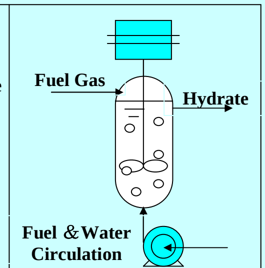
Formation, Dehydration and Characterization of Hydrate

(~2000)

- Hydrate formation
  - Determined a method of formation
  - Laboratory scale test
- Dehydration of hydrate slurry
  - Determined a method of dehydration
  - Laboratory scale test
- Additional formation to contact with gas and dehydrated methane hydrate in high pressure
- Measurement of the behavior of compressed methane hydrate in high pressure
- Measurement of physical properties of hydrates

Type of Gas Hydrate Formation System

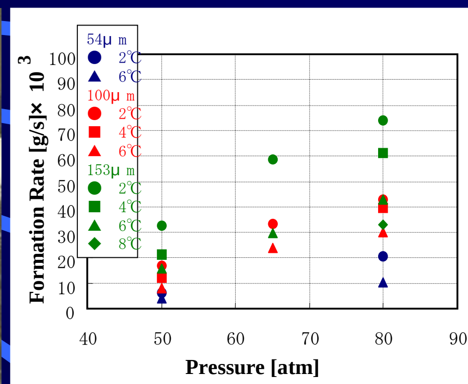
MITSUBISHI HEAVY INDUSTRIES, LTD.

System			
Type	Spraying Type	Bubbling Type	Mixing Type
Power	○	○	△
Simplification	○	△	△
Scale Up	◎	○	△

Hydrate Formation Test in Lab. Scale

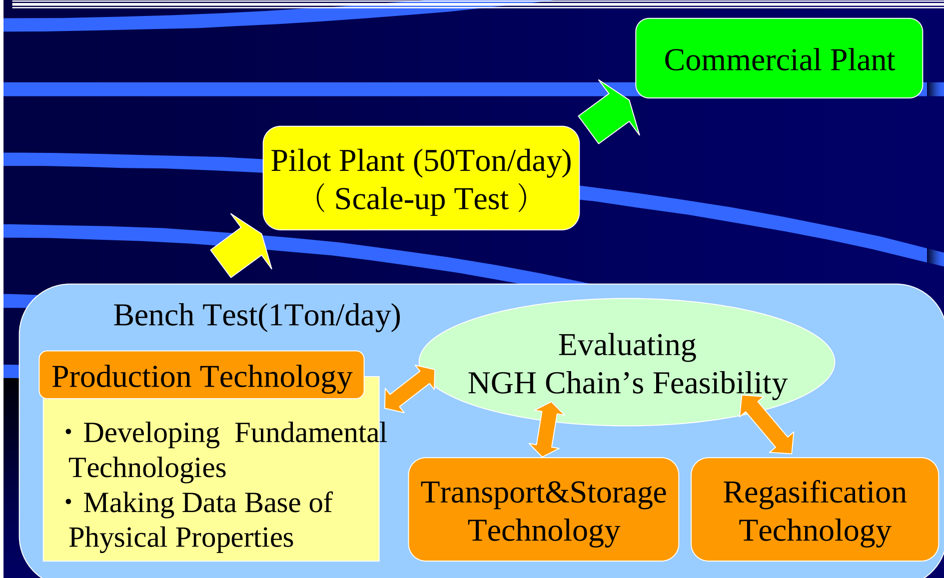
MITSUBISHI HEAVY INDUSTRIES, LTD.

Assessed a spray system for temperature, pressure, droplet size and others by methane gas



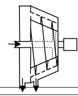
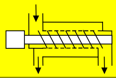
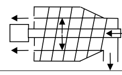
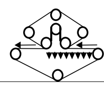
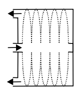
MHI Development Plan for NGH Chain

MITSUBISHI HEAVY INDUSTRIES, LTD.



Type of Dehydrator

MITSUBISHI HEAVY INDUSTRIES, LTD.

No.	Type	Continuous Operation	Low Density	Installation in High Pressure	Evaluation
1	**Centrifuge Filter** 	○	○	○	○
2	**Screw Press** 	○	○	○	◎
3	**Decanter** 	○	△	○	△
4	**Belt Press** 	○	○	×	×
5	**Filter Press** 	×	○	×	×

Dehydration of Hydrate Slurry

MITSUBISHI HEAVY INDUSTRIES, LTD.

Results (gas ; R143a at atmosphere)

Water Content : 20～30 wt%
Hydrate Recovery Rate : 80～90 wt%
Screw Rotation Speed : ~10 rpm

Water content : 95%

Outline

1. Concept of natural gas transportation and storage system using natural gas hydrate

2. Laboratory scale experiments by methane gas (~2000)

3. Bench scale test (1Ton/day) by R143a hydrate (2001~)

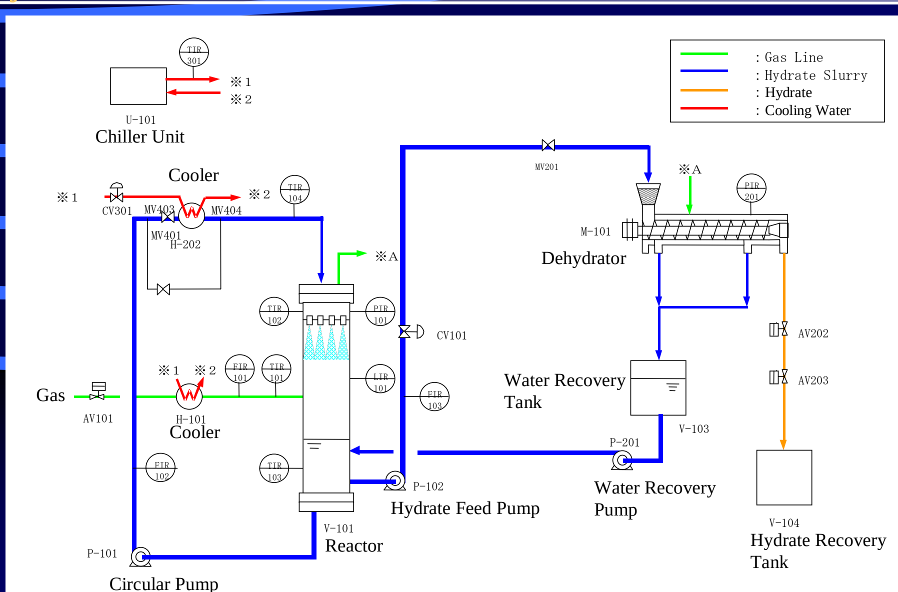
Situation of Bench Scale Test (1Ton/d)

- **Formation Test**
  Evaluate the effect of flow rate, number of nozzles, droplet size, etc
- **Dehydration Test**
  Evaluate the water content and hydrate recovery efficiency
- **Combined Test**

⇓

Develop to the high pressure methane system (2002~)

Continuous Formation and Dehydration System



Outlook of Continuous F & D System

Specification of Formation Reactor

MITSUBISHI HEAVY INDUSTRIES, LTD.

	Bench Scale	Lab. Scale
Gas	R143a	CH_4
Size	$1m^3$ φ 800× 2000H	$4300cm^3$ φ 100× 550H
Flow rate	0.3～$1.8m^3/h$	Max 0.06 m^3/h
Droplet	0.15～1.1mmφ	50～150μ mφ
Pressure	Max 0.4 MPa	Max 10 MPa
Formation Rate	Max 1.0 ton/day	7 Kg/day

Specification of Dehydrator

MITSUBISHI HEAVY INDUSTRIES, LTD.

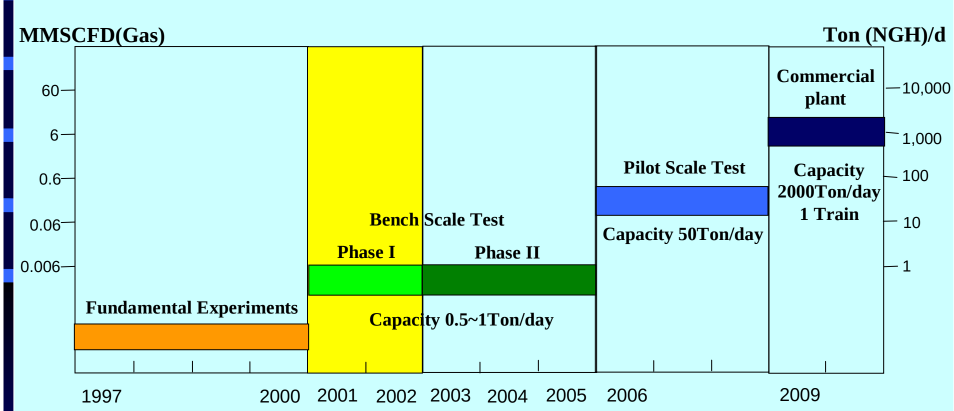
Method	Screw Press
Pressure	Max 0.4 MPa
Power	Pressurized Oil

Summary

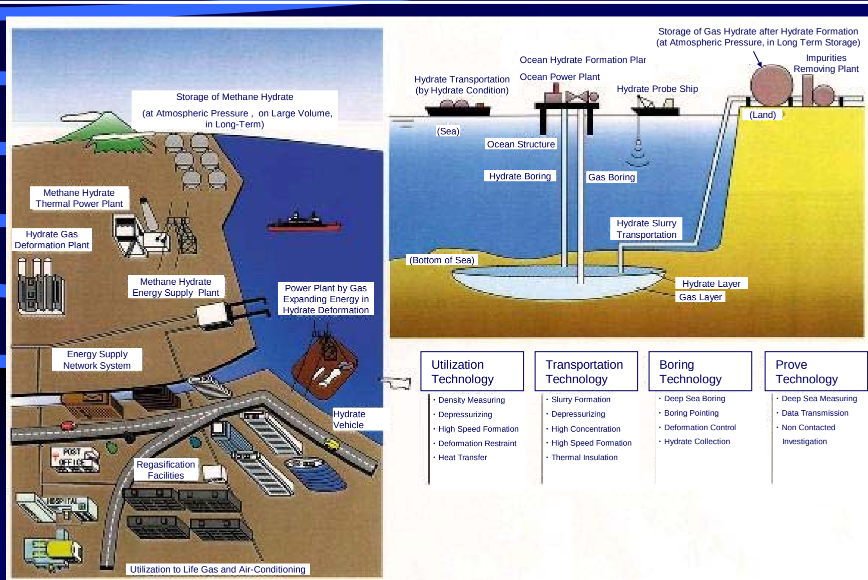
- Achieved 1Ton/day GH spray type formation system
- Achieved continuous dehydration system in 2 Kg/cm^2 pressure

Develop to the high pressure methane system (2002~)

Research & Development Schedule



Conception of
NGH Transportation and Storage System



"Natural Gas Transportation System using Gas Hydrate Pellets"
October 30, 2002
Washington Plaza Hotel, Washington DC

Hajime Kanda
NGH (Natural Gas Hydrate) Project Department
Mitsui Engineering & Shipbuilding Co., Ltd.

In accordance with the future energy perspectives by several sources such as IEA, the world demand of natural gas in 2030 is likely to be twice more than that in 2000 mainly because of both economic growth of developing countries and international efforts to cut greenhouse gas emissions.

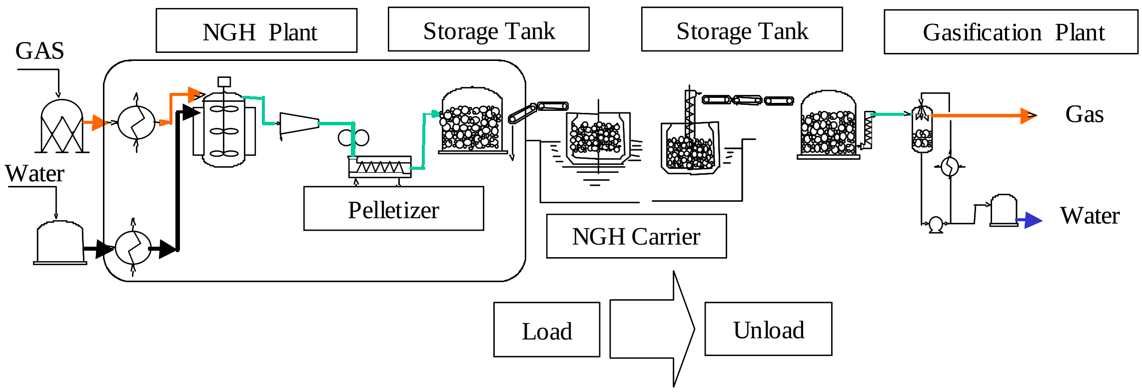
On the other hand it is well known that Natural gas hydrate (NGH) contains large amount of natural gas about 170 times (in case of pure methane) as much as its volume and it is easy to be stored and transported safely at about minus 15 degree C under the atmospheric pressure due to so called self-preservation effect. As a result, specifications of facilities including production plants are expected to be simpler and total cost of gas transport is lower in comparison with Liquefied Natural Gas (LNG) case.

Focusing on these advantages of NGH properties Mitsui Engineering & Shipbuilding Co., Ltd. is working on the comprehensive NGH technology development to complete the gas supply system, such as NGH generation, dewatering, pelletizing, storage, sea transportation, loading/unloading and gasification. In particular Mitsui is concentrating the NGH pellet system, which is superior in many points including high filling ratio in the ship hold, good fluidity and enhanced self-preservation effect, and that is one of the best solutions to make NGH transport more feasible.

Recently Mitsui has joined in three Japanese governmental researches on NGH transportation which are financially supported by three organizations of Japanese ministries, Corporation for Advanced Transport and Technology (CATT), New Energy and Industrial Technology Department Organization (NEDO) and Japan National Oil Corporation (JNOC) respectively. Taking this opportunity Mitsui has started to construct a demonstration plant in its Chiba Works in Japan with production rate of 600kg NGH per day. The plant is scheduled to start operation in 1st quarter 2003.

In this presentation the presenter shows advantages of NGH pellet system and how Mitsui's research and development on NGH are promoted through current activities.

Mitsui's Concept on Gas Transport System using NGH Pellets



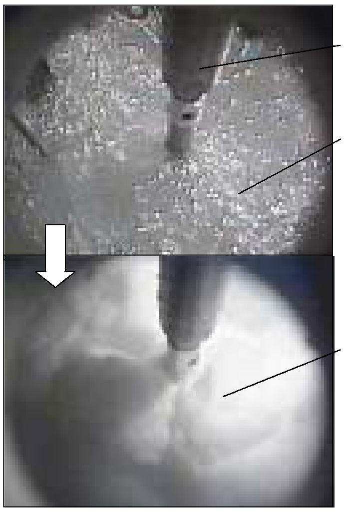
MES MITSUI ENGINEERING & SHIPBUILDING CO., LTD.

"Mitsui's NGH Production Technology"

Mitsui has successfully achieved in 2000 to generate NGH with higher speed by means of "Mixing and Bubbling Method". Followings are the photographs showing a bench scale NGH production facility installed at Mitsui's Chiba Laboratory in Japan. The left photograph shows the whole view of facility which has the production capacity of 5kg NGH per hour. The right photographs are taken by a video camera set on the top side of the reactor observing inside of the reactor. Temperature is set at about three or five degree C and pressure is about 5MPaG. After starting operation of facility, white and snowy NGH is rapidly generated in the reactor.

Bench Scale NGH Production Equipment
(Capacity is about 5kg NGH per hour)

at Mitsui's Chiba Laboratory



"Advantage of NGH Pelletizing Technology"

After NGH is generated in the reactor, it is generally dewatered, super-cooled and depressurized to be powdery particles. However such powdery NGH is porous, and filling ratio, which is how much NGH is contained in the given space, is more or less 0.4. To solve this problem and make NGH transport system more economical, Mitsui is researching and developing NGH pellet system, in which powdery NGH is pressurized to be NGH pellets as shown in following photographs. Each pellet is typically sphere shape in multi size. After pelletized, filling ratio is expected to increase up to over 0.7. In addition, pelletized NGH is expected to be quite fluid to handle and the self-preservation effect enhanced.

1. Larger Amount of Net Gas Transportable
2. High Fluidity & Easy Handling
3. Enhanced Self Preservation Effect

20mm dia.NGH Pellets
manufactured by Mitsui

Ice(NGH pellets) to fire

The Second Workshop of the International Committee on Gas Hydrates SESSION V

“Natural Gas Transportation System using Gas Hydrate Pellets”

October 30, 2002

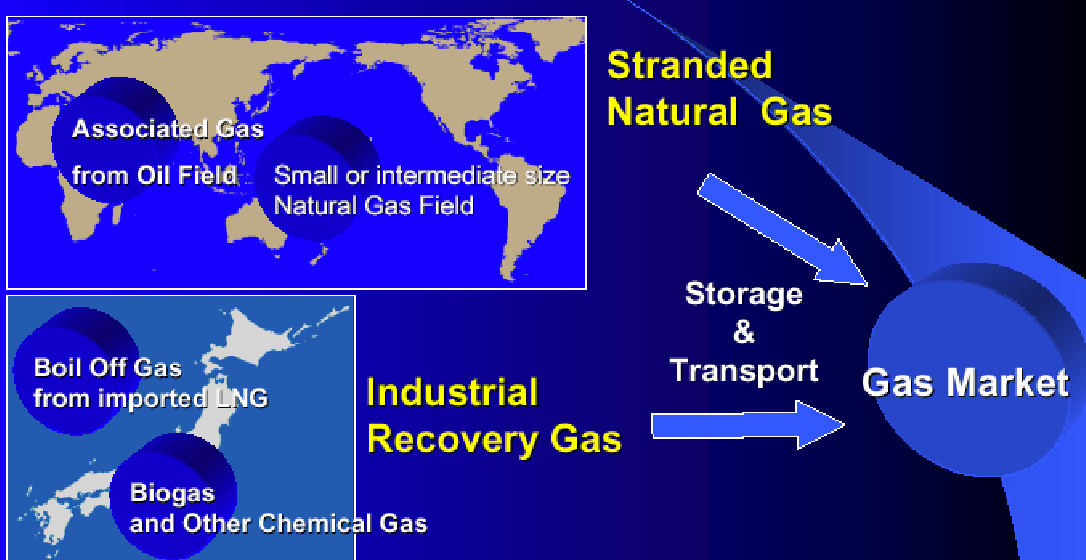
Washington Plaza Hotel, Washington DC

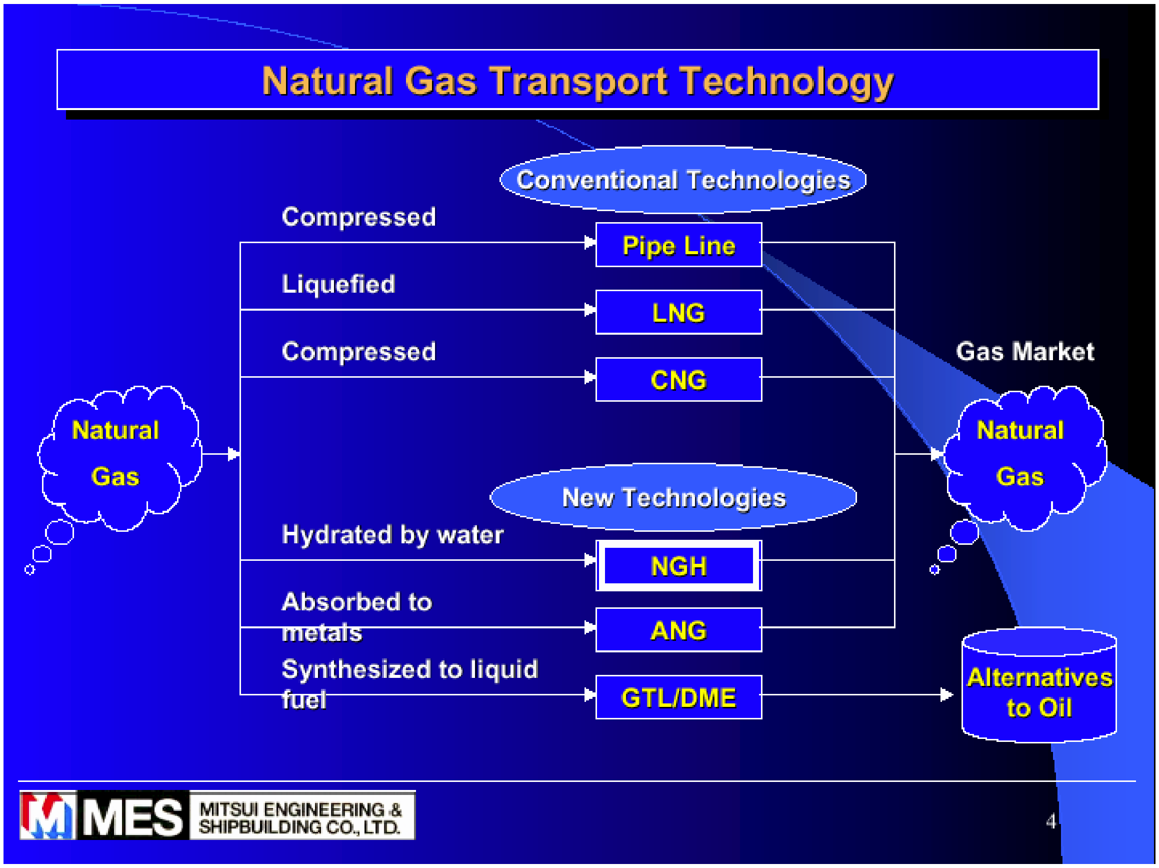
HAJIME KANDA

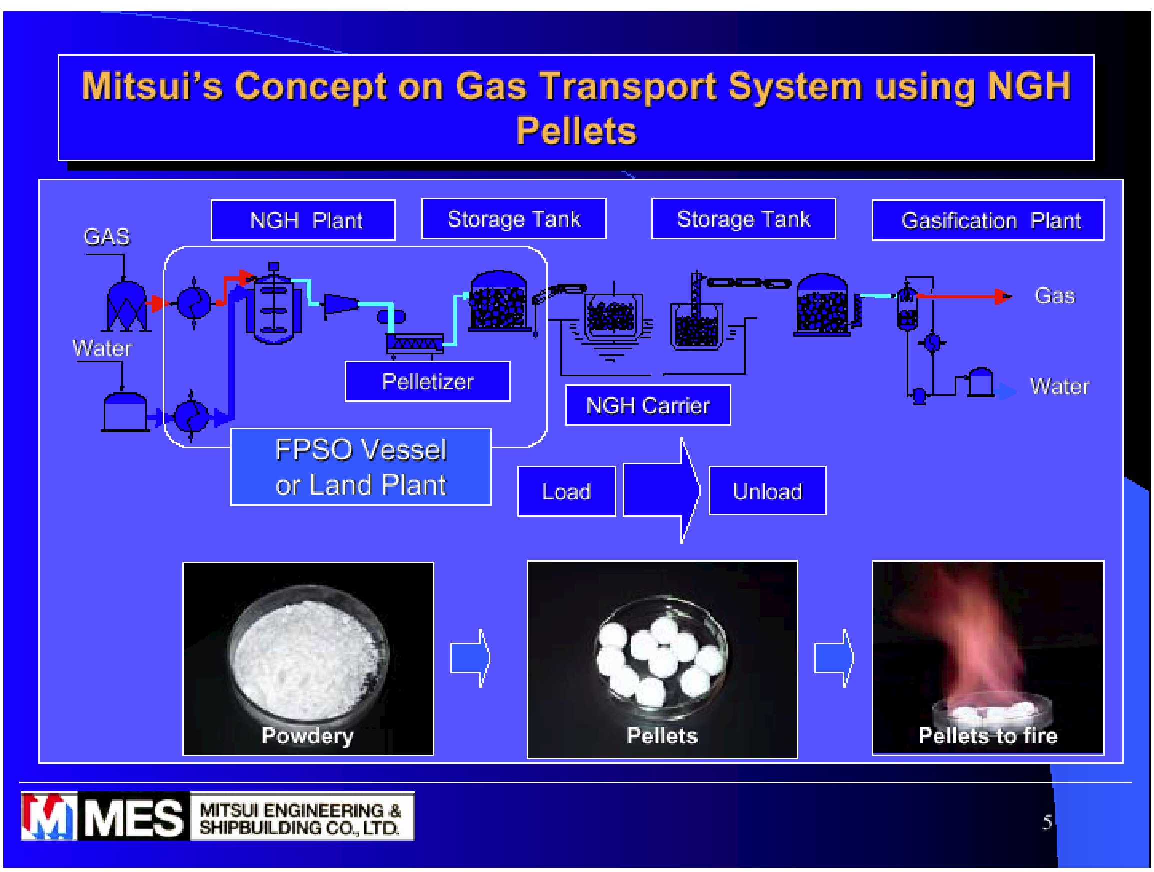
Natural Gas Hydrate Project Department

MITSUI ENGINEERING & SHIPBUILDING CO., LTD.

Utilization of Stranded and Undeveloped Potential Gas Sources




Natural Gas Transport Technology
Conventional Technologies
Compressed
Pipe Line
Liquefied
LNG
Compressed
CNG
Gas Market
Natural Gas
Natural Gas
New Technologies
Hydrated by water
NGH
Absorbed to metals
ANG
Synthesized to liquid fuel
GTL/DME
Alternatives to Oil
MES MITSUI ENGINEERING & SHIPBUILDING CO., LTD.
4


Mitsui's Concept on Gas Transport System using NGH Pellets
NGH Plant
Storage Tank
Storage Tank
Gasification Plant
GAS
Water
Gas
Water
Pelletizer
NGH Carrier
FPSO Vessel or Land Plant
Load
Unload
Powdery
Pellets
Pellets to fire
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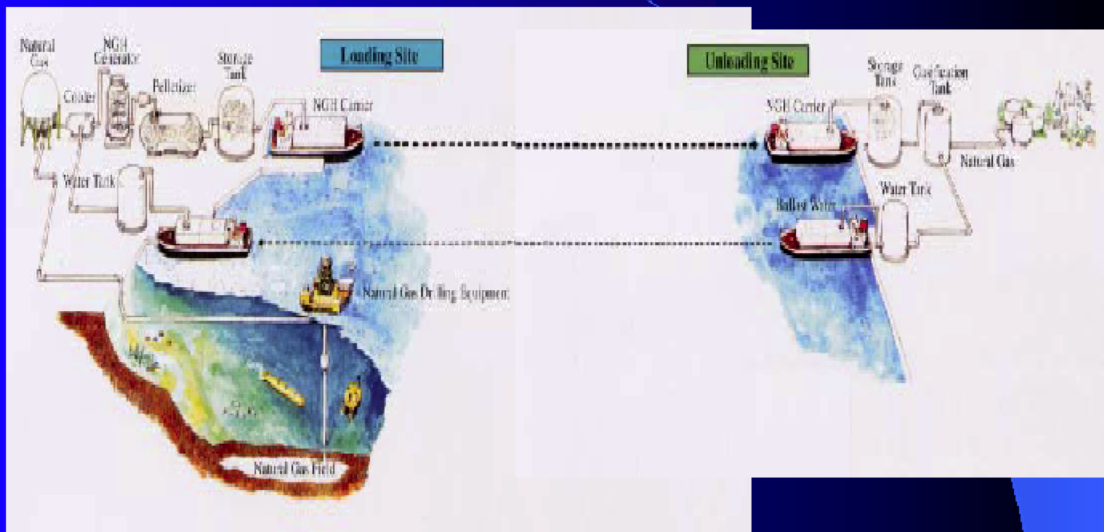
5

Illustration of Mitsui's Concept on Gas Transport System using NGH Pellets



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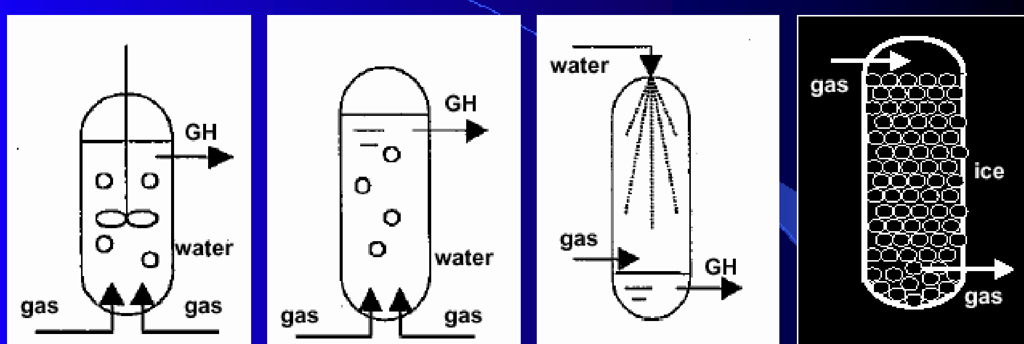
Methods of NGH Generation



Mixing | Bubbling | Spray | Ice particles

Mixing & Bubbling → **High Speed Generation**

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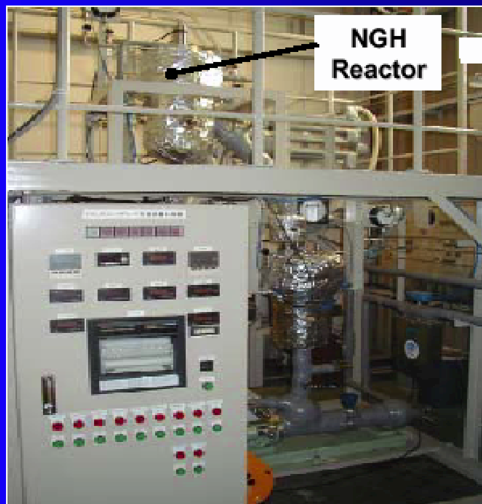
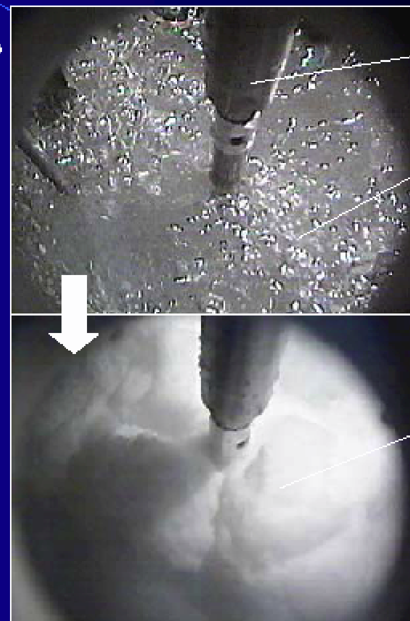
High Speed NGH Production Technology



Bench Scale NGH Production Equipment
(Capacity is about 5kg NGH per hour)

in Mitsui's Chiba Laboratory



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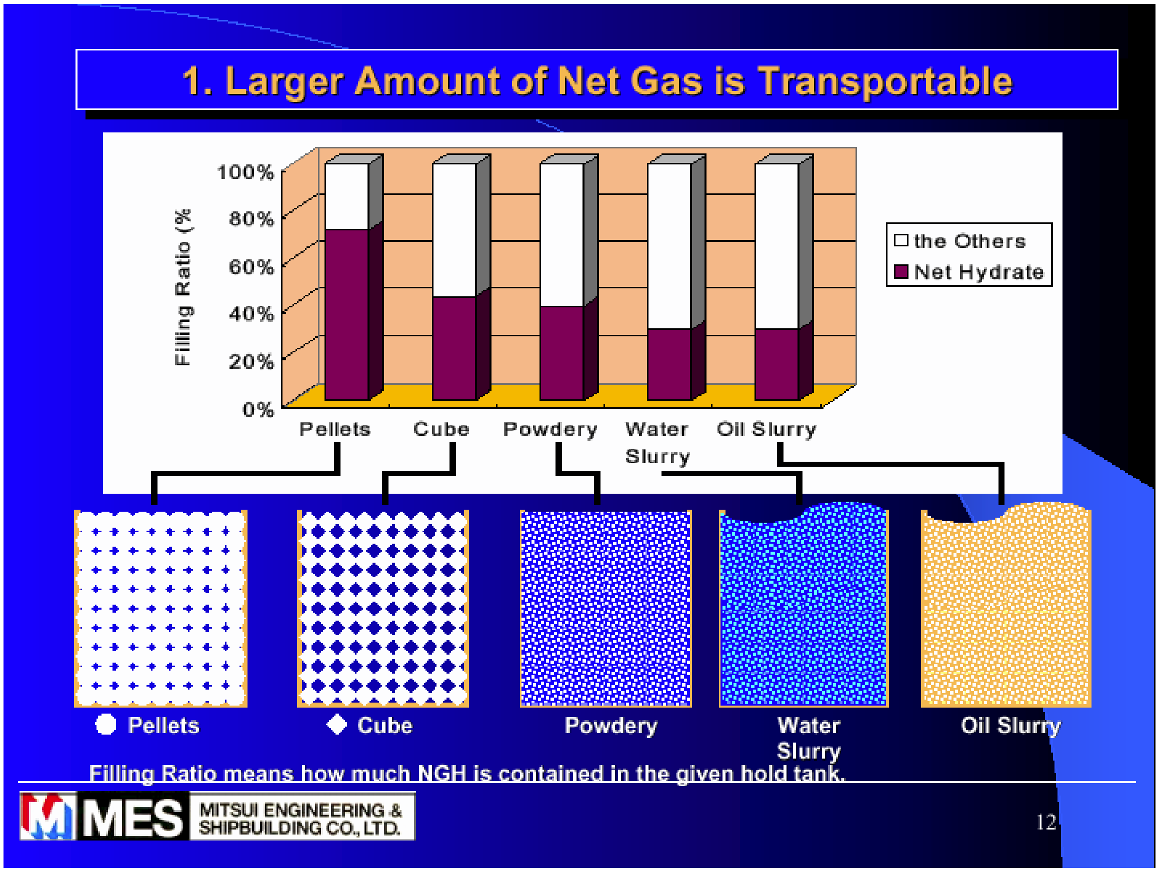
Advantage of NGH Pelletizing Technology

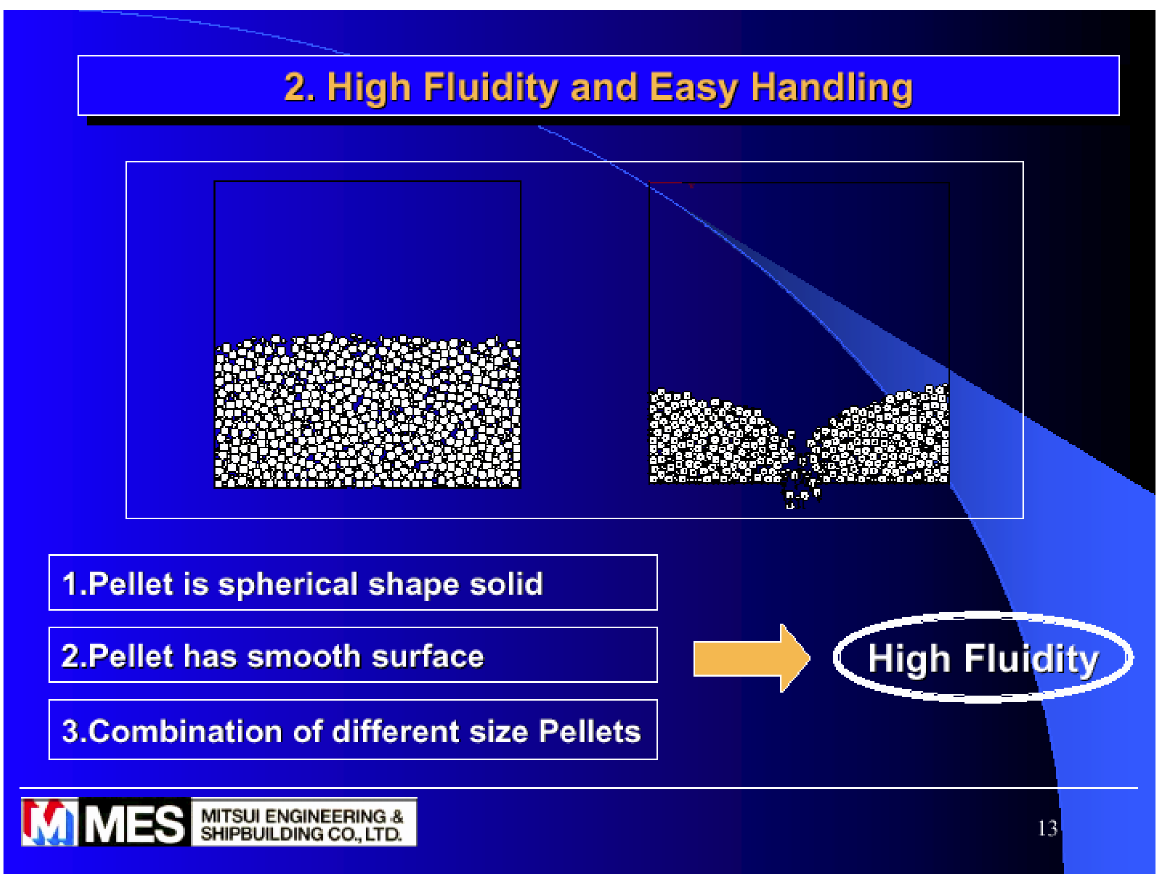
1. Larger Amount of Net Gas Transportable
2. High Fluidity & Easy Handling
3. Enhanced Self Preservation Effect

20mm in diameter NGH Pellets manufactured by Mitsui

Low temperature room in Chiba Laboratory

MES MITSUI ENGINEERING & SHIPBUILDING CO., LTD.


1. Larger Amount of Net Gas is Transportable
100%
80%
60%
40%
20%
0%
Filling Ratio (%
Pellets
Cube
Powdery
Water
Slurry
Oil Slurry
the Others
Net Hydrate
Pellets
Cube
Powdery
Water
Slurry
Oil Slurry
Filling Ratio means how much NGH is contained in the given hold tank.
MES
MITSUI ENGINEERING &
SHIPBUILDING CO., LTD.
12


2. High Fluidity and Easy Handling
1.Pellet is spherical shape solid
2.Pellet has smooth surface
3.Combination of different size Pellets
High Fluidity
MES
MITSUI ENGINEERING &
SHIPBUILDING CO., LTD.
13

Industrial Applications using NGH properties

Gas Hydrate has many interesting properties for industrial applications.

1. Much Gas is contained in itself
2. Much cold heat is recovered after dissociation
3. High pressure gas is recovered after dissociation
4. Mixed gas is separated to each

Applications	Property	Property	Applications
BOG Storage Gas transportation	170 times gas	Much cold heat	Cooling for Gas turbine Supply of cold heat
Power generation Energy saving	High pressure gas	Gas Separation	Gas purification process

Company Profile

Founded	In 1917 as one division of MITSUI & CO.
Sales	457 billion yen (about 3.8 billion USD) in 2002 fiscal year
Employee	10,737 as of March 2002
Head Office	Tokyo, Japan

Current Mitsui's R&D Organization on Gas Hydrate

NGH Project Dept. *Organized in Sept. 2001*

- Technology Development HQ
  - Chiba Laboratory
  - Akishima Laboratory
  - Tamano Laboratory
- Plant Engineering HQ
- Shipbuilding & Marine Systems HQ
- Machinery Systems HQ
- Steal Structure & Construction HQ

For more information please contact us through

ngh@mes.co.jp

URL http://www.mes.co.jp

Thank you.

Research on Use of Gas Hydrate for Natural Gas Transportation

Y. Nakajima[1)], H. Shirota[1)], S. Ota[1)], and T. Takaoki[2)]
1) National Maritime Research Institute
6-38-1 Shinkawa, Mitaka, Tokyo, 181-0004, Japan
2) Mitsui Engineering and Shipbuilding Co., Ltd.
5-6-4 Tsukiji, Chuo-ku, Tokyo, 104-8439, Japan

Introduction

A research project on natural gas hydrate (NGH) transportation system has been conducted since the fiscal year of 2001 by the cooperation of Mitsui Engineering and Shipbuilding Co., Ltd. (MES), National Maritime Research Institute (NMRI) and Osaka University, under the financial support by the Corporation for Advanced Transport & Technology. In this system, natural gas hydrate is synthesized, using natural gas produced from gas fields, and transported to consuming countries by NGH carriers. Our feasibility study suggests that NGH transportation system would be feasible as the means for carrying natural gas from small or middle-scale gas fields in Southeast Asia to Japan although LNG transportation from those fields to Japan is not feasible due to the huge cost of LNG production plant. Compared with LNG transportation system, NGH transportation system would have advantage of decrease in initial cost for the production plant while it has disadvantage of high shipping cost. One of the important subjects of the research on NGH transportation system is control of dissociation properties of NGH, as well as improvement of NGH production efficiency, which is a major subject of R & D by MES. Thus, NMRI has been investigating the dissociation properties, i.e., self-preservation effect of NGH as bulk cargo on ships.

In this report, we describe the outline of the main topics in the research project: 1) NGH processing for shipment, 2) design of an NGH carrier and cargo-handling systems and 3) evaluation of the self-preservation effect of NGH pellets. In this project, we have used methane hydrate instead of NGH.

NGH processing for shipment

We prepare methane hydrate by bubbling method, in which methane gas is injected into a reactor filled with water to form methane hydrate on the surface of methane gas bubbles. After removing of the residual water, methane hydrate powder is taken out. Then, we pelletize the methane hydrate powder to obtain methane hydrate pellets.

We found that methane hydrate pellets would have the advantages of not only easy cargo-handling but also prevention of dissociation by casting of methane hydrate powders into the form of pellets. It is supposed that dissociation of methane hydrate pellets is slower than that of methane hydrate powders. In other words, the self-preservation effect of methane hydrate is expected to be enhanced by pelletization. The appearances of methane hydrate pellets are shown in Fig. 1.

Fig. 1 Appearances of methane hydrate pellets

In addition, we are applying combination of large and small sized pellets to improve the filling efficiency, which can be represented by the amount of gas per unit volume of cargo holds.

Design of NGH Carrier and Cargo-handling Systems

An NGH Carrier would be a double-hull bulk carrier with cargo holds insulated from the inner hull. An example of sectional area of a preliminarily designed NGH carrier is illustrated in Fig. 2. The conceptual design of an NGH carrier depends on several factors such as gas field, minimum water depth of ports of loading and discharging, voyage route, cargo quantity, etc.

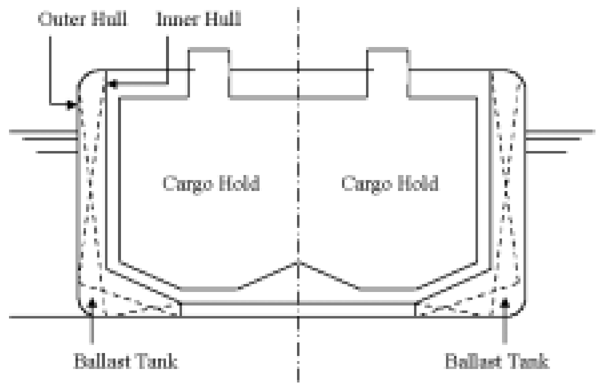


Fig. 2 Preliminary design of NGH carrier

Furthermore, cargo-handling systems should be developed. As loading systems, slurry, belt conveyor and pneumatic system are expected to be applicable. As discharging systems, slurry, grabbing and re-gasification are expected. However, each method has some advantages and disadvantages to apply to NGH transportation, and are under investigation by MES.

Evaluation of Self-preservation Effect

Self-preservation effect is an important feature of methane hydrate for evaluation of feasibility and safety analysis of NGH transportation system. Then, we measured the dissociation rate of methane hydrate pellets at several temperatures below 273K. The dissociation curves of methane hydrate pellets measured through the preliminary experiments are shown in Fig. 3.

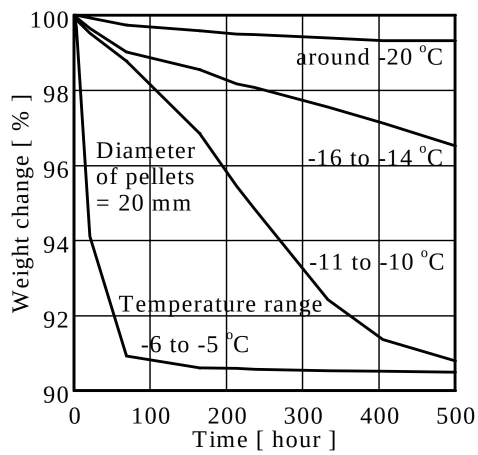


Fig. 3 Dissociation curves of methane hydrate pellets

The methane hydrate pellets dissociated at 253K slowly enough for two-week voyage while those almost completed the dissociation at 268K by 4 days passed. The samples were made by MES through the research on mass-production of NGH and the properties of samples will change in future.

We are investigating the detailed features of the self-preservation effect of methane hydrate pellets by experiments varying ambient conditions. Furthermore, we are investigating the dissociation properties of methane hydrate pellets under compressed condition, which represents the conditions of NGH pellets in cargo holds on ships taking into account acceleration resulted from ship motion in waves.

Summary

The outline of main topics in our research project on NGH transportation system is described. We found some features of methane hydrate for development of NGH transportation as follows:

1) NGH processing for shipment

Pelletization of methane hydrate improves not only cargo-handling but also self-preservation effect;

2) Design of NGH carrier and cargo handling systems

An NGH Carrier would be designed as a double-hull bulk carrier with insulated cargo holds; and

3) Evaluation of self-preservation effect

By measuring the dissociation rate of methane hydrate pellets at several temperatures, methane hydrate pellets dissociated at 253K slowly enough for two-week voyage.

Acknowledgement

We highly appreciate all members in the research projects for their contribution and other people related to this research, in particular to the Corporation for Advanced Transport & Technology for its financial support.

Research on Use of Gas Hydrate for Natural Gas Transportation

Y. Nakajima, H. Shirota, S. Ota
National Maritime Research Institute

T. Takaoki
Mitsui Engineering and Shipbuilding Co., Ltd.

AGENDA

- Introduction
    Scope & Overview
- NGH Processing for Shipment
    Synthesis
    Pelletization
    NGH Carrier
    Cargo-handling Systems
- Evaluation of Self-preservation Effect
    Measurement of Dissociation Rate
    Properties of Self-preserved Hydrate Pellets
- Summary

INTRODUCTION

Application of Natural Gas Hydrate (NGH) to Natural Gas Transportation

Proposed by Gudmundsson et al (1996)

Collaboration for Research Project

Corporation for Advanced Transport & Technology

Financial Support

(FY2001 - 2003)

Osaka Univ.

Thermodynamics & Structure of Binary Hydrate*
Fine Structure of Methane Hydrate Pellet

****: Methane + Ethylene/Cyclopropane***

National Maritime Research Inst. (NMRI)

<u>Evaluation of Self-preservation Effect</u>

Safety Measures and Management

Mitsui Engineering & Shipbuilding (MES)

<u>Processing of NGH Pellet</u>

Design of NGH Carrier

Development of Cargo-handling Systems

Scope

- *Control of NGH dissociation during transportation*
- *Dissociation is controlled by Self-preservation Effect*

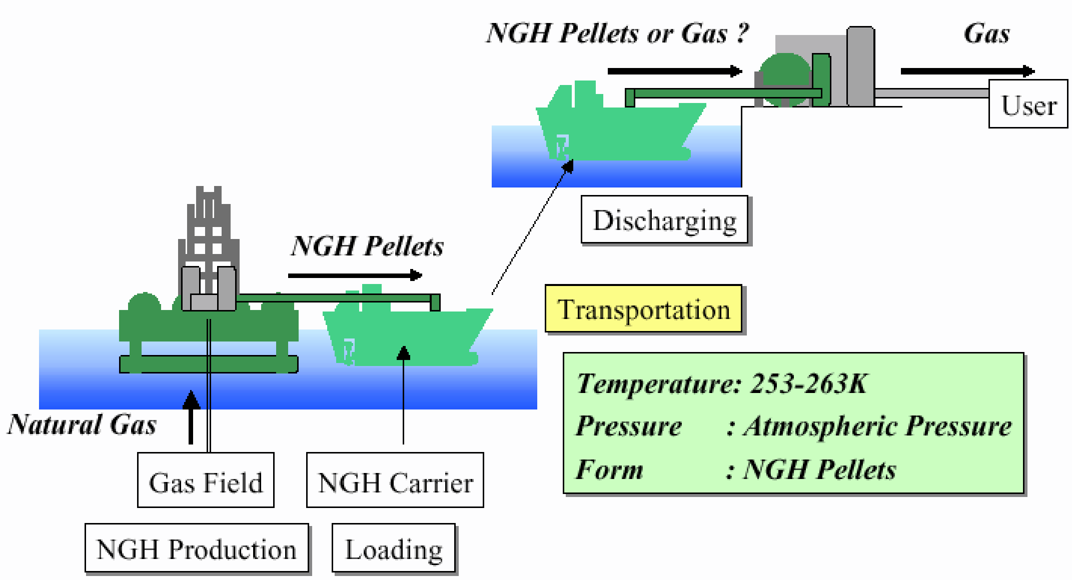
Enhancement & Evaluation of Self-preservation Effect

↓

Enhancement
Processing of Synthesized (Powdery) Hydrate to Pellet Form

Evaluation
Measurement of Dissociation Rate and Properties of NGH Pellets

Overview of NGH Transportation System



NGH PROCESSING FOR SHIPMENT

Scheme of Methane Hydrate Synthesis & Processing

In this project, we use Methane Hydrate in stead of NGH.

Methane Gas

Synthesis by Bubbling Method

Powdery Methane Hydrate

Pelletization

Methane Hydrate Pellet

Synthesis of Methane Hydrate

Bubbling Method

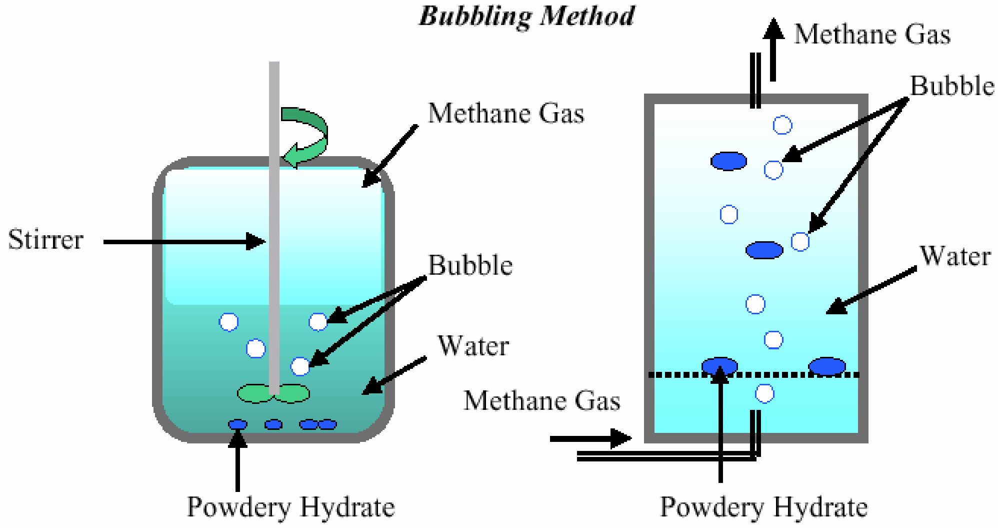


Photo of Methane Hydrate Pellets

Pellet Diameter: 20mm

By Mitsui Engineering &Shipbuilding

Merits of Pelletization

Easy Cargo-handling

Improvement of Filling Efficiency in Cargo Holds by Combination of Large and Small Pellets

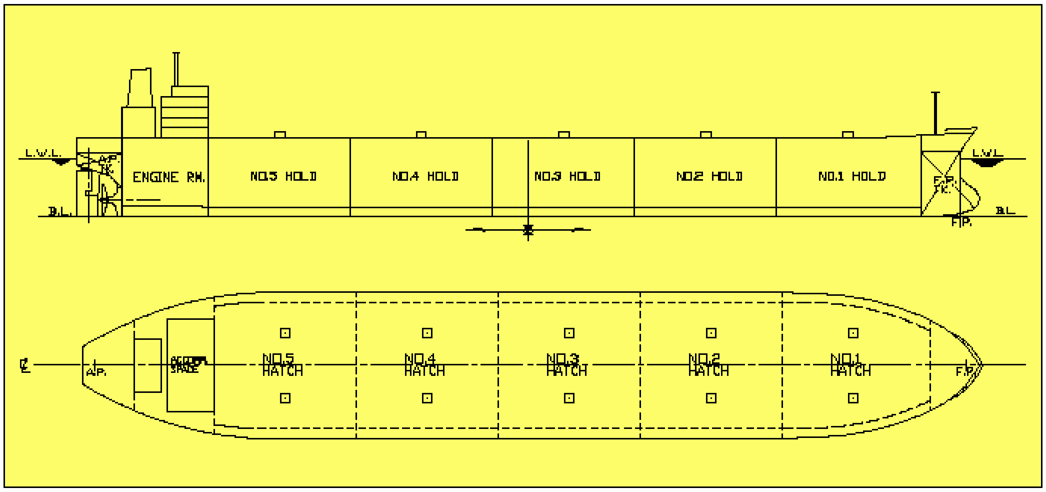
Slower Dissociation than Powders

Is Self-preservation Effect Enhanced by Pelletization?

↓

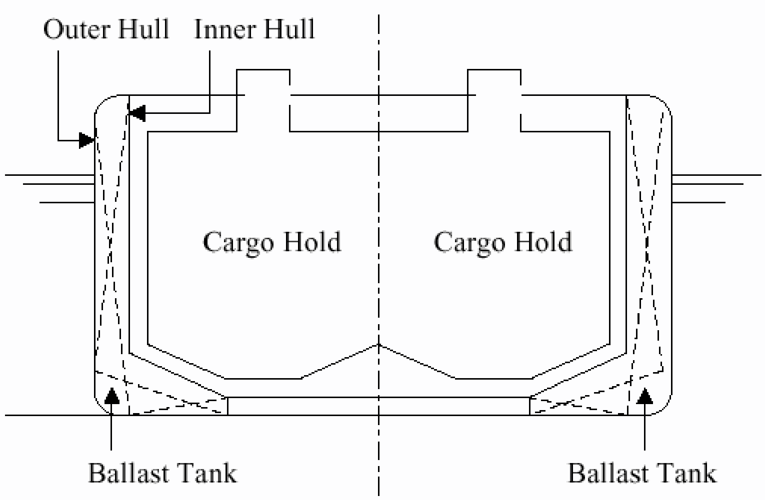
Measurement of Dissociation Rate

Design of NGH Carrier



Conceptual Design of NGH Carrier

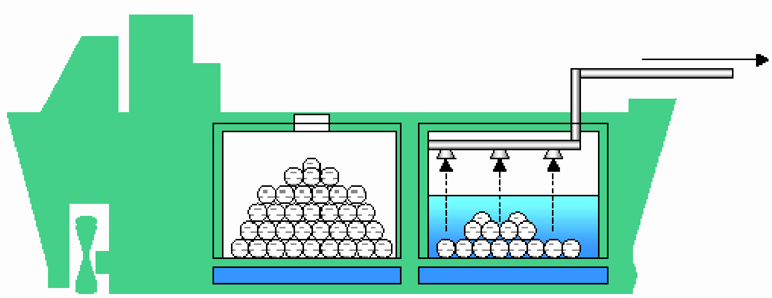
Design of NGH Carrier



Vertical Cross-section of NGH Carrier

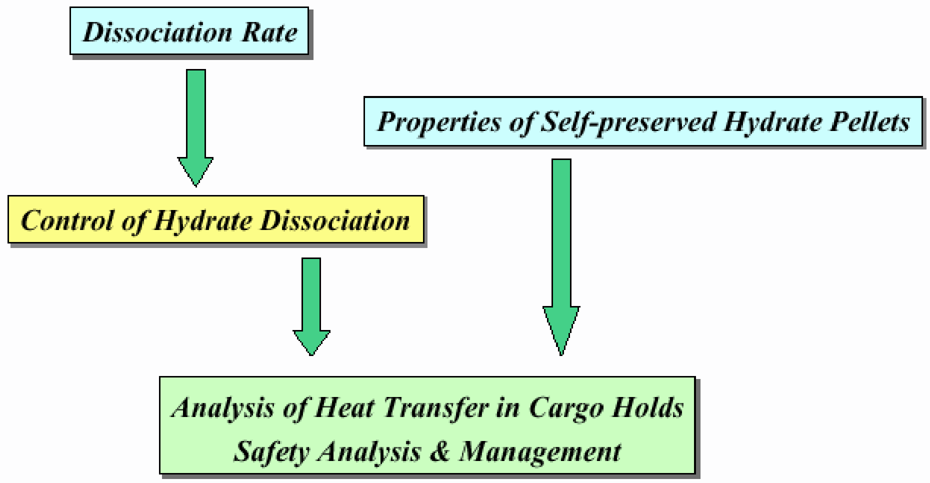
Cargo-handling Systems

Discharging Systems

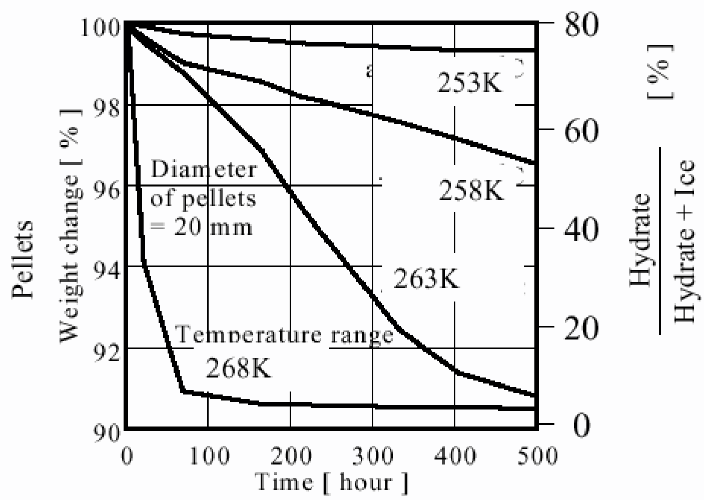


- Naked Pellet
  Re-gasification
  Conveyor
- Slurry
  Pump

EVALUATION OF SELF-PRESERVATION EFFECT



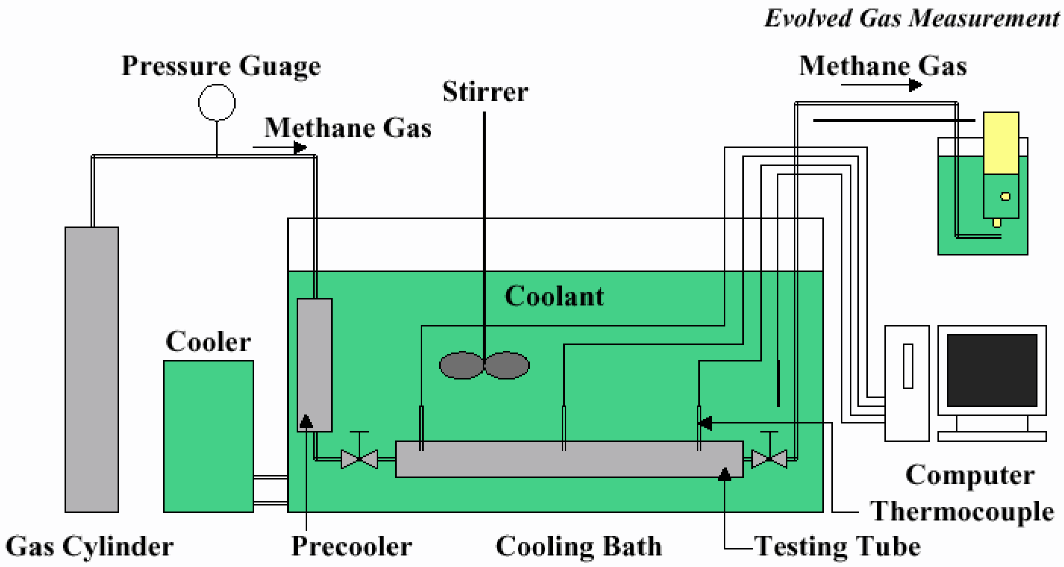
Measurement of Dissociation Rate



Preliminary Experiments
(Ambient gas is not controlled)

Calculated by Evolved Gas Amount
Stoichiometric Composition of Hydrate

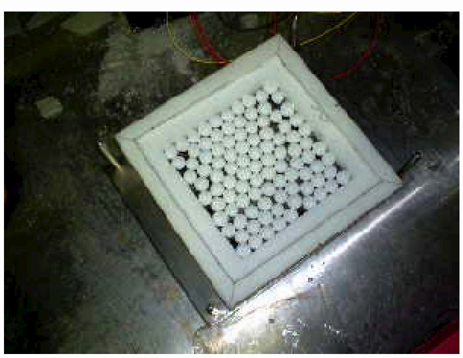
Future Experiment of Dissociation Rate



Hydrate Pellets in Testing Tube are dissociated in well-controlled ambient gas

Properties of Self-preserved Hydrate Pellets

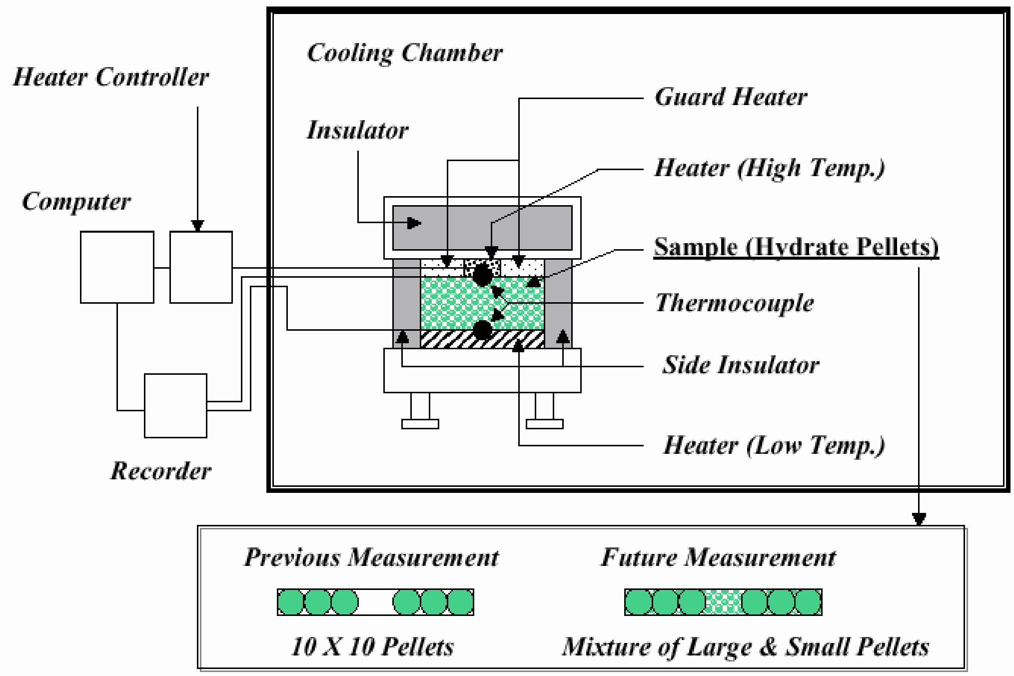
Thermal Conductivity



Thermal Conductivity of Single Layer of Hydrate Pellets

0.29W/mK@253K
0.34W/mK@258K

Schematic Diagram of Thermal Conductivity Measurement



Future Work

Measurements at Conditions that Simulate Real Situation of Transportation

Thermal Conductivity of Size-Mixed Pellet Layer

Compression Strength of Size-Mixed Pellet Layer

Dissociation Rate of Compressed Hydrate Pellets

For Control of Hydrate Dissociation,

Analysis of Heat Transfer in Cargo Holds

Safety Analysis & Management

Compression Test

Compression Testing Apparatus
(Static Loading Test)

SUMMARY

We are investigating
enhancement and evaluation of self-preservation effect of methanehydrate
for a research of NGH Transportation System.

1) NGH processing for shipment
Pelletization improved self-preservation effect of methane hydrate.

2) Evaluation of self-preservation effect
Measurement of dissociation rate at several temperatures showed methane hydrate pellets dissociated at 253K slowly enough for two-week voyage

ACKNOWLEDGEMENT

We appreciate all members in the research projects for their contribution and other people related to this research, in particular to the Corporation for Advanced Transport & Technology for its financial support.

"JNOC's Research Projects for Natural Gas Transportation with Gas Hydrates"

Toshiharu Okui

Japan National Oil Corporation

ABSTRACT

There are many middle and small gas fields in Asian countries but those fields are considered difficult to be developed by conventional techniques, such as LNG and pipelines, because of the balance of its gas amount and initial cost of those facilities. In future, when all large gas fields are consumed, more economical technology to develop those many smaller gas fields will be essential. Japan has very small amount of domestic oil and gas resources; therefore, it is important to have some options to import energy resources.

Natural Gas Hydrates (NGH) has drawn much attention as one of the new economical gas transportation methods these days. NGH contains 170 times as much gas as its volume under milder conditions, such as at much higher temperature than LNG and lower temperature than pressure cylinders. Therefore, initial cost of NGH process is estimated lower than LNG. There are many reports about basic properties of gas hydrates and some reports about the cost estimation of NGH chain but almost no engineering data in industrial scale.

Japan National Oil Corporation (JNOC) has started research programs to evaluate industrial efficiency of NGH as a gas transportation medium in 1999 with some Japanese colleagues. First, a special attention was paid to collect engineering data of fast continuous production of hydrates. As a result, we found many difficulties to form large amount of hydrate in a big facility, but some of them were successfully overcome. Knowledge of basic properties of hydrates was often very helpful to solve the problems.

Finally other companies joined us and now the program is basically composed of three parts, production, shipping, and gasification. From now, more detailed cost estimation from experimental data and technical developments for reducing operation cost are scheduled.

30 October 2002

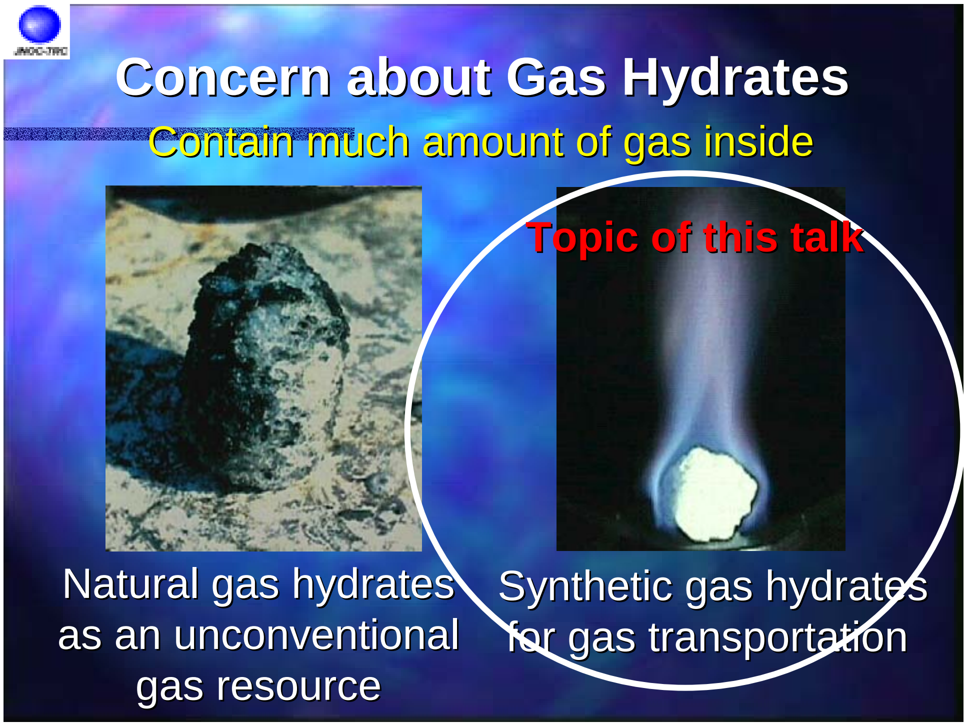
JNOC's Research Projects for Natural Gas Transportation with Gas Hydrates

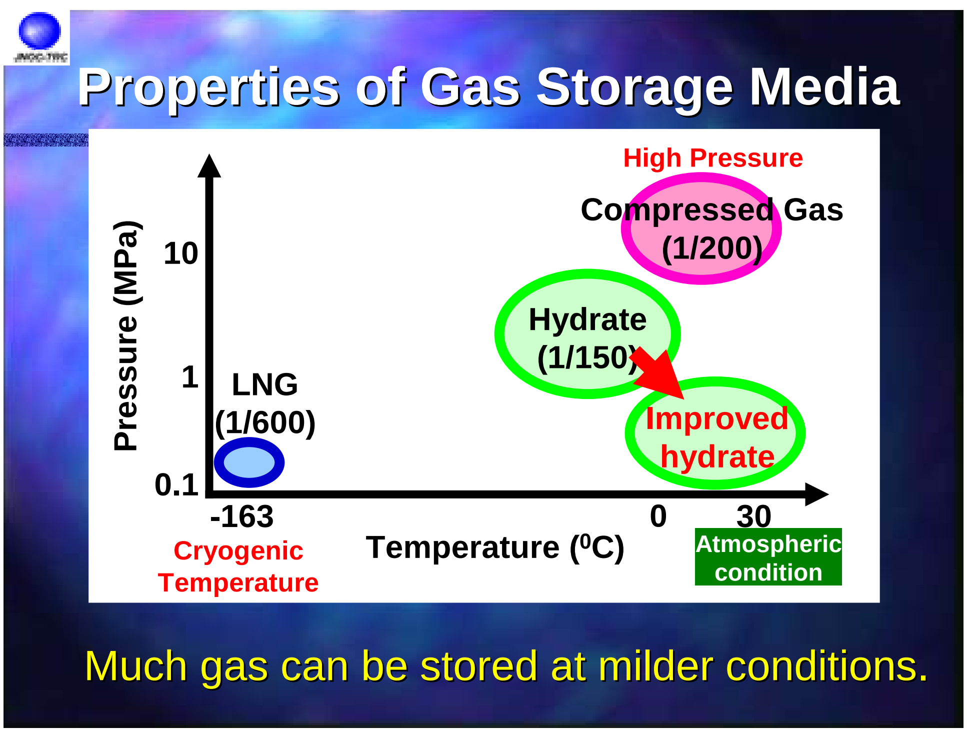
Toshiharu Okui

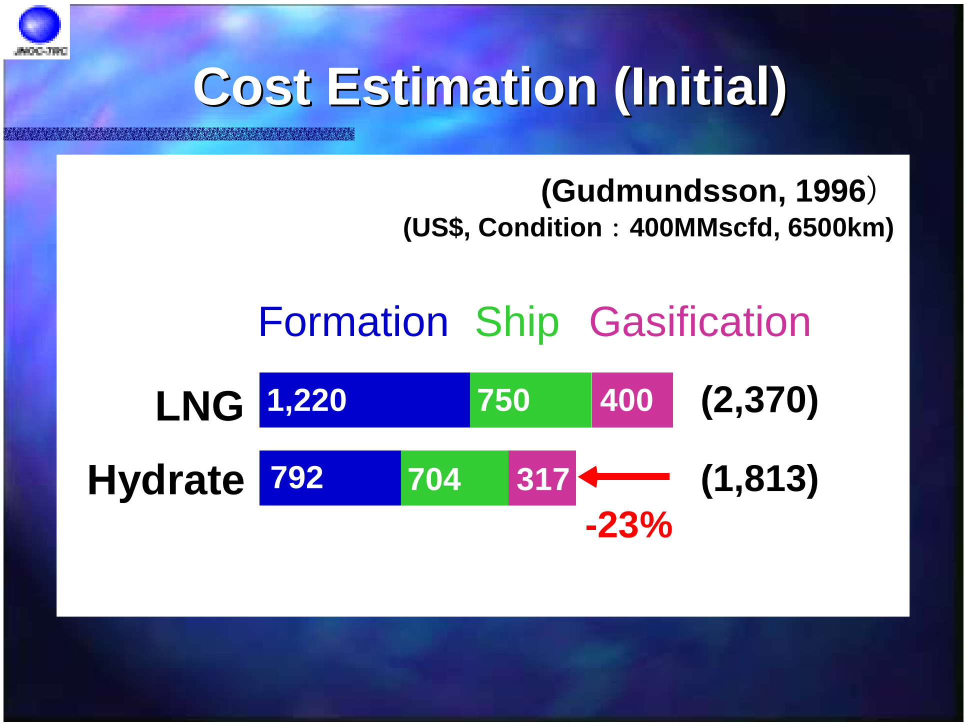
Japan National Oil Corporation
Technology Research Center

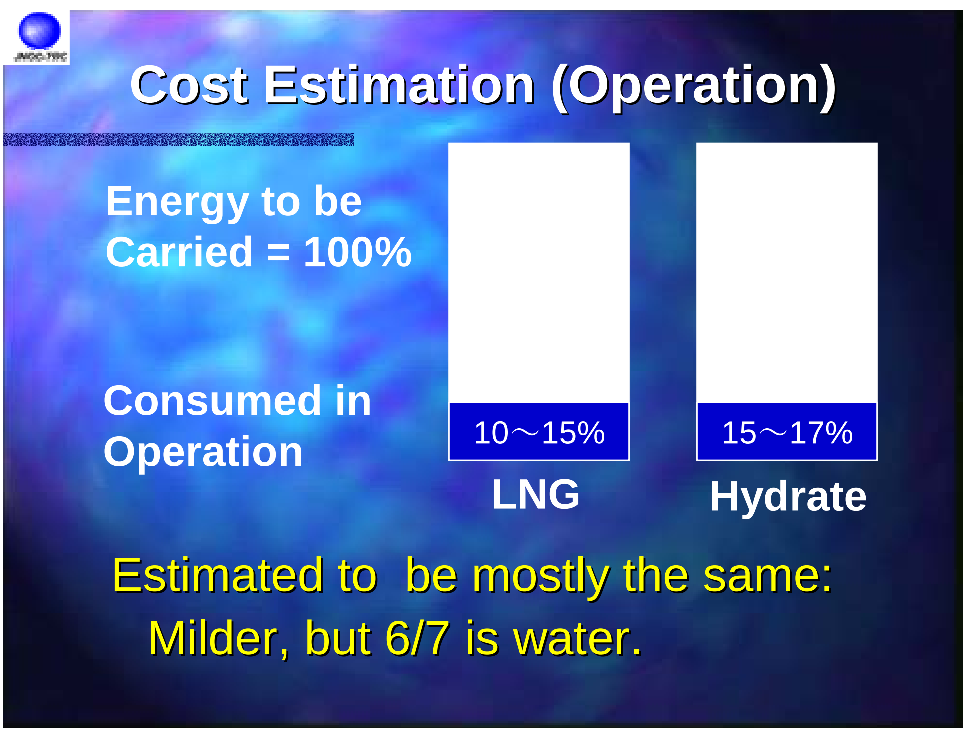
Outline

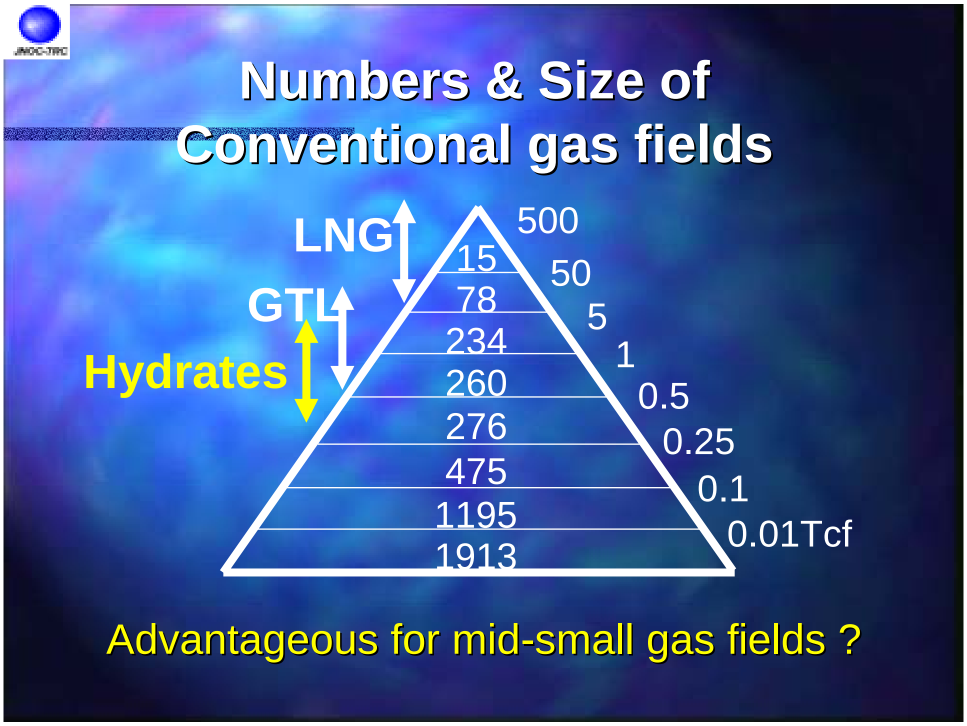
- Properties for Gas Transportation
- Cost Estimations
- Targets
- Research Projects
  - Concept and Organization
  - Contents
  - Subjects

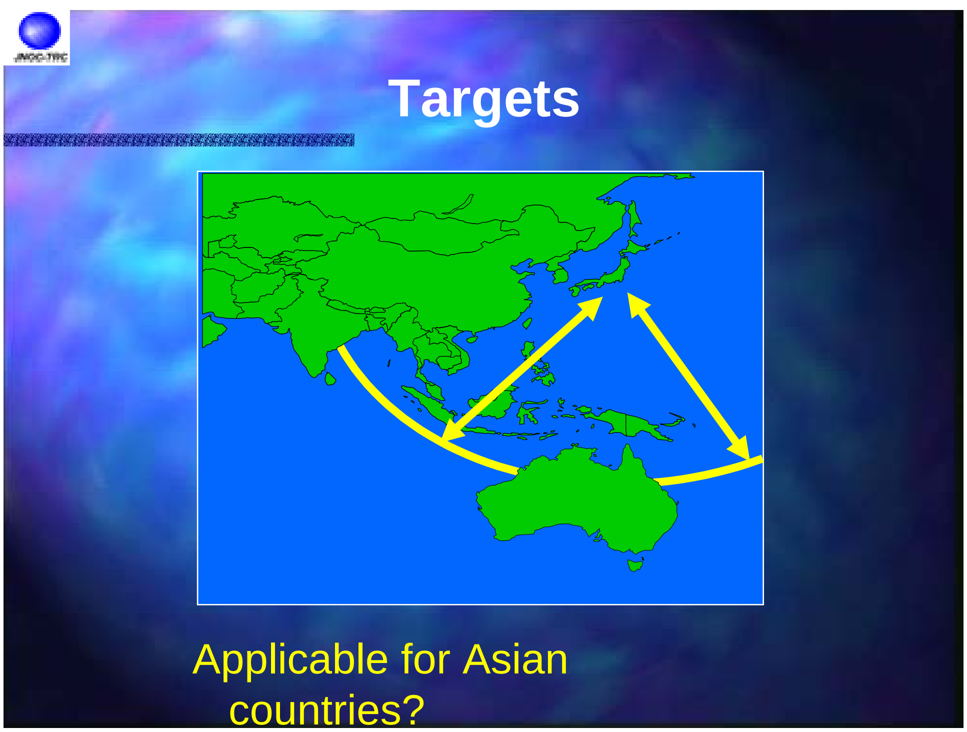

Concern about Gas Hydrates
Contain much amount of gas inside
Topic of this talk
Natural gas hydrates as an unconventional gas resource
Synthetic gas hydrates for gas transportation

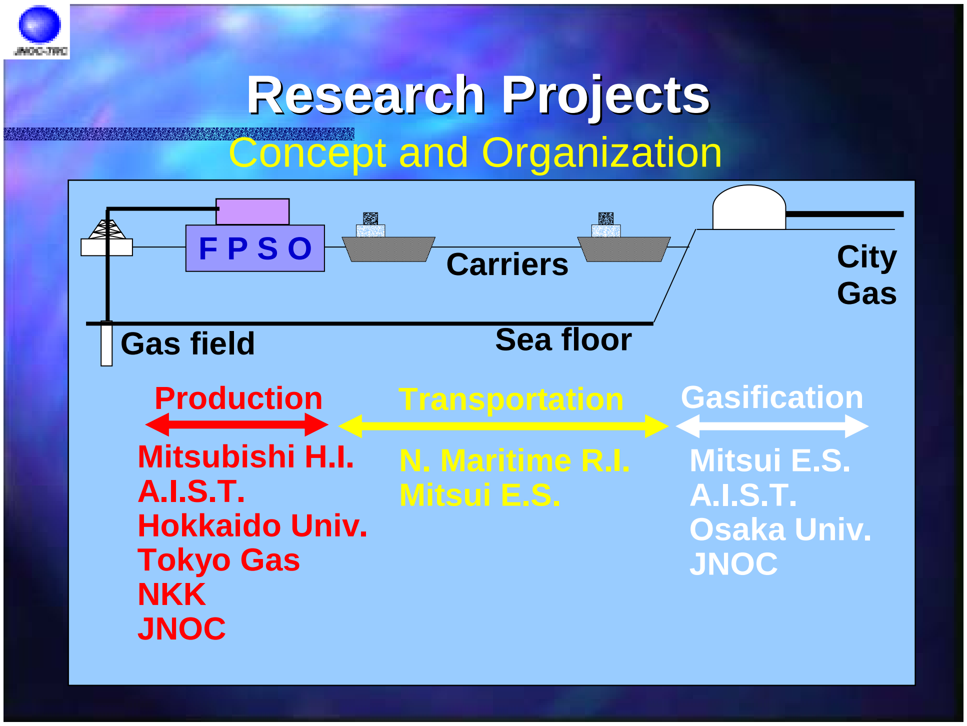

Properties of Gas Storage Media
High Pressure
Compressed Gas (1/200)
Hydrate (1/150)
Improved hydrate
LNG (1/600)
Pressure (MPa)
10
1
0.1
-163
0
30
Cryogenic Temperature
Temperature (⁰C)
Atmospheric condition
Much gas can be stored at milder conditions.


Cost Estimation (Initial)
(Gudmundsson, 1996)
(US$, Condition : 400MMscfd, 6500km)
Formation
Ship
Gasification
LNG
1,220
750
400
(2,370)
Hydrate
792
704
317
(1,813)
-23%

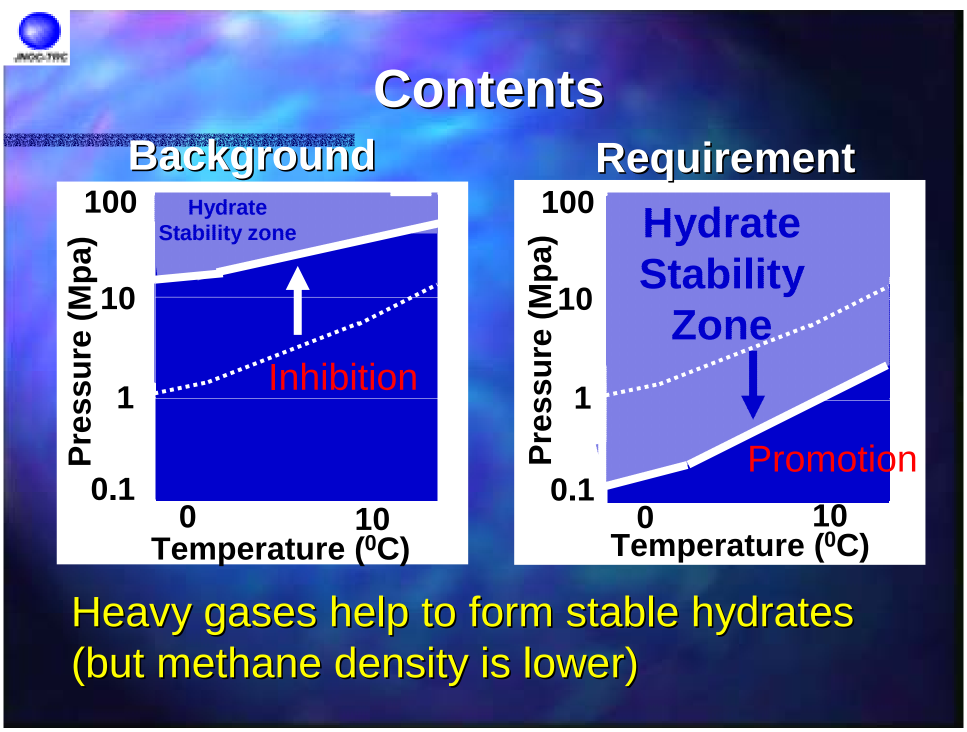

Cost Estimation (Operation)
Energy to be Carried = 100%
Consumed in Operation
10～15%
15～17%
LNG
Hydrate
Estimated to be mostly the same:
Milder, but 6/7 is water.


Numbers & Size of Conventional gas fields
LNG
GTL
Hydrates
500
15
50
78
5
234
1
260
0.5
276
0.25
475
0.1
1195
0.01Tcf
1913
Advantageous for mid-small gas fields ?

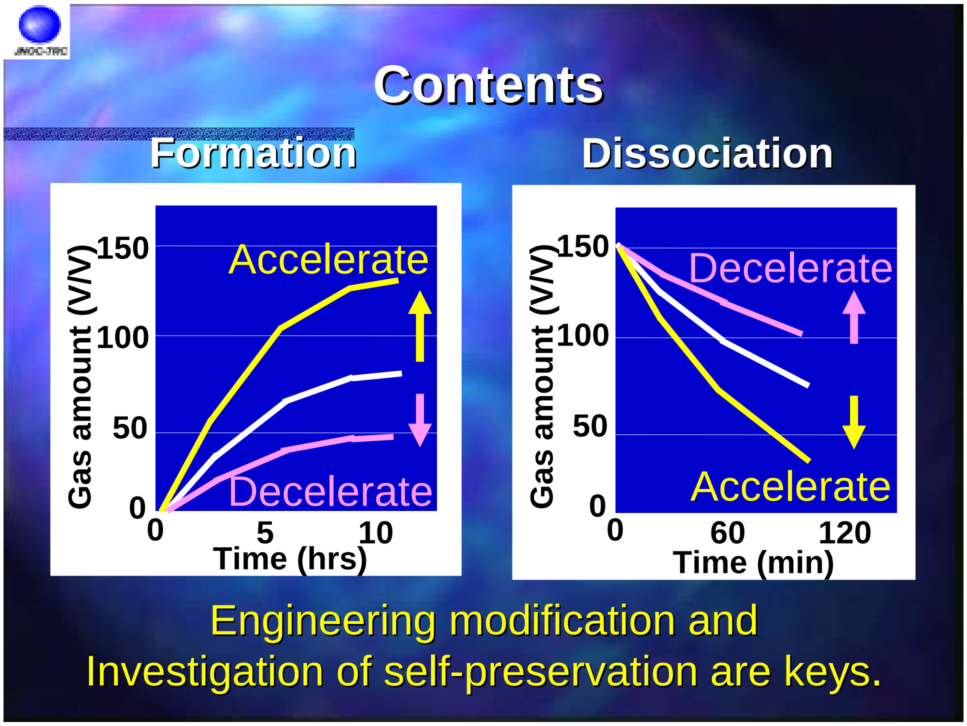

Targets
Applicable for Asian countries?

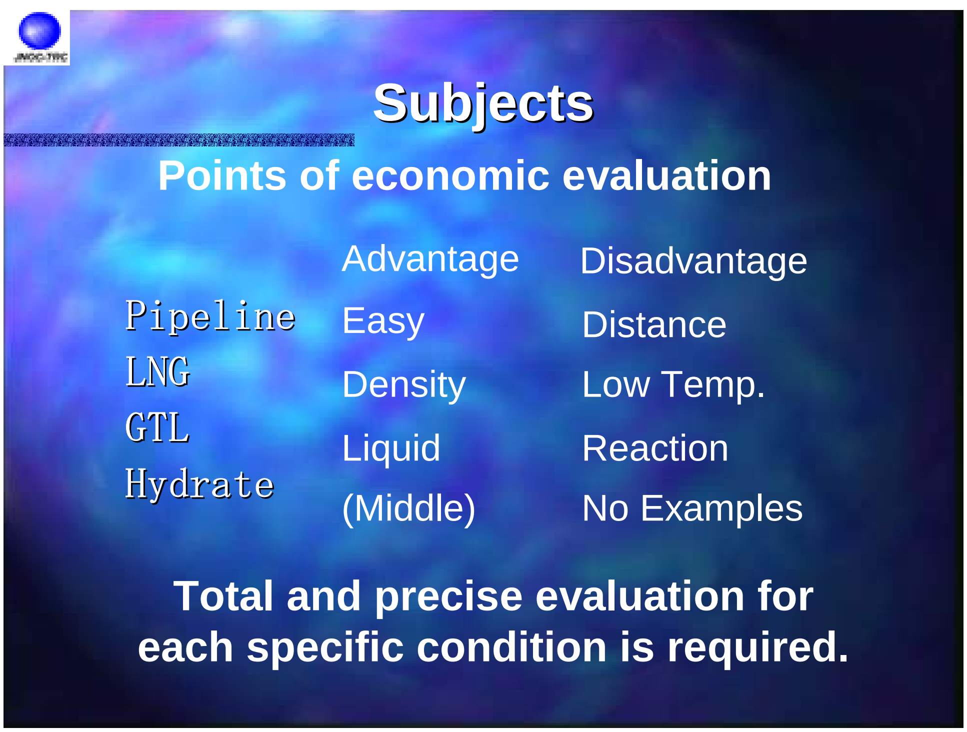


JNOC-TRC
Research Projects
Concept and Organization
F P S O
Carriers
City Gas
Gas field
Sea floor
Production
Transportation
Gasification
Mitsubishi H.I.
A.I.S.T.
Hokkaido Univ.
Tokyo Gas
NKK
JNOC
N. Maritime R.I.
Mitsui E.S.
Mitsui E.S.
A.I.S.T.
Osaka Univ.
JNOC



JNOC-TRC
Contents
Background
Requirement
Hydrate Stability zone
Inhibition
Hydrate Stability Zone
Promotion
Pressure (Mpa)
100
10
1
0.1
0
10
Temperature (⁰C)
Heavy gases help to form stable hydrates
(but methane density is lower)


JNOC-TRC
Contents
Formation
Dissociation
Gas amount (V/V)
150
100
50
0
0
5
10
Time (hrs)
Accelerate
Decelerate
Gas amount (V/V)
150
100
50
0
0
60
120
Time (min)
Decelerate
Accelerate
Engineering modification and
Investigation of self-preservation are keys.


JNOC-TRC
Subjects
Points of economic evaluation
Advantage
Disadvantage
Pipeline
LNG
GTL
Hydrate
Easy
Density
Liquid
(Middle)
Distance
Low Temp.
Reaction
No Examples
Total and precise evaluation for
each specific condition is required.

SESSION VI

International Interdisciplinary Scientific Network

Chairman: Mr. Art Johnson
Hydrate Energy International
Kenner, LA

Rapporteur: Dr. Michael Max
Marine Desalination Systems, L.L.C.
Washington, DC

2nd International Workshop on Methane Hydrate R&D
Washington Plaza Hotel - Washington, D.C.
October 29-31, 2002

"ODP Coring Equipment and Procedures for Studying Methane Hydrate on Leg 204 and a Proposal for Future Hydrate Research"

Dr. Frank R. Rack, Joint Oceanographic Institutions
1755 Massachusetts Ave., NW; Suite 700;
Washington, D.C. 20036-2102
Tel: (202) 232-3900, ext. 216; Fax: (202) 462-8754
Email: frack@joiscience.org
http://www.joiscience.org

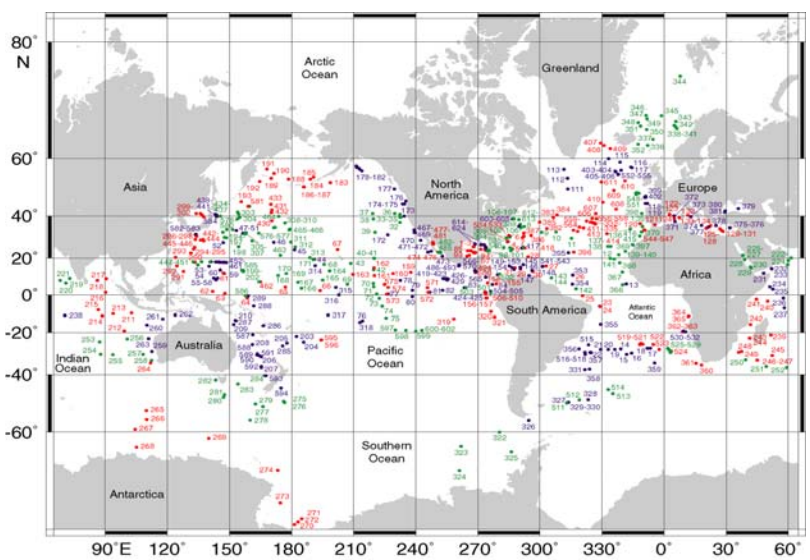
Achievements in scientific ocean drilling have set the stage for understanding the complex linkages among the different parts of the dynamic Earth system.

"The Deep Sea Drilling Project (DSDP:1968-1983) validated the theory of plate tectonics, began to develop a high-resolution chronology associated with study of ocean circulation changes, and carried out preliminary exploration of all of the major ocean basins except the high Arctic.

The Ocean Drilling Program (ODP: 1985-2003), capitalizing on DSDP's momentum, probed deeper into the ocean crust to study its architecture, analyzed convergent margin tectonics and associated fluid flow, and examined the genesis and evolution of oceanic plateaus and volcanic continental margins. ODP has also greatly extended our knowledge of long- and short-term climate change." **from "Earth, Oceans and Life" (2001) IODP Initial Science Plan, 2003-2013**

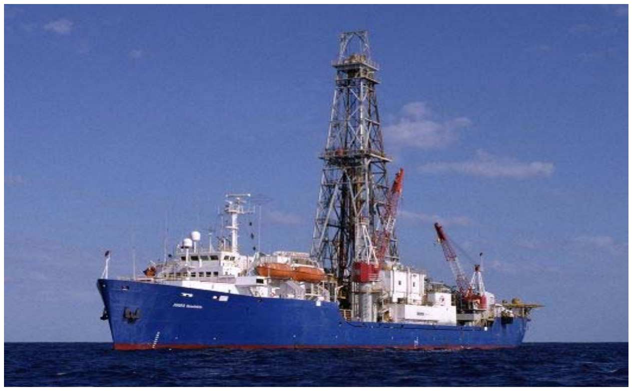
D/V *Glomar Challenger*

Deep Sea Drilling Project (DSDP) Sites



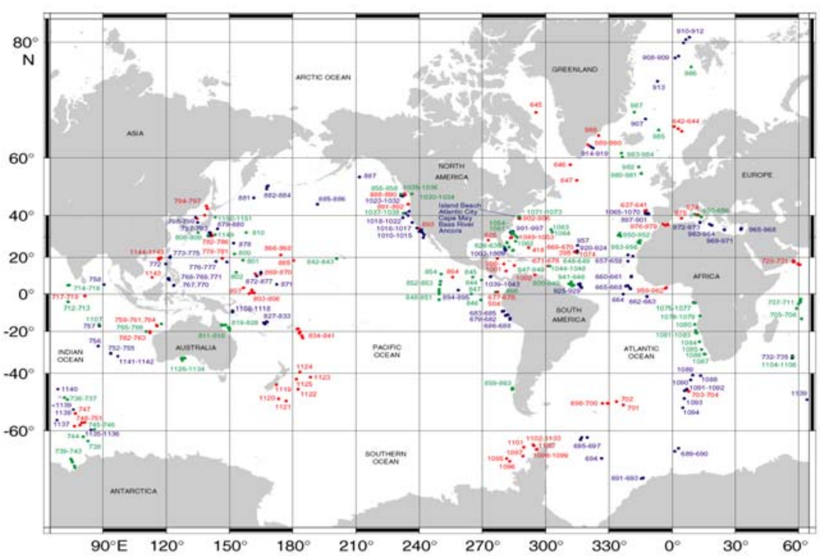
DSDP Legs 1-96, Sites 1-624

D/V JOIDES *Resolution*



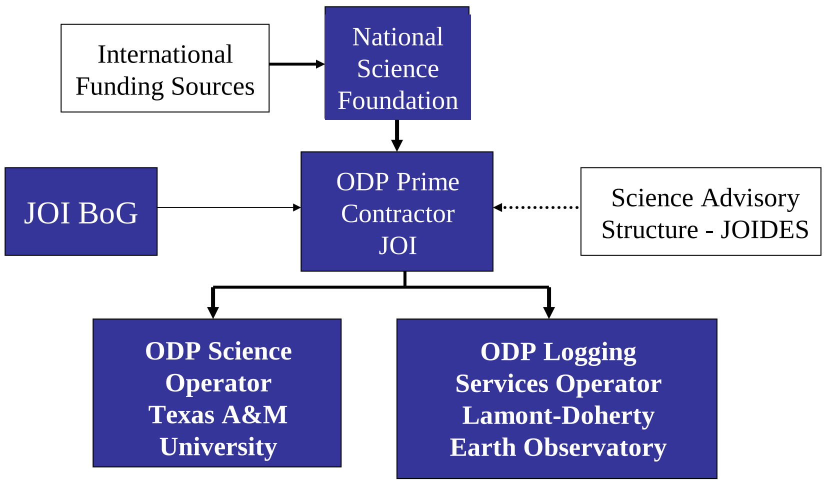
The JOIDES *Resolution* is a uniquely outfitted dynamically-positioned drill ship, that has a seven-story laboratory complex onboard. This vessel has been contracted for the Ocean Drilling Program (ODP) since 1985 to conduct worldwide scientific coring operations.

Ocean Drilling Program (ODP) Sites



ODP Legs 100-186, Sites 625-1151

ODP Management Structure



Joint Oceanographic Institutions (JOI)

- **A private, non-profit corporation based in Washington, D.C. that manages cooperative research programs for the international oceanographic and geoscience communities.**

- **JOI is a consortium of 18 U.S. academic/research institutions represented by the JOI Board of Governors (BoG).**

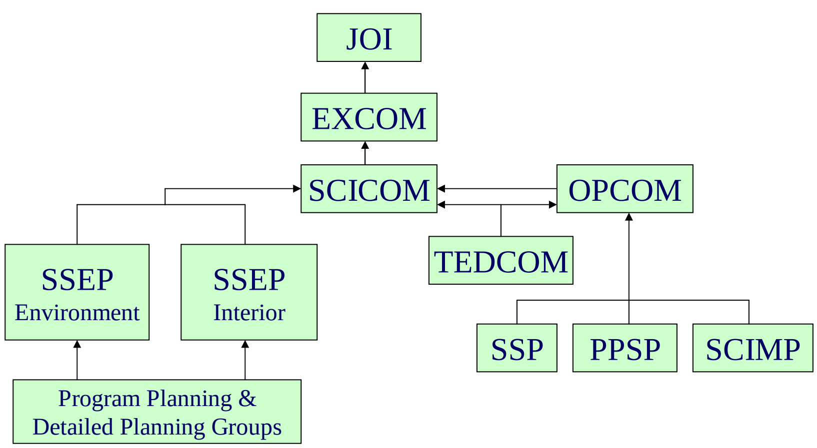
- **JOI is Prime Contractor to NSF for management of ODP, and for the cooperative agreement with NSF to manage the JOI/U.S. Science Support Program which funds the participation of U.S. scientists on the D/V *JOIDES Resolution*.**

JOI Board of Governors (BoG)

Chair: Robert Detrick

- **University of California, Santa Cruz - Department of Earth Sciences**
- **University of California, San Diego - Scripp's Institution of Oceanography**
- **University of Florida - College of Liberal Arts and Sciences**
- **Florida State University**
- **University of South Florida - *new**
- **University of Hawaii - School of Ocean and Earth Sciences and Technology**
- **Lamont Doherty Earth Observatory - Columbia University**
- **University of Miami - Rosenstiel School of Marine and Atmospheric Sciences**
- **University of Michigan - College of Literature, Science, and the Arts**
- **Oregon State University - College of Oceanic and Atmospheric Sciences**
- **Pennsylvania State University - *new**
- **University of Rhode Island - Graduate School of Oceanography**
- **Rutgers, The State University of New Jersey - Institute of Marine and Coastal Sciences**
- **Stanford University**
- **Texas A& M University - College of Geosciences and Maritime Studies**
- **University of Texas at Austin - Institute of Geophysics**
- **University of Washington**
- **Woods Hole Oceanographic Institution**

JOIDES Scientific Advisory Structure



Ocean Drilling Program (ODP)

- JOIDES Scientific Advisory Structure
- Drilling Platform(s)
- Core Repositories
- Databases
- Publications
- Information Services
- Web Sites
- Engineering Services
- Technology Development
- Logging Services
- Public Affairs
- Education and Outreach
- Site Surveys

Ocean Drilling Program
D/V JOIDES *Resolution*

Shipboard/Shorebased Database Environment

Ingest Data →

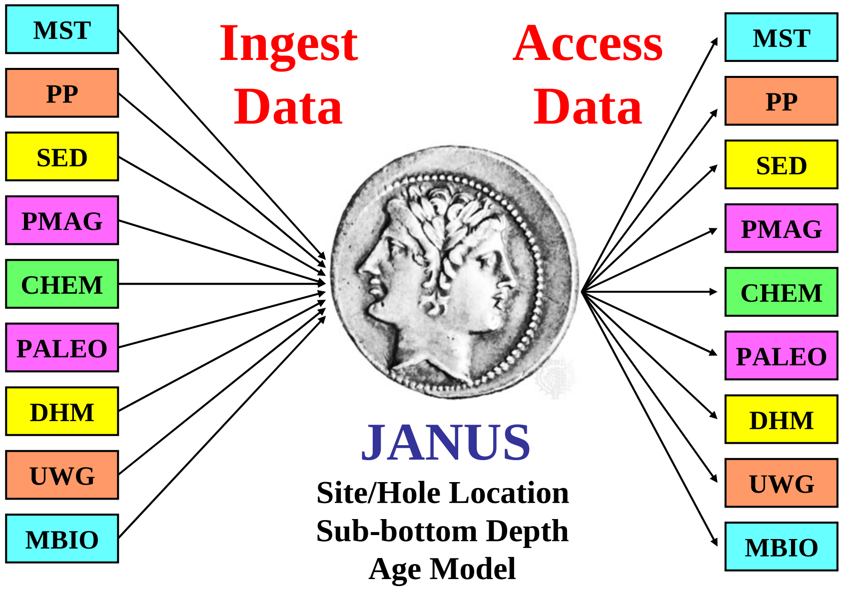
Calibration Data
Measurements
LabVIEW Interface
Data management

JANUS

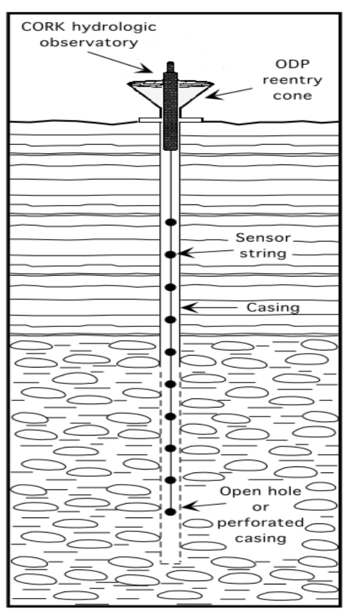
→ **Access Data**

Perform Queries
Generate Reports
Data Analysis
Data Visualization

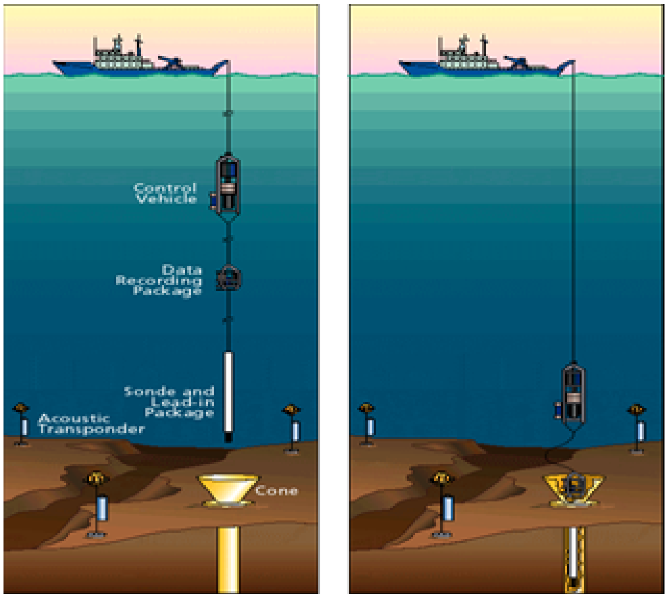
ODP Shipboard Database Environment

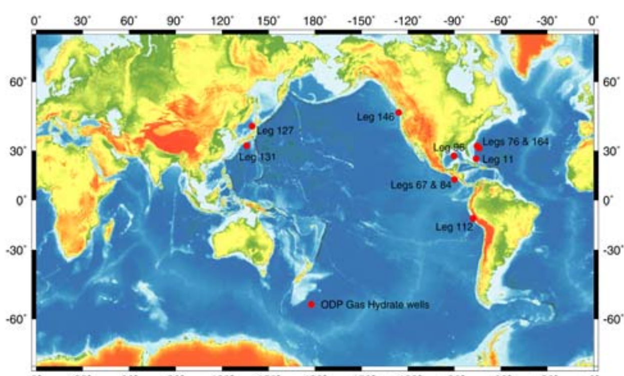


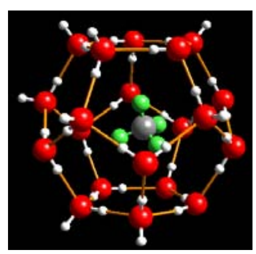
Schematic of CORK Hydrologic Observatory



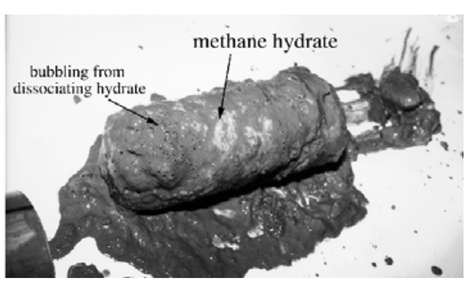
Wireline Re-entry into an ODP Borehole







ODP Studies of Oceanic Methane Hydrate Deposits



ODP Gas Hydrate Research Accomplishments

- **1970 - First BSR Drilled, Leg 11, Blake Ridge**
- **1979 - First Hydrate Core Recovered, Leg 67, Guatemala**
- **1980 - First Use of the PCB, Leg 76, Blake Ridge**
- **1982 - 1.5 m-long Massive Hydrate, Leg 84, Guatemala**
- **1983 - Microbes & Hydrates, Leg 96, Gulf of Mexico**
- **1986 - Hydrates in Lower Slope Seds (PCS), Leg 112, Peru**
- **1989 - Hydrates in Sea of Japan, Leg 127, near Japan**
- **1990 - Hydrates in Nankai Trough, Leg 131, near Japan**
- **1992 - Drilled through BSR, Leg 146, Cascadia**
- **1995 - 1st Dedicated Hydrate Leg, Leg 164, Blake Ridge**
- **2002 - 1st Dedicated Microbiology Leg, Leg 201, Peru Margin**

ODP/IODP Gas Hydrate Proposals

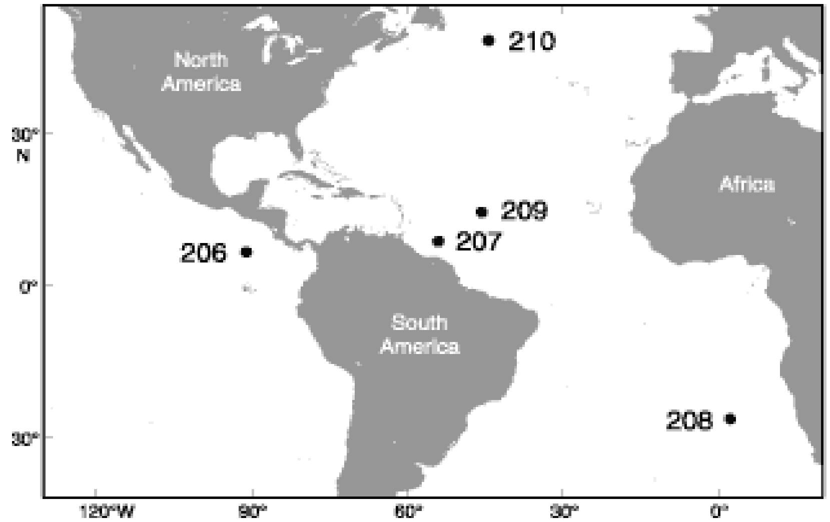
ODP Legs Drilled in 2002:

- **Peru Margin - BSR calibration & properties of hydrates; redefined as a dedicated microbiology leg - ODP Leg 201**
- **Oregon Margin - BSR calibration & characterization of gas hydrates on Hydrate Ridge - ODP Leg 204**

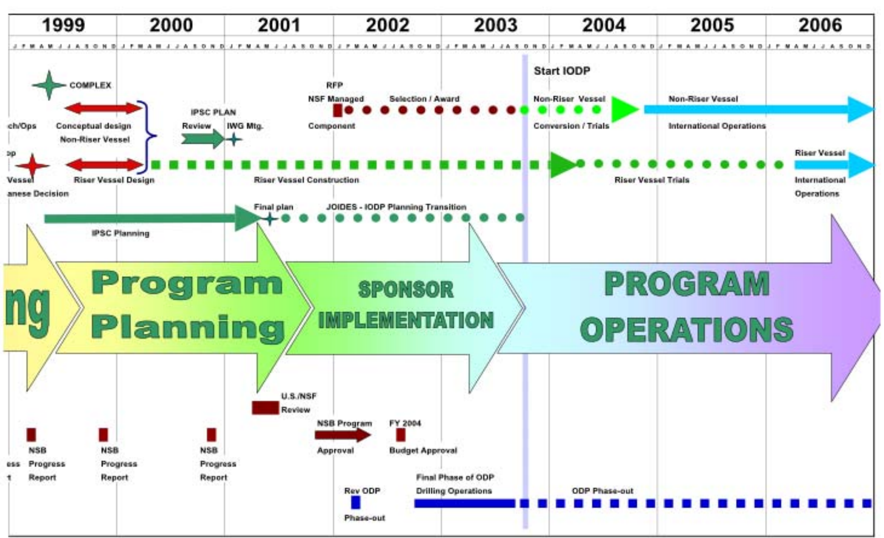
IODP Proposals being considered for drilling (post 2005):

- **Norwegian Margin - slope stability of the Storegga Slide**
- **Cascadia Margin - In situ measurements to constrain hydrate formation models**
- **Gulf of Mexico - Study of hydrates in a petroleum province**
- **Blake Ridge - Study of the dynamics of a large hydrate reservoir**
- **Nankai Trough - Study of hydrates in accretionary prism**

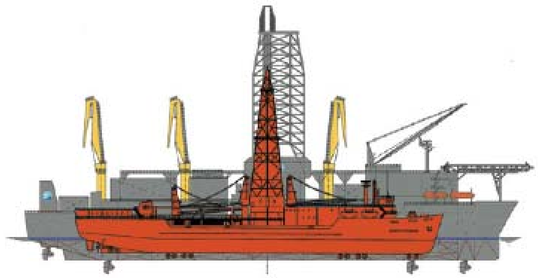
ODP Legs during FY03 using the D/V JOIDES Resolution (through September 2003 when ODP field programs end)



IODP SCHEDULE



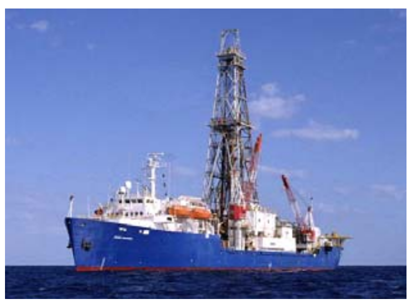
IODP - Multiple Drilling Platforms



- **Riserless drilling vessel**
- **Riser-equipped drilling vessel**
- **Mission specific platforms**

Riserless (continuous coring) Drillship
Capitalized by the United States

- **Currently used in ODP:** ***JOIDES Resolution***
- **NSF to release a request for proposals**
- **Operations begin 2005**



Riserless (continuous coring) Drillship
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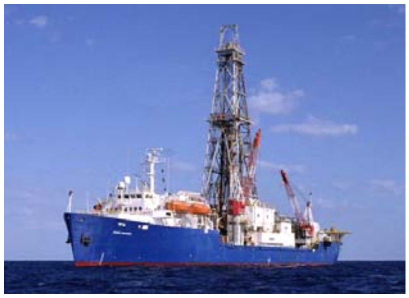


Mission Specific Platforms
Europe intends to provide

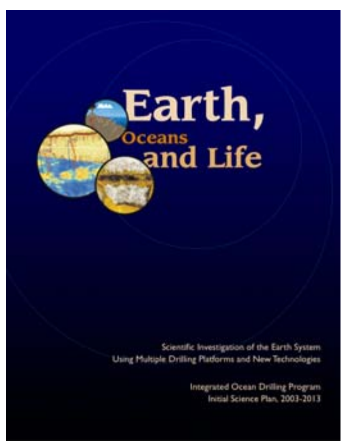
- Areas inaccessible to riserless and riser ships
- Necessary to accomplish goals of the Science Plan
- Case-by-case basis

International Working Group
Funding agency representatives planning the IODP

- Japan (co-chair)
- Germany
- UK
- European Commission
- Canada
- US (co-chair)
- China
- France
- Sweden
- Australia

Integrated Ocean Drilling Program
Initial Science Plan

- The Deep Biosphere and the Subseafloor Ocean
- Environmental Change, Processes and Effects
- Solid Earth Cycles and Geodynamics



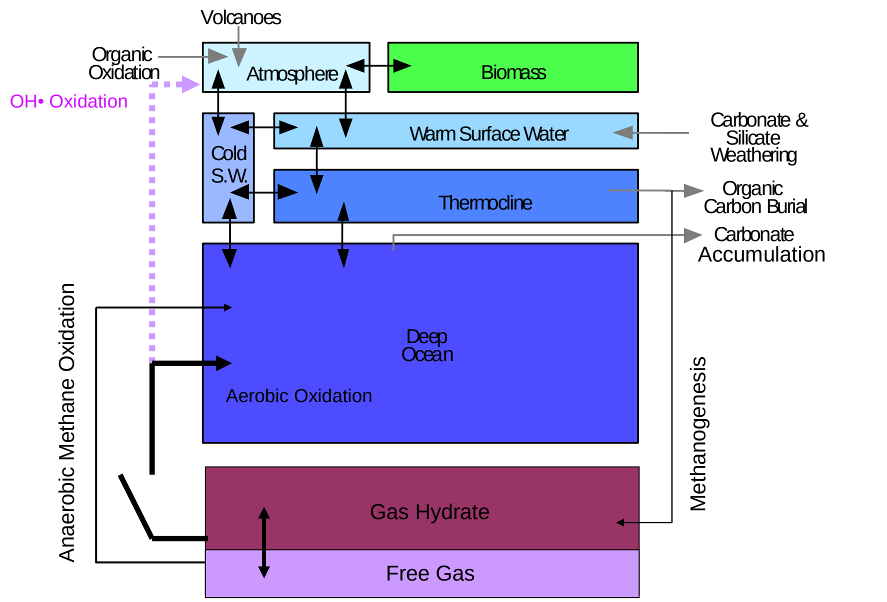
For more information: **http://www.iodp.org**

Interdisciplinary Collaborative Expeditions for a Year of Hydrate Observation and Perturbation Experiments (ICEY HOPE)

Proposal to use the D/V *JOIDES Resolution* (including shipboard laboratories, sampling, logging and downhole measurement tools) during a "window of opportunity" that begins immediately after September 30, 2003.

Focus on basic research to reduce uncertainties and improve our understanding about the role of natural gas hydrates (e.g., global carbon cycle, climate change, seafloor stability, resource potential, ocean observing systems, time series to examine dynamics of physical and biogeochemical processes).

A Global Carbon Cycle with a Gas Hydrate Capacitor



Dickens, AGU Monograph 124, 2001

What Is the Estimated Cost?

ODP Leg 204

NSF/ODP	**$5.3 Million U.S. Dollars**	**Shipboard Operations**
DOE/NETL	**$1.3 Million U.S. Dollars**	**JOI Cooperative Agreement**
NSF (Ewing)	***$0.5 Million U.S. Dollars (est.)***	**Offset/Walkaway VSPs**
EC-HYACINTH	***$1.0 Million U.S. Dollars (est.)***	**Pressure Coring Tests**
Subtotal	**$8.1 Million U.S. Dollars**	**Direct Operational Costs**
NSF/JOI-USSSP	**$0.8 Million U.S. Dollars**	**U.S. Science Support**
USGS/DOE	***$1.0 Million U.S. Dollars (est.)***	**Interagency Science Support**
International	***$1.0 Million U.S. Dollars (est.)***	**International Science Support**
Subtotal	**$2.8 Million U.S. Dollars**	**Science Support Costs**
Total Cost (est.)	**$10.9 Million U.S. Dollars**	**Shipboard & Postcruise**

A dedicated program of scientific drilling, installation of natural laboratories, and preliminary postcruise science studies for 1 year would cost approximately $50 Million U.S. dollars for a series of geographically distributed projects.

What Is the Timeframe for Action?

ODP field activities using JR will end on September 30, 2003.

For ICEY HOPE to be viable, planning needs to happen now and requests for funding by interested groups needs to be fast-tracked. Scientific justifications and relevant geophysical survey data should be available to locate sites to be drilled/cored/logged.

Commitments for field programs need to be in place by early 2003. Collaborations with other FY04 programs being planned may be possible (e.g., USGCRP, CCRI, CCTI).

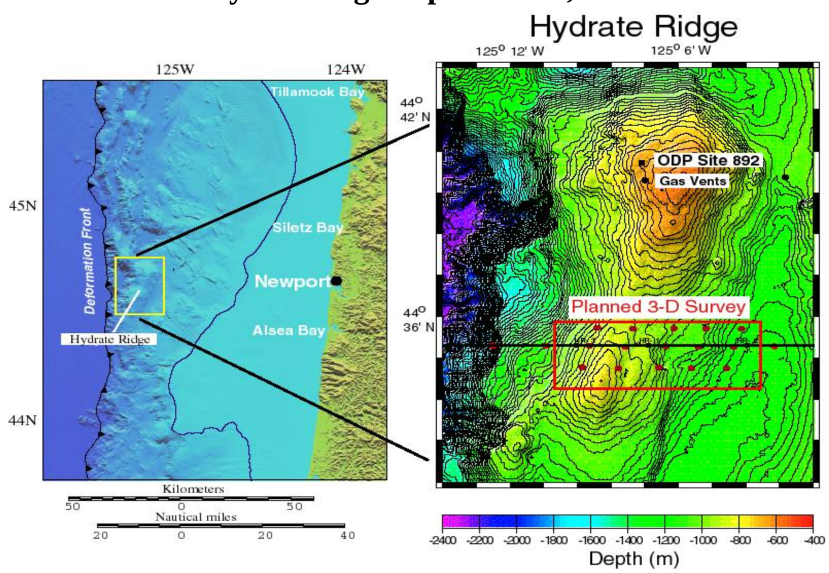
International projects are being sought (e.g., U.S., Japan, India, Canada, Germany, Norway, Central America, others?).

ODP Leg 204 can be used as a demonstration project for the type of activities that could be accomplished in other projects.

A hydrate database linked to a GIS framework will assist R&D.

ODP Leg 204: Hydrate Ridge

July 8 through September 6, 2002



Objectives for ODP Leg 204

(1) Compare the source region for gas and the physical and chemical mechanisms of hydrate formation between accretionary ridge and slope basin settings.

(2) Calibrate estimates of hydrate and underlying free gas concentrations determined with geophysical remote sensing techniques.

(3) Test, using geochemical tracers, physical properties measurements, and microstructural analysis, whether variations in bottom-simulating reflector (BSR) and sub-BSR reflectivity observed in seismic data result from tectonically induced hydrate destabilization.

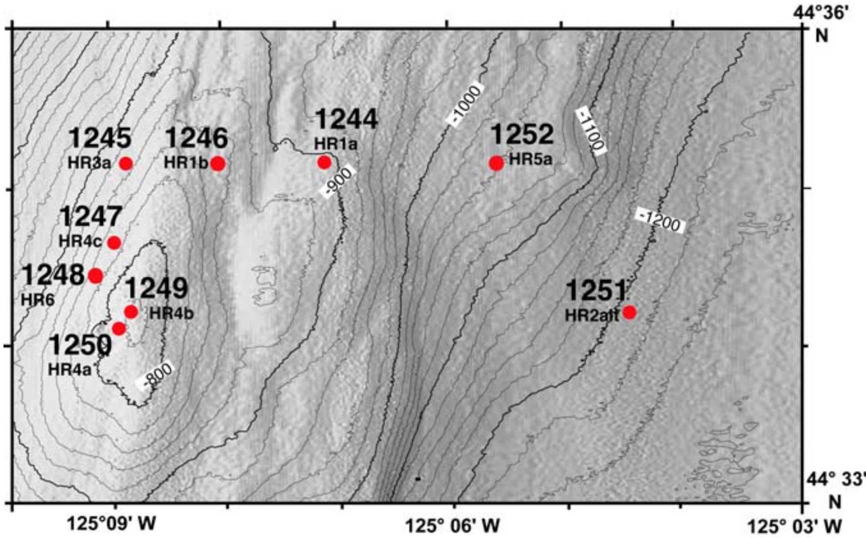
Objectives for ODP Leg 204

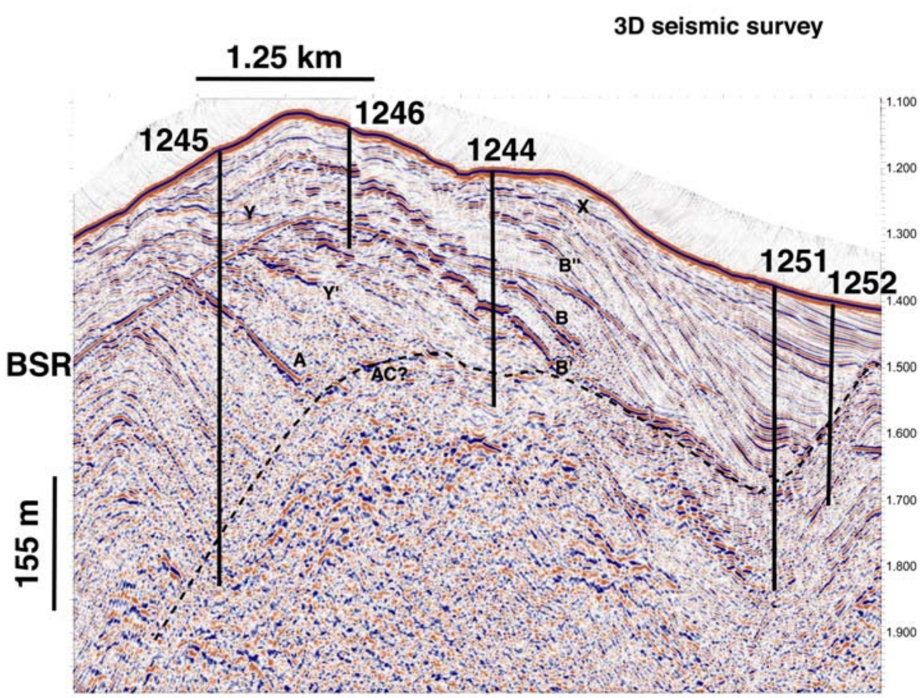
(4) Develop an understanding of the geochemical effects of hydrate formation in order to identify paleoproxies for methane release that can be used to integrate the geologic data into climate models.

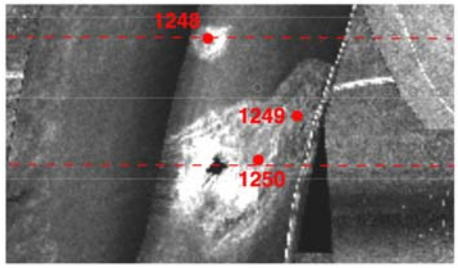
(5) Determine the porosity and shear strength of hydrate-bearing and underlying sediments in order to evaluate the relationships among hydrates, fluid flow and slope stability.

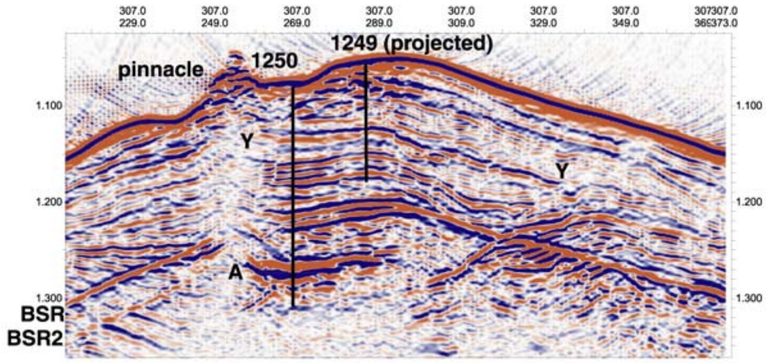
(6) Quantify the distribution of methanogenic and methanotropic bacteria in the sediments in order to evaluate their contribution to hydrate formation and destruction, and to sediment diagenesis.

ODP Leg 204 Site Locations

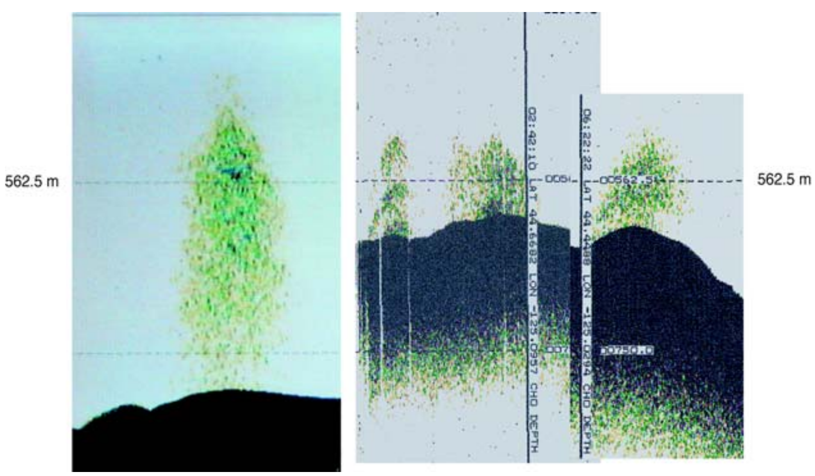




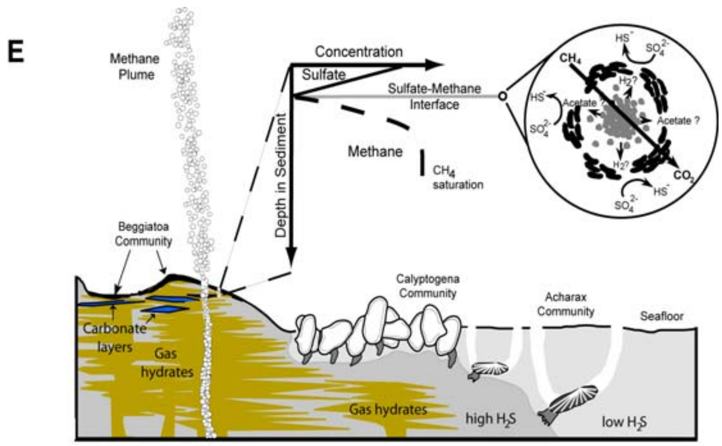




ODP Leg 204 - Hydrate Ridge
Plumes of Natural Gas at the Ridge Crest



ODP Leg 204 - Hydrate Ridge
Schematic of Biogeochemical Processes



Summary of Leg 204 Gas Hydrate Coring

- **Leg 204 began and ended in Victoria, B.C., Canada. The leg was planned as a 59.4 day leg - actually was 57.1 days long.**
- **50.4 days (88.3%) was spent operating; 6.7 days (11.7%) were spent in port and/or in transit to/from Hydrate Ridge.**
- **Overall, 9 Sites were drilled/cored, with a total of 45 Holes.**
- **Water depths of sites ranged from 788.5 mbrf to 1228.0 mbrf.**
- **Penetration depths varied from 9.5 mbsf to 540.3 mbsf.**
- **8 of 9 sites were drilled using LWD (resistivity-at-bit, NMR, density/neutron) technology.**
- **Eleven (11) holes were drilled using a tricone bit for LWD or wireline logging. Thirty-three (33) holes were cored using APC and/or XCB coring systems; 1 hole was cored with RCB.**

Summary of Leg 204 Gas Hydrate Coring

- Over 3674.5 meters of sediment were cored and 3068.3 meters of sediment was recovered (83.5% core recovery).

- Nine rendezvous with the D/V *JOIDES Resolution* took place during Leg 204; including 7 helicopters and 2 supply boats.

- 42 personnel were exchanged on/off the ship.

- A series of holes were dedicated to the rapid recovery and preservation of hydrate-bearing sediment cores for a "geriatric study" co-funded by DOE-NETL and NSF/ODP.

- 50 meters of hydrate-bearing core was recovered and stored in steel pressure vessels at 4ºC and 600 psi using methane gas. PVs are 3" I.D. rated to 3000 psi; Core is 2.66" O.D.

- 35 meters of hydrate-bearing core was recovered and stored in 8 liquid nitrogen cryo-freezers (160 liter capacity each).

Hydrate Core Samples Preserved in Liquid-Nitrogen at ODP Gulf Coast Repository, College Station, TX

Hydrate Core Samples Preserved in Liquid-Nitrogen at ODP Gulf Coast Repository, College Station, TX

ODP Technology for Characterizing Hydrates

- Advanced Piston Corer (APC); Extended Core Barrel (XCB); Rotary Core Barrel (RCB)
- In Situ Temperature Probes (APC-T; DVTP)
- In Situ Pore Pressure Dissipation Tool (DVTP-P)
- APC-Methane (P, T, C) Tool
- Shipboard Laboratory Facilities
- Pressure Core Sampler (PCS); PCS gas manifold
- HYACE/HYACINTH (cooperative relationship with European Commission); HRC, FPC, transfer chambers, pressure core logging system.

“Ocean Drilling Program (ODP) Engineering Tools and Hardware” ODP Technical Note #31

Tool Description Sheets are available online as PDFs.

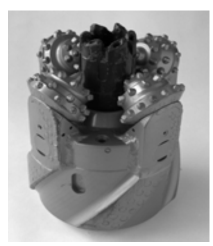
http://www-odp.tamu.edu/publications/tnotes/tn31/INDEX.HTM

Additional information about shipboard labs, drilling equipment, policies and procedures are available online at:
http://www-odp.tamu.edu/

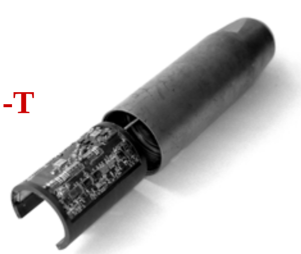
ODP Standard Coring Bits and Cutting Shoes

APC

XCB



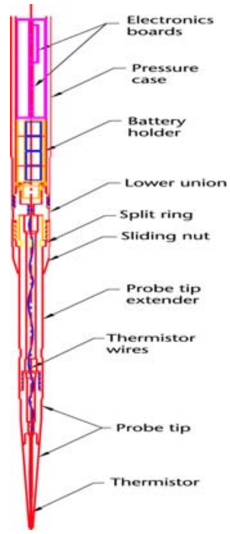
APC-T



RCB

Davis-Villinger Temperature/Pressure Probe (DVTP and DVTP-P)

The DVTP-P provides in situ pore pressure measurements, in addition to measurements of formation temperature.



Davis-Villinger Temperature Probe (DVTP)

APC-Methane Tool - TPC Sensors in APC Piston

Summary of Leg 204 Specialty Tool Deployments

- 81 out of 81 successful runs with the APC-Temperature Tool (memory tool that fits into APC coring shoe).

- 8 out of 8 successful runs with the Davis-Villinger Temperature Probe (DVTP).

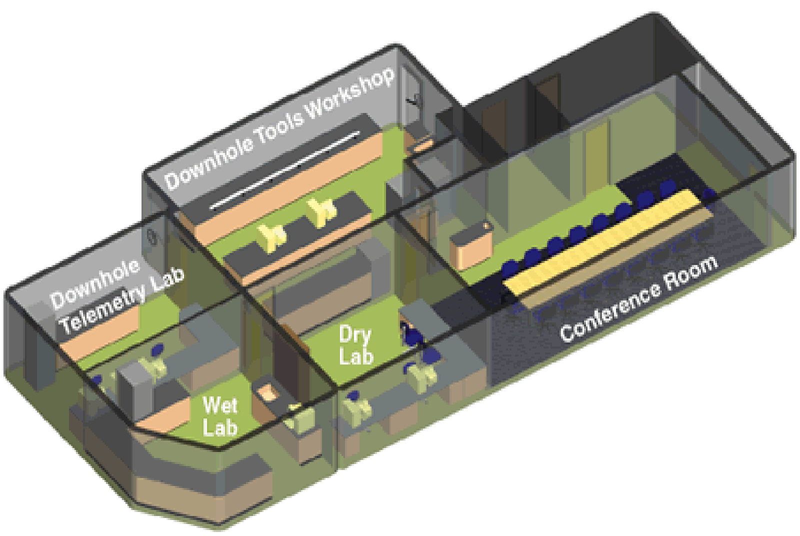
- 16 out of 16 successful runs with the Davis-Villinger Temperature Probe with Pressure (DVTP-P).

-1 out of 2 successful runs with the Fugro Piezoprobe tool, which measures pore pressure dissipation *in situ*. This tool is run on the Schlumberger logging cable (real-time) as opposed to the wireline deployment of the DVTP-P (data in memory).

- 107 out of 110 successful runs with the APC-methane Tool, which includes Temperature, Pressure, and Conductivity sensors in the APC piston head (time series measurements).

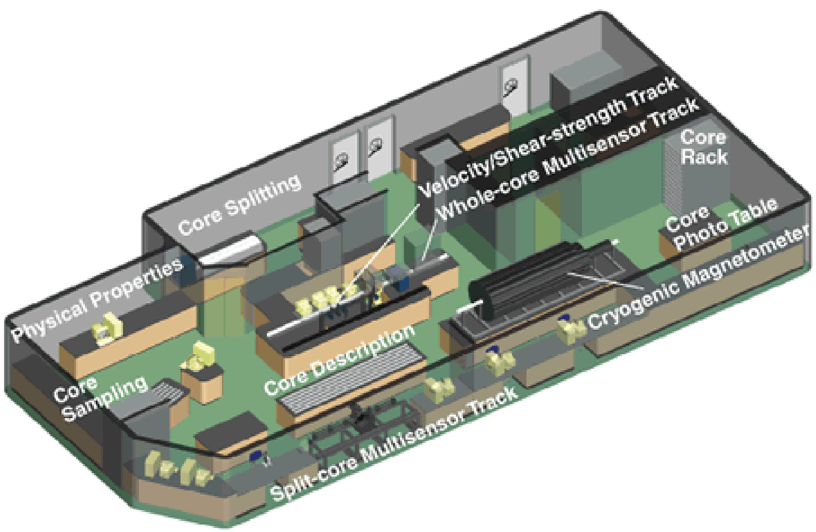
D/V *JOIDES Resolution* Labstack
"A Floating University for Geoscience Research"

7th Level - D/V *JOIDES Resolution* Labstack



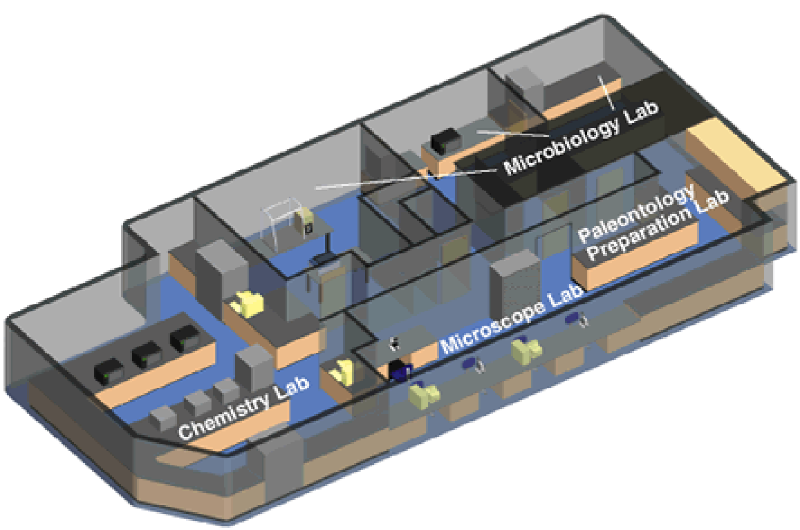
Leg 204 Post-Site Scientific Results Discussion

6th Level - D/V *JOIDES Resolution* Labstack

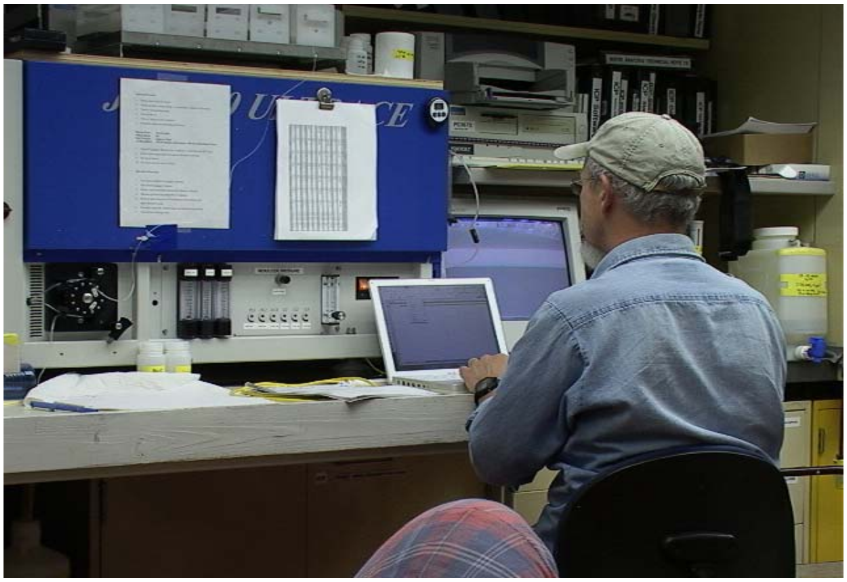


Catwalk Handling of Sediment Cores after Recovery

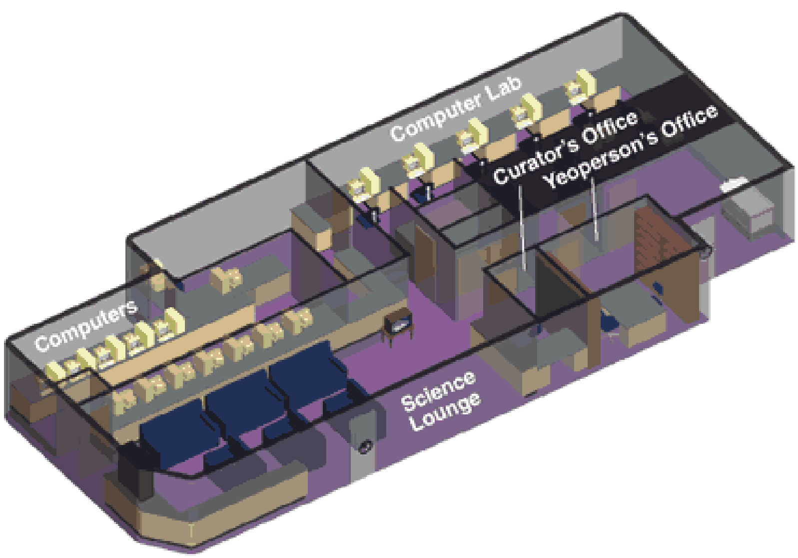
5th Level - D/V *JOIDES Resolution* Labstack



Geochemical Analysis of Samples using ICP-ES



4th Level - D/V *JOIDES Resolution* Labstack



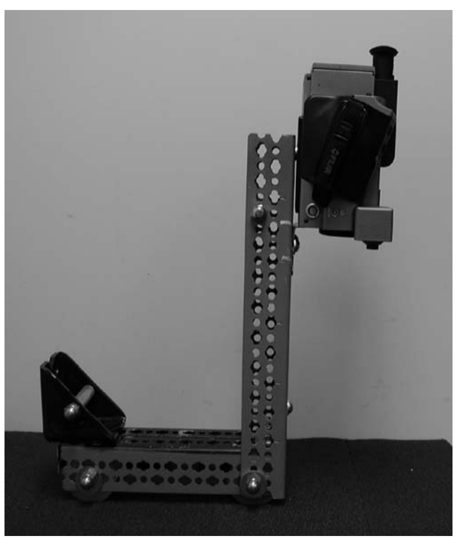
JOI/ODP Proposal to U.S. DOE “Methane Hydrates” Solicitation

“In-Situ Sampling and Characterization of Naturally Occurring Marine Methane Hydrate Using the D/V JOIDES Resolution”. $1,288,202 awarded (including cost-share) in Phase 1 of this cooperative agreement.

Make upgrades to the ODP Pressure Core Sampler (PCS), PCS gas manifold, ODP memory tools (DVTP, DVTP-P, APC-methane, APC-T tools) for use on Leg 204.

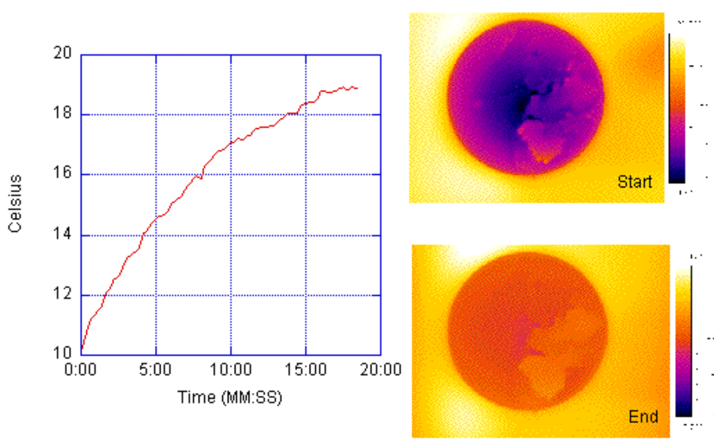
Acquire equipment to characterize methane hydrates (e.g., G/GI Seismic Guns, Infrared Thermal Imaging System); modify the FUGRO piezoprobe tool for use with the ODP bottom hole assembly (BHA).

Infrared Thermal Imaging of Sediment Cores to Detect Gas Hydrates in the Core Liner.



Infrared Thermal Imaging of Sediment Cores to Detect Gas Hydrates in the Core Liner.

Infrared Thermal Imaging of Sediment Cores to Assess Core Handling Protocols.



Anaerobic Sampling for Microbiology in a Nitrogen Glove Box

ODP Radioisotope Van for Microbiological Investigations

Technical Advancements - ODP Leg 204

Provided by DOE-NETL funding to JOI, LDEO and National Labs

IR Imaging Track - Automated acquisition of thermal imaging data

PCS Gas Manifold Data Logging System

ODP-Logging Chamber (ODP-LC) for use with GEOTEK Vertical-Multi-Sensor (pressure) Core Logger

GI guns - seismic energy source for VSP experiments

Schlumberger Nuclear Magnetic Resonance (NMR) LWD Tool - LDEO/BRG

X-Ray Linear Scanner - Lawrence Berkeley National Laboratory (Barry Freifeld)

Geriatric Study - Cores preserved in refrigerated van using Cryo-Freezers and Pressure Vessels (at 4ºC and 600 psi)

Pressure Coring of Methane Hydrates on Leg 204

ODP Pressure Core Sampler (PCS): wireline-retrievable, top-drive rotary/push; standard tool; 42 mm diameter, up to 86 cm-long core; 10,000 psi (690 bar) max. pressure; 2 sampling ports. Gas manifold system mates to tool for measuring gas volume and composition of gas.

FUGRO Pressure Corer (FPC): wireline-retrievable, percussion/push; prototype tool; 50 mm diameter, up to 100 cm-long core; 3625 psi (250 bar) max. pressure; 1 sampling port.

HYACE Rotary Corer (HRC): wireline-retrievable, downhole mud motor rotary/push; prototype tool; 58 mm diameter, up to 100 cm-long core; 3625 psi (250 bar) max. pressure; 1 sampling port.

JOI/ODP Proposal to U.S. DOE
"Methane Hydrates" Solicitation

Task 1.1: Preliminary Evaluation of Existing Pressure/Temperature Coring Systems.

Report available online at DOE/NETL website.
http://NETL.CERTREC.COM
Login: NETL
Password: ARCHIVE
Go to Bottom of List (52.4 MB file)
HYD_00037_2001.PDF

739 page summary of information available from Technical Notes, JOIDES meetings, Web Pages, and other information sources.

ODP Pressure Coring System (PCS)