Preprint
UCRL-JC-145774

Final Report for the September 2001 Workshop on Physical and Chemical Property Measurements for the Gas Hydrate R&D Community

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This article was submitted to
2001 Workshop on Physical and Chemical Property Measurements for the Gas Hydrate R&D Community, Moss Landing, CA, September 17-18, 2001

U.S. Department of Energy
Lawrence Livermore National Laboratory

October 1, 2001

Approved for public release; further dissemination unlimited

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This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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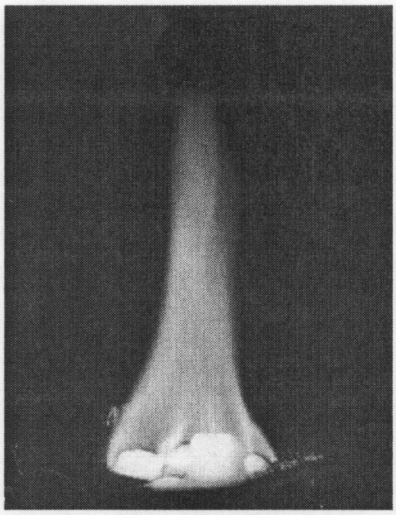
Final Report for

the Workshop on

PHYSICAL AND CHEMICAL PROPERTY MEASUREMENTS FOR THE GAS HYDRATE R&D COMMUNITY

17 –18 September 2001

Monterey Bay Aquarium Research Institute (MBARI)
Moss Landing, California



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SUMMARY

A 2-day workshop "Physical and Chemical Property Measurements for the Gas Hydrate R&D Community" was held on 17-18 September 2001. Putting together this workshop was a joint effort by LLNL, MBARI and the USGS, Menlo Park. Twenty-two people from a wide variety of institutions and backgrounds participated. An additional eighteen people were forced to cancel at the last minute due to the events of 11 September 2001.

The premise of the workshop was that progress in nearly every aspect of gas hydrate research depends fundamentally on the availability of high-quality property data and the development of laboratory insights into the physics and chemistry that govern gas hydrates in nature. One objective of the workshop was to develop a dialogue between laboratory scientists who make property measurements of gas hydrates and scientists who use these data for quantitative modeling. A second objective was to help facilitate research among experimentalists and the acquisition of reliable gas hydrate properties. The latter focused mainly, but not exclusively, on researchers from institutions in the San Francisco Bay Area to energize a community that has a geographic advantage in collaborative relationships.

The workshop was successful at meeting both of these objectives, although the unique perspectives of the invitees who weren't able to attend were missed. After reviewing the current state of gas hydrate R&D with respect to property measurements, there was general agreement that it is time to move forward with new approaches (e.g., seafloor experiments, lab experiments with hydrate-sediment aggregates) and new applications of techniques (e.g., improved seismics, in situ x-ray and neutron diffraction and tomography, and NMR scanning). The workshop consensus is summarized at the end of this document in a table of fundamental questions pertaining to natural gas hydrates and possible experimental lab and seafloor approaches to answering them.

TEXT FROM PRE-WORKSHOP BROCHURE

Organizing Committee
Nina Rosenberg (LLNL)
William Durham (LLN)
Stephen Kirby (USGS, Menlo Park)
Peter Brewer (MBARI)

Background
Experiments on gas hydrates include studies of the processes of formation, dissociation, and dissolution, as well as relevant physical properties (e.g., thermal, acoustic, strength and rheological, electrical and magnetic). Issues for discussion are identification of data gaps; the quality, internal consistency and relevance of existing data; and comparison between man-made and natural hydrates and their mixtures with sediments.

Gas hydrate applications include estimation of gas hydrate distribution using seismic exploration and other methods; development of methods for gas production from hydrate-bearing sediments; assessment and reduction of deep-water seafloor hazards; and understanding the natural formation and decomposition of gas hydrates and their interactions with Earth's climate.

Progress in each of these areas depends fundamentally on the availability of high-quality property data and development of laboratory insights into the physics and chemistry that govern gas hydrates in nature.

The workshop will include mainly researchers from institutions in the San Francisco Bay Area to energize a community that has a geographic advantage in collaborative relationships, but will include a few close colleagues from outside this area. Participation in this workshop is limited and by invitation only.

Objectives
The objectives of this workshop are to:
(1) Develop a dialogue between laboratory scientists who make property measurements of gas hydrates and scientists who use these data for quantitative modeling and (2) Help facilitate research among experimentalists and the acquisition of reliable gas hydrate properties.

(Original) Program Schedule

Monday 17 September

730-830	Registration/Continental Breakfast

830-900	Introductory Remarks

900-1200 (*break included*)

PANEL 1. Hydrates: Measurement Challenges

Co-Chairs: Kirby and Durham

Ripmeester	Instrumental methods for the analysis of hydrate structure, composition and kinetics
Chou	Transformations and characterizations of methane hydrates at elevated pressures
Chakoumakos	Physical and thermodynamic properties of gas clathrate hydrate determined by *in situ* neutron scattering
Kirby	Towards a robust, self consistent and critical reference suite of physical properties of sI methane hydrate and mixed hydrocarbon sII hydrates: inter-lab standards, thermodynamic constraints and coordination recommendations
Durham	Deformation-induced gas hydrate decomposition
Dvorkin	Rock physics of sediments with gas hydrate

1230-1330	LUNCH (*catered*)

1330-1530

PANEL 2. Data Needs and Gaps

Co-Chairs: Buffet and Brewer

Speakers

Buffet	The role of numerical models in integrated studies of the formation and decomposition of marine gas hydrates
Ruppel	Constraining the hydrodynamics of gas hydrate reservoirs through models and observations
Moridis	Knowledge gaps in gas hydrate simulation for resource recovery
Colwell	Experimental needs of the microbiologist studying gas hydrates

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1530-1700	Tour of R/V *Western Flyer*

1700-1730	Keynote Speech: Keith Kvenvolden (USGS), Gas hydrate in the global organic carbon cycle
1730-1800	Open Discussion

1800-1930	DINNER at Phil s Fish Market

1930-2130	Poster Session
2130	Adjourn for the day

Tuesday 18 September

730-830	Continental Breakfast

830-1200 (*break included*)

PANEL 3. Hydrates in the Real World

Co-Chairs: Paull and Kleinberg

Speakers

Brewer	Physical properties of CO_2 Hydrate films
Winters	Physical properties of samples containing natural and laboratory formed gas hydrate
Kleinberg	Nuclear magnetic resonance of hydrate-bearing rock and sediment: assay, pore size control, and hydraulic permeability
Rector	Seismic identification of gas hydrates: laboratory experiments and real world issues
Paull	Gas hydrates: What we need to know versus what we can currently measure.

1200-1300	LUNCH (catered)

1300-1530

PANEL 4. Putting a Measurements Program Together

Co-Chairs: Rosenberg and Durham

Speakers

Max	Development of an applied hydrate research program
Jones	Proposed work plans for the Gulf of Mexico hydrate joint industry project

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1530-1545	Closing Remarks
1545	End Formal Workshop
1545+	Informal Discussions

SUMMARY OF WORKSHOP PRESENTATIONS

(Note: Some changes were made to the original program because of the fact that several of the original speakers were not able to attend at the last minute. Gregor Rehder (MBARI), Laura Stern (USGS/Menlo Park), Izou Aya (Maritime Research Institute, JAPAN), David Scholl (USGS/Menlo Park) and Jeff Wright (Chevron) were added to the program as speakers.)

PANEL 1. HYDRATES: MEASUREMENT CHALLENGES

Chakoumakos (ORNL), Physical and thermodynamic properties of gas clathrate hydrate determined by in situ neutron scattering

Bruce Chakoumakos discussed the work he and Claudia Rawn have been doing at Oak Ridge National Laboratory (ORNL) on gas hydrates using neutron scattering and synchrotron x-ray methods to study the structure and dynamics of synthetic clathrate hydrates. This method allows for the determination of crystal structure data as a function of temperature, pressure and composition, which can be used to calculate thermal expansion, compressibilities, hydrate number, cage filling, quantitative phase analysis, and other structural parameters. They have found that, in practice, diffraction data from samples that are fully deuterated (or with a deuterated molecular-water framework) yield the lowest background intensities and the most precise results. They have also started doing *in situ* scattering studies using custom designed sample cells that can be used for kinetic studies of phase formation, and decomposition, and polymorphic phase transformations.

Kirby (USGS, Menlo Park), Towards a reliable, self consistent and relevant reference suite of physical/chemical properties of hydrocarbon clathrate hydrates

Steve Kirby asked three basic questions about gas hydrates property measurements: Are measured properties reliable? Are measurements self consistent? Are lab measurements relevant to real-world hydrates? With respect to the issue of reliability, he stressed that results should be independent of measurement method when made on comparable, well-characterized sample material and that verification of the reliability of a measurement method should be made using standard materials, such as water ice, for which physical properties are well known. Preference should be given to methods involving measurements inside the hydrate synthesis pressure vessel and avoiding measurements involving the preservation by immersion in liquid nitrogen and 1-atm handling, a method that tends to reduce measurement reproducibility. With respect to the issue of self-consistency, he stressed that there are several thermodynamic constraints that can and should be used linking independent measurements (e.g., comparing values for thermal diffusivity vs. thermal conductivity, and adiabatic vs. isothermal elastic bulk moduli). With respect to the relevancy issue, he stressed that we need to stay mindful of the fact that recovered natural hydrate samples are partially decomposed and that we don't fully appreciate how structures, hydrate numbers, and gas compositions of natural hydrates drill core and grab samples might be altered during sample recovery, transport,

and storage, and whether these alterations are significant with respect to property measurements. These present limitations of our present knowledge of natural hydrates make it difficult to determine how closely lab-made hydrates compare with those in nature.

Durham (LLNL), Gas hydrates: Lab measurement principles

Bill Durham stressed that gas hydrates in natural systems represent a level of complexity that does not lend itself to straightforward experimental investigation of physical properties. He emphasized that at this early stage of research there are two experimental principles that are important to follow: (1) Keep it simple, and (2) Expect the unexpected, particularly for gas hydrates. Laboratory measurements are easiest to interpret when experimental conditions and sample composition are closely controlled and precisely defined. Understanding physical and chemical behavior of unknown systems should begin with characterizing the properties of end-member compositions. For example, the thermal conductivity of an aggregate of sediment, water, and gas hydrate, is a function of the conductivity of the individual phases, the concentration and distribution of those phases and perhaps the properties of the interfaces between phases. Regarding unexpected behavior of gas hydrates in the lab, he talked about his observations of instability during handling and long-term storage, anomalous preservation, very low thermal conductivity, very high ductile strength and recent evidence that methane hydrate even deep within its stability field can dissociate during inelastic deformation.

Dvorkin (Stanford), Rock physics of sediments with gas hydrate

Jack Dvorkin first reviewed some of the basics of rock physics and seismology as applied to studies of gas hydrates. He stressed the importance of using well logs for calibrating the interpretation of seismic measurements, and asked the group to think about laboratory experiments that might make gas hydrates in sediments in ways similar to nature. He also stressed the importance of understanding the physics behind the trends of physical properties with changes in phase composition of mixed-phase aggregates, such as the effects of gas hydrate saturation on wave speeds and the important roles of hydrate/sediment textures in determining how hydrates affect the properties of sediment columns. Such insight will allow extension of knowledge to other settings. His message for estimating the effects of hydrates is: Measure, Relate, and Understand.

PANEL 2. DATA NEEDS AND GAPS

Moridis (LBL), Knowledge gaps in gas hydrate simulation for resource recovery

George Moridis reported on the challenges of simulating methane production by heating gas hydrates reservoirs and on the results of his numerical modeling of this process. These models have shown him which property parameters are the most important. Key parameters include: enthalpy values for hydrate dissociation (which can be different from values for hydrate formation due to hysteretic behavior), methane solubility in this system (especially near the hydration point), thermal conductivity of the hydrate-sediment medium, and the effect of hydrate on the fluid flow properties of the medium

(e.g., permeability), including identifying and formulating the roles of capillary effects. He emphasized that, although the mathematics of these simulations are not a problem, gaps in knowledge of these properties are a problem. He is leading an effort at LBNL and USGS to use x-ray scanners and x-ray tomography to track hydrate breakdown fronts inside pressure vessels and thereby verify the results of numerical modeling. An initial encouraging result from this effort suggests that hydrate and ice have significantly different x-ray attenuation properties and hence suggest that a decomposition front may be imaged.

Rehder (MBARI) & Stern (USGS Menlo Park), Dissolution rates of synthetic hydrates

Gregor Rehder and Laura Stern reported on tests of specimens of laboratory-grown CH_4 and CO_2hydrate that were transported to the ocean in a pressurized transport vessel for dissolution experiments in undersaturated seawater at about 1000 m depth. Key video segments of these experiments were shown to the group. The CO_2 hydrates were completely dissolved after less than 4 hours. The CH_4 hydrates dissolved much more slowly. The ratio of the dissolution rates of the CO_2 and CH_4 hydrates was about 11 and they explained this result using a diffusive sublayer model for gas hydrate dissolution. The results of this work may have major implications. The fast dissolution rate of CO_2-hydrate is comparable to the rate of dissolution of liquid CO_2, which implies that gas hydrate formation does not significantly affect the residence time of CO_2 in a "deep-sea lake" CO_2-sequestration scenario. The measured dissolution rate of several mm methane hydrate per day in undersaturated seawater suggest that long-term survival of seafloor hydrate outcrops observed today must be sustained by continued hydrate regrowth.

Rehder (MBARI), Enhanced lifetime of methane bubble streams within the deep ocean

Gregor Rehder reported on direct comparisons of the dissolution and rise rates of methane and argon bubbles experimentally released in the ocean at depths from 440 to 830 m. The bubbles were injected from the ROV Ventana into a box open at the top and the bottom, and imaged while in free vertical ascent. The vehicle was piloted upwards at the rise rate of the bubbles. Methane and argon showed closely similar rise rates and shapes at depths above the methane hydrate stability field. Below that boundary (~520 m) methane bubbles tended to be much more spherical and markedly enhanced methane bubble lifetimes were observed, probably because a layer of methane hydrate formed around the bubbles. This effect greatly increases the ease with which methane gas released at depth, either by natural or industrial events, can ascend through the shallow ocean layers and perhaps enter Earth's atmosphere.

Scholl (USGS, Menlo Park), Large deposits of massive hydrate in the Bering Sea: wonderments about an acoustic image of a formation process

Dave Scholl discussed acoustic signatures of large (1-2 km in diameter, 0.1-0.2 km in thickness) bodies of massive (i.e., >30% of available pore space) accumulations of

methane hydrate beneath the Bering Sea. These anomalous velocity signatures, termed VAMP (Velocity-Amplitude) structures, reveal evidence of regional, localized, and smaller scale processes of the *in situ* formation of hydrate deposits. His modeling of the seismic reflection records shows that each of these VAMP targets probably represents a major submarine gas field and that there are probably several thousand such VAMPs beneath the Bering Sea. Unlike the low-yield disseminated hydrate deposits beneath continental margins, VAMPs probably represent concentrated, high-yield deposits that are easily prospected by seismic methods. He urges that lab measurements be used to calibrate and refine estimates of the hydrate deposits in these structures.

KEYNOTE SPEECH

Kvenvolden (USGS, Menlo Park), Gas hydrate in the global organic carbon cycle
Keith Kvenvolden talked about natural gas hydrate reservoirs in the shallow geosphere and their role as both a sink for and a source of methane. He compared this action to a capacitor (or, as he prefers to call it, a condenser) in a simple electrical circuit. A resonant circuit analogue couples the condenser with a resistor and inductor to attempt to describe the consequences of the charging and discharging of the gas hydrate condenser on global change, including global climate change. He presented carbon-isotopic evidence from both the marine and terrestrial record provides support for the role of gas hydrates in global surficial processes but doubts that methane from decomposing hydrates ordinarily gets into the atmosphere in large enough quantity to affects climate as a greenhouse gas. He suggests that the exceptionally warm period near the beginning of the Cenozoic may have been an exception.

PANEL 3. HYDRATES IN THE REAL WORLD

Brewer (MBARI), Physical properties of CO_2 hydrate films

Peter Brewer discussed a series of experiments in which his team directly injected liquid CO_2 into the deep ocean at depths >3000 m. (At this depth, the liquid CO_2 density exceeds that of seawater.) He reported on evidence of likely chaotic behavior in that apparently identical experiments can yield grossly differing outcomes depending upon very small changes in initial conditions. Examples of such seafloor experiments include the deployment of seafloor pools of ~ 20 liters of CO_2. In one run, liquid penetration into sediment was followed by subsurface hydrate nucleation and growth and the formation of a solid hydrate "frost heave" occurred within 24 hours. A second nearby experiment involving an identical CO_2 deployment remained in the liquid state for 14 days, with no massive hydrate formation. Observations made while penetrating this film with a pH electrode suggest that rapid rebuilding of a thin hydrate film occurs (~1 μm thick) and that this process provides the only explanation of the seemingly chaotic behavior. He predicts that similar chaotic behavior and similar gas-water interface properties will be observed for CH_4 hydrates, and will be scaleable in expected ways, and urged attention to the fluid dynamic problems associated with hydrate formation.

Aya (Maritime Research Institute, JAPAN), Maximum rebuilding rate of CO_2 hydrate membrane under stress

In a talk directly relevant to the previous presentation by Peter Brewer, Izou Aya gave a report on experiments that showed how the deformation behavior of CO_2 hydrate membrane between liquid CO_2 and liquid water varies in its response to stress depends on the state of saturation of the water on one side of the membrane. If the water side of the membrane is undersaturated with respect to CO_2, the membrane shows a very large permanent stretching deformation when loaded with a platinum loop. In contrast, if the surrounding water is saturated with respect to CO_2, the membrane shows a small, mainly elastic deformation and abruptly breaks when the stress reaches a maximum limiting value. Dr. Aya explained this behavior by assuming that the deformation in undersaturated water involves driving cracks through the membrane, a process that requires excess free water (hence the cracks can not propagate unless the surrounding water is undersatuated). Once the crack penetrates the membrane, the CO_2 on the other side of the membrane combines with this free water to "rebuild" the hydrate strcuture of the membrane.

Winters (USGS, Woods Hole), Physical properties of samples containing natural and laboratory formed gas hydrate

Bill Winters summarized physical property results obtained using the gas hydrate and sediment test laboratory instrument (GHASTLI) at the USGS Woods Hole laboratory. The measurements were made on samples recovered from the Malik 2L-38 gas hydrate well drilled in the Makenzie Delta, NWT Canada, and on samples in which gas hydrate was formed in the lab. He discussed systematic increases in P-wave velocity and strength changes in the presence of gas hydrate and ice in sediment compared to sediment without those phases. He also discussed storage techniques for preserving and transporting samples containing gas hydrate.

Kleinberg (Schlumberger-Doll Research), Nuclear magnetic resonance of hydrate-bearing rock and sediment: assay, pore size control, and hydraulic permeability

Bob Kleinberg talked about his work using nuclear magnetic resonance (NMR) measurements to provide quantitative information about hydrate in porous rock and sediment. He suggests that NMR is one of the best ways to determine hydrate content (NMR can detect liquid water, but not ice or hydrate.) Relaxation time analysis gives pore size control of hydrate, and provides estimates of how hydrate affects hydraulic permeability. He talked about seafloor NMR experiments that are underway at MBARI that may provide insights into the formation of hydrate deposits.

Wright (Chevron-San Ramon)

Jeff Wright talked about Chevron's interest in gas hydrates, focusing largely on a proposed $13M joint industry project (JIP) with DOE that is led by Chevron, in cooperation with four other companies, to drill, core, log and record seismic data specifically for hydrates in the Gulf of Mexico. This proposed project (not yet finalized

and approved for funding) would be financed primarily (~80%) by DOE. The main goals of this project are to characterize the hydrate deposits to address potential safety concerns (if any) associated with drilling through hydrate intervals in pursuit of long term production of deeper conventional hydrocarbons, as well as evaluating the natural-gas potential from gas hydrates beneath the Gulf of Mexico. He also outlined some of the proposed cooperative projects, in the areas of geophysics and seismology, with universities and government labs that will likely be supported by Chevron independently and with its JIP partners.

Paull (MBARI), Gas hydrates: What we need to know versus what we can currently measure.

Charlie Paull began his talk with the statement that the main measurement need is the distribution of gas and gas hydrates, at all spatial scales, in natural settings. He then discussed the limitations of current approaches in drilling and logging, and stressed the need for the development of better tools for in situ pore water extraction and for recovery of hydrate samples from gas-hydrate intervals without gross decomposition of the gas hydrates. He also emphasized that we need better baseline models of sediment properties with depth so that the changes in properties caused by hydrates can be better estimated. This need is evident in trying to interpret resistivity and salinity logs for hydrate content.

Several speakers who were not able to attend the workshop at the last minute sent summaries of the talks they had planned to give.

Max (Marine Desalination Systems, Inc.), Development of an applied hydrate research program

Until recently, the majority of applied gas hydrate research has been focused on developing ways to stop hydrate from forming as part of flow assurance programs. Following incessant prodding from hydrateophyllic scientists, however, recognition that the vast gas hydrate deposits may provide the next generation hydrocarbon energy source has energized gas hydrate research and brought government funding to bear in a number of countries. In addition, new areas of hydrate research are emerging. Applications of hydrate physical chemistry in the fields of water treatment and separation of components of aqueous systems offer a number of industrial opportunities, but research bearing on these issues must take into account ownership of intellectual property rights. This is because the research is being driven by private companies to which the rights to new technology are vital for commercial success. The major difficulty that any company has in carrying out hydrate research at present is that National Laboratories and State Universities own research carried out by their staff by law and companies must make other arrangements to have their focused research carried out at private companies and private universities if they are to maintain control of patent rights.

Chou (USGS, Reston), Transformations and characterizations of methane hydrates at elevated pressures

Detailed study of pure methane hydrate in a diamond cell with *in situ* optical, Raman, and x-ray microprobe techniques reveals two previously unknown structures, structure II (SII) and structure H (SH), at high pressures. The SII methane hydrate at 250 MPa has a cubic unit cell of a = 17.158(2) Å and volume V = 5051.3(13) Å^3; SH at 600 MPa has a hexagonal unit cell of a = 11.980(2) Å, c = 9.992(3) Å, and V = 1241.9(5) Å^3. These structures were determined by *in situ* energy dispersive x-ray diffraction scans of the single crystals in the diamond cell at beamline X17C of NSLS, Brookhaven National Lab. The compositions of these two investigated phases are still not known. The invariant point for the assemblage ice VI-water-SI methane hydrate-SH methane hydrate is at 16.6°C and 842 MPa, and the invariant point for the assemblage ice Ih-water-SI methane hydrate-SII methane hydrate is at –8.7°C and 99 MPa. The SH methane hydrate is the high pressure phase reported by Dyadin and Aladko (1996; Proc. of the 2nd Conf. on Gas Hydrates, 67-70) and the MH-II phase reported by Loveday et al. (2001; Nature, 410, 661-663) and Shimizu et al. (in press; J. Phys. Chem. B). However, the SII methane hydrate phase has not been observed or confirmed by any other investigators. We recently observed and characterized the MH-III phase reported by Loveday et al. (ibid.) and Shimizu et al. (ibid.).

Colwell (INEL), Experimental Needs of the Microbiologist Studying Gas Hydrates
The experimental needs of a microbiologist studying gas hydrates reflect the conceptual models that have been developed to describe the involvement of microorganisms in gas hydrate-related processes. Results of the experiments will be essential for completion of mathematical models which describe these processes. Key microbial processes of interest include methanogenesis, anaerobic methane-oxidation, and possible microbial contribution to hydrate formation. The ability to evaluate microbial biomass, activity, distribution, physiology, and diversity associated with natural or synthetic gas hydrates is a practical goal for field and laboratory experiments. For collection of natural gas hydrates in the environment, pressure-temperature coring tools that preserve the hydrate and minimize sample alteration are required for stabilizing the indigenous microbial communities. The ability to collect these samples will eventually allow characterization of such sensitive microbial parameters as the amount of messenger RNA present within cells, an indicator of the types of enzymes being made in response to specific environmental conditions. Opportunities to conduct experiments in pre-existing boreholes in marine or sub-permafrost settings will be facilitated by devices that allow non-disruptive multi-level static sampling (in place incubation) in marine sediments and ultimately real-time sensing of chemical and physical properties indicative of microbial activities in the sediments. Physical models including bioreactors, pressure vessels of various sizes (some with view ports), and glass micromodels will permit replicated laboratory studies of microorganisms under in situ conditions. Close coordination among scientists of different disciplines during such investigations will be required to fully examine those processes that rely upon microorganisms.

INVITED WORKSHOP PARTICIPANTS

People who attended the workshop

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Group photo taken at workshop

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WORKSHOP DISCUSSIONS

Fundamental Questions in Hydrate Science & Technology that are in Principle "Answerable" by Relatively Simple and Evocative Laboratory and Seafloor Experiments

FUNDAMENTAL QUESTIONS	POSSIBLE APPROACHES
1.How long do seafloor hydrates survive on the seafloor in contact with undersaturated seawater? Does such contact change the compositions of surviving hydrates?	Measure dissolution rates of lab-made hydrate on seafloor (some experiments already begun at MBARI). Gas and water analyses of gas hydrate samples sealed and transported at pressure after prolonged exposure to undersaturated seawater.
2. How are hydrates formed in nature? How do formation environments and processes correlate with gas hydrate morphologies (nodules, veins, finely-disseminated, vein filling, massive, etc.)? How do diagenetic processes change gas hydrate after their formation?	Optical-cell comparisons with natural gas hydrates. Long-term near-seafloor growth experiments. SEM observation of changes in gas hydrate morphology. Gas hydrate growth in slow flow-through settings. Could also impregnate porous sediments to preserve pore texture.
3. How do the characteristics of natural hydrates compare to those gas hydrates formed in the lab (structure, hydrate number, n, gas composition)?	Improved methods for natural gas hydrate recovery and transfer to observation vessels. SEM observations on natural & synthetic gas hydrates. Geochemical comparisons.
4. How do the characteristics of natural gas hydrates change when retrieved from natural environments and brought to the lab?	Lab emulations using P, T, and time retrieval pathway.
5. What are the effects of hydrate formation and decomposition on the fluid flow properties (e.g., permeability) of hydrate-media?	Long-term seafloor gas hydrate growth experiments in pressure vessels with seawater flow-through. Corresponding lab experiments.
6. What are the roles of microbes in hydrate formation and dissociation?	Seafloor formation and decomposition experiments in the presence of microbes. Culture microbes optical cells and observe population dynamics & monitor metabolism.

FUNDAMENTAL QUESTIONS (continued)	POSSIBLE APPROACHES (continued)
7. What is fine seismic structure of the hydrate interval and its boundaries? How does this structure reflect the processes that formed it?	Near seabottom deep tow surveys *(check NRL activities)*. Seafloor seismic surveyer (sources & receivers) & possible coordination as site survey for drilling.
8. How can well logs be made more useful, specifically in discriminating hydrate from non-hydrate components and in verifying rock-physics models?	Logging measurements of lab-made sediment/hydrate samples in the lab and on the seafloor. Quantify amount of hydrate in sediment samples and use as a ground truth for logging.
9. What is the nature of the base of the hydrate stability zone?	Lab emulation by slowly heating lab-made hydrate-sediment aggregates and observing the sample response.
10. Are interfacial gas hydrate properties important compared to those of bulk material?	Lab measurements on properties of polycrystalline hydrates or granular aggregates with different grain sizes. Optical-cell measurements of interfacial angles.
11. What are the effects of decomposition of marine gas hydrate-bearing formations that are under gravitational stresses on continental slopes? Do such stresses alter the P-T phase stabilities of natural gas hydrates?	Lab investigations of the mechanical and phase stability of gas hydrates simultaneously under non-hydrostatic stress and elevated P and T both inside and outside the hydrostatic stability field.
12. How may we best test and verify numerical gas production models that are intended to emulate thermal-stimulation methods?	*In situ* x-ray or neutron attenuation tomography of hydrate/sediment samples inside pressure vessels with internal temperature sensors. Logging during production and post-production in test wells.
Needed: More perspectives from molecular physics and chemistry, climate change, other oil and gas perspectives (seafloor stability & resource potential), biology, ...	

Progress in Measuring the Properties of Well-Characterized sI Methane Hydrate

Property	Experiments Started	Experiments Completed	Temperature Effects	Pre E
Basic Phase Characterization				
Bulk polycrystal synthesis method for > 99% purity	X	X	N/A	!
As-synthesized composition CH_4*nH2O, **n** = 5.89±0.02	X	X		
Re-equilibration rate law for **n** with changes in P and T	X			
Structure confirmed by diffraction or Raman spectroscopy	X	X	X	
Density, ρ, and molar volume, V_m, at a standard state (Quadruple point, T = 272.9 K, $P_{methane}$ = 2.563 MPa)				
Phase stability limits of sI including limits for P>100 MPa	X	X	X	
Decomposition rates of porous hydrate	X (1 atm)	X	X	
Fine Structure and P-T-V Equation of State				
Structure refinement, ND on methane deuterate	X	X		
Thermal expansion, α_v (T), T<180 K. ND at 1 atmosphere	X	X		
Thermal expansion, α_v (T), T>180 K, ND at elevated P				
Isothermal bulk modulus, K_T, from cell volume compression using ND at elevated P. ND = neutron diffraction.				
Elastic Properties				
Single-crystal elastic stiffness matrix: c_{11}, c_{12}, and c_{44}				
Bulk elastic wave speeds: V_P and V_S, compacted hydrate	X	X	X	
Bulk elastic properties: G, K_S, and υ (from V_P and V_S)	X	X	X	
Dielectric constant, K, and refractive index, n = √K				
Heat Storage and Transport				
Thermal conductivity, k, compacted hydrate	X		X	
Thermal diffusivity, κ, compacted hydrate	X		X	
Heat capacity, C_P (P, T)				
Latent heat of decomposition, hydrate → methane + ice				
Latent heat of decomposition, hydrate → methane + Lw				
Inelastic Mechanical Properties				
Steady-state creep rate laws (n, H*, and V*)	X	X	X	
Coefficient of static friction, μ				
Coefficient of internal friction, φ				
Fracture surface energy, γ				
Rate law for fracture healing				
Rate law for compaction of granular hydrate aggregates				
Crystal/Fluid Properties				
Crystal-interface growth law in saturated seawater				
Equilibrium crystal morphology in saturated seawater				
Interfacial energy in saturated seawater, γ_i^{sw}				
Seafloor dissolution rates in undersaturated seawater	X			
Long-term chemical stability in liquid nitrogen				
Gas-liq/solid-hydrate diffusional exchange rates (CO_2-CH_4)	X			
Molecular Physics and Chemistry: Incomplete				

***Studies in which starting phase purity, gas composition, hydrate number, crystal structure, and grain structure have all been independently measured or verified for the sample material.**