Hydrate Formation and Dissociation in Simulated and Field Samples

Methane Hydrates Research at Oak Ridge National Laboratory

C.J. Rawn, PI
T.J. Phelps, Co-PI
M. Elwood-Madden, collaborator
Current Personnel

Tommy Phelps
Co-PI, microbiology, large vessel experiments, and safety engineering

Claudia Rawn
Co-PI, material science, X-ray/neutron diffraction and crystallography

Miguel Rodriguez, Jr
R&D Associate and Technical Resource

Jonathan Alford
Post-graduate, starting September 08

Ji-Won Moon
Postdoctoral Fellow

Megan Elwood-Madden
University of Oklahoma
Hydrate background of PI’s

**T. J. Phelps**, Distinguished staff scientist, 16 yrs at ORNL
Published ~15 papers on gas hydrates, total of ~150
Trained 25 post-graduates

Related service includes 1st microbiologist and 1st DOE rep on IODP/ODP USSAC and committees 1999-2002
Since 2006 has served DOT in pipeline related issues

**C. J. Rawn**
Senior staff scientist with 11 yrs at ORNL
Joint Faculty at the University of Tennessee

Published ~12 papers on gas hydrates, total of ~80
Interacts daily with DOE facility users, undergraduates and graduate students

Collaborative publications with SNS, NIST, USGS, INL, Ga Tech, Texas A&M, Univ. of Oklahoma, Oregon State Univ.
Training since 2006 Hydrate Review

Megan Elwood Madden
Assistant Prof. at the University of Oklahoma

Scott McCallum – post masters student
geosciences - 2003 - 2006
Petro-geologist, PA

Phillip Szymcek – post masters student
Petro-geologist, AR

Patricia Taboada-Serrano –
2005 – 2008 (Former Fulbright Fellow)

Shannon Ulrich – post bachelors student
2006 - 2008 Colorado School of Mines
Environmental Science and Engineering
Facilities and Equipment

• In-Situ Diffraction
  – Neutron *Time, Temp, Pressure*
  – XRD

• Hydrate synthesis capabilities
  – Deuterated samples for neutron diffraction

• Seafloor Processing Simulator
  – housed in a temperature controlled explosion-proof cold room
  – capable of simulating deep seafloor pressures and temperatures

• Luna Distributed Sensing System (DSS) for observation of hydrate formation/dissociation

In-Situ neutron diffraction provides capabilities to do combined time, temperature, and pressure decomposition studies (spallation at the SNS provides the time component).

Two neutron powder diffraction patterns collected on samples provided by the USGS. Red: hydrogenous (H₂O), Black: deuterated (D₂O) showing how deuteration decreases the background and increases the Bragg scattering detailing atomic positions, lattice parameters, etc.

![Methane Hydrate 15K neutron powder diffraction patterns (selected region, lambda = 1.50 Å)](image)
Spallation Neutrons and Pressure (SNAP)

Collaborators: Chris Tulk and Bryan Chakoumakos

SNAP Diffractometer allows studies of a variety of samples under extreme pressure and temperature conditions.

Applies up to 100 GPa on an ~1mm³ sample.

This enables us to collect temperature/pressure/time dependent data:
- Thermal expansion
- Bulk modulus (compressibility)
- Dissociation kinetics (formation?)

This new beamline has
- Increased neutron flux
- Large-volume pressure cells
- Next-generation detectors
In-Situ X-ray Powder Diffraction

- PANalytical (Phillips) X’Pert Pro Diffractometer
  - Anton Paar TTK 450 low temperature chamber
  - X’Celerator detector for fast data collection

Time/ Temperature dependent dissociation studies
On natural samples

Center for Nanophase Materials Sciences
A Highly Collaborative and Multidisciplinary
U.S. DOE Nanoscale Science Research Center

OAK RIDGE National Laboratory
Low Temperature X-ray Diffraction Studies of GOM Hydrates

Collaborator: R. Sassen (Texas A&M) GOM samples with ~30 – 50% sII hydrate

Temperature dependent data showing dissociation of sII hydrate to water ice

sII gas hydrate, from a GOM natural gas, dissociated ~188 K (-85 C)

Only sII and water ice, no sI noted

Future studies to determine rate constants and reaction parameters

Collect time dependent data at multiple constant temperatures until 100% decomposition

Gas Chromatography/Mass Spectrometry to analyze gases for gas mass balance
Need for Distributed Sensing System

- 2000 – 2006 hydrate tracked by bulk measurements or visually

- Purchased fiber optic Distributed Sensing System (DSS)

- DSS uses fiber optics to observe temp changes corresponding to hydrate formation (exothermic) or dissociation (endothermic)

Time-Resolved 3-D temperature monitoring
Distributed Sensing System (DSS)

The Luna® Distributed Sensing System (DSS) laser pulses down an optical fiber determine changes due to temperature and strain.

Temperature and strain cause the fiber to expand or contract which are noted in the reflection time.

Time for the reflection to return is translated into a hybrid temperature strain value (TSV).

Sensors are at 1-cm intervals.
Integrated analysis of hydrate formation in heterogeneous systems

In situ optical, pressure, and temperature observations of hydrate in free gas systems

Model of hydrate growth from free gas phase

- Hydrate films observed along the surface of methane gas bubbles
- Films crystallized to form hydrate nodules in sediment
- Massive hydrate deposits form initially in areas of gas bubble accumulation

Suggests in systems containing free gas the stratigraphy, tectonic, and sedimentary structures likely control the location of massive gas hydrate deposits

Corroborates Indian Ocean hydrates observed in sands and fractures (Kastner, Goldschmidt 2008)
Data Collection with the DSS

• Fibers were coiled in a spiral
  – Attached to a circle of plastic mesh
  – Beginning of fiber on the outside of the spiral
  – End of fiber at the center of the spiral

Synthetic sediment experiments
Ottawa Sand/Silt

- Saturated to 30% with H₂O
- Homogeneous experiments
- Heterogeneous experiments
  With a 3” layer of silt
Ex-Situ Fiber test

- Four fibers and thermocouple exposed to same conditions

![Graph showing Thermocouple data with Time (h) on the x-axis and Temperature (°C) on the y-axis.](image1)

Room temp H₂O

Addition of ice H₂O

Ice melting and gradual warming

DSS data

![Diagram showing fiber 115 with Distance along fiber (cm) on the x-axis, Time (h) on the y-axis, and Temperature (°C) on the z-axis.](image2)
Nitrogen Control Experiments

- Four homogeneous sediments experiments
  - Two where temperature increases
  - Two where pressure decreases (one shown at right)

Fibers show similar overall trends
Some fibers could be more sensitive to changes than others

Note: Fiber 115 always shows reproducible variability despite location in SPS, possibility more sensitive to changes
Methane Experiments

- Four homogeneous sediment experiments
- CH₄ gas at T/P
- < 50 g of hydrate expected to form
- ~1 L of CH₄ added at 0.6 mL/min via HPLC pump

- Initial vessel cooling
- System reaches equilibrium
- Depressurization
- Warming

Possible hydrate formation indicated by upward arrows and dissociation by downward arrows
FY09 – FY11 Directions for SPS - DSS Experiments

• Homogeneous and Heterogeneous sediment experiments pressuring with CH₄

• Large data set analysis
  • Temp/strain monitored every 60 sec
  • Plotting the distance as polar coordinates
  • Igor Pro, Origin, MatLab (subcontract with University of Oklahoma)

• Massive amounts of hydrate to compare to earlier CH₄ experiments

• Examining relationships between overheating and depressurization for gas production
FY09 – FY11 Diffraction Directions

• More in-situ XRD work on natural (hydrogeneous) samples from Texas A&M
  • Time dependent studies (kinetics)
  • Lattice parameters as a function of temperature (thermal expansion)

• In house synthesis of deuterated samples for neutron powder diffraction
  – ORNL’s High Flux Isotope Reactor (HFIR) powder diffractometer upgrades to be completed in FY09
  – SNAP open for general users in FY09
  – Data collection as a function of pressure
    • Dissociation pressures
    • Bulk modulus from analyzing lattice parameters as a function of pressure
Productivity – Publications 2007 and 2008


Proceedings:

Productivity – Presentations

- 6th ICGH Vancouver July 2008 (Two Presentations)
- AGU Fall meetings both in 2006 and 2007
- GSA Annual Meeting 2007

- Science and Technology Issues in Methane Hydrate R&D workshop, Hawaii, 2006
- Inter-Laboratory Hydrates Workshop, Sept 2006, CSM

- Hosted Tim Grant at ORNL December 2006

- ORNL Gas Hydrates Workshop February 2007 to inform the ORNL community of special capabilities and ongoing hydrate research conducted at the laboratory, and provided a platform for future collaborations
Other Publications, Milestones, and Quarterly Reports

• Publication planned for the Review of Scientific Instruments on the data collection and processing with the DSS with Luna Technologies

• Publication planned on the time/temperature dependent x-ray diffraction data once more experiments at different temperatures are completed

• All milestones from FY08 FWP completed:
  – 12/07 Collected data with the DSS with heterogeneous sediment column
  – 3/08 submitted report on homogeneous sediment column experiment (precursor to ICGH paper)
  – Switched 6/08 (conduct neutron diffraction experiment) with 3/09 (publication on time dependent xrd studies) milestones – ICGH paper on time dependent xrd studies

• Quarterly reports sent to Robert Vagnetti (NETL)
Budget Considerations

• In FY08 reduced budget by 15% and delayed capital equipment request

• FY09 Capital Equipment to design and build a cold-loading system for Paris-Edinburgh pressure cells used on the SNAP beamline
  – ORNL has several PE cells, and the cooling capability, but lack a method/system to load cold samples
  – This cold loading system would give us the ability to pre-cool and load ices and gas hydrates at liquid nitrogen temperature, into the anvil package
Collaborations: Ga Tech/ORNL

With Costas Tsouris, Joint ORNL/GA Tech Faculty
Department of Civil and Environmental Engineering

Methane Recovery from Hydrate-Bearing Sediments
With J. Carlos Santamarina
GA Tech Faculty

Coalbed Methane Produced Water Treatment
by Hydrate Formation and Dissociation
Geochemistry of shales associated with methane seep mounds

Analyzing:
- Oxidation state
- C, O, H, and S isotopes
- Carbonates
- Redox gradients (below)

Geologic indicators of gas hydrate formation and dissociation in the lab and field—examining ~65 million year old carbonate seeps for geochemical and sedimentological traces of gas hydrates

Collaborations: University of Oklahoma
Megan Elwood-Madden

Funded through Oak Ridge Associated Universities
High Pressure in the Paris-Edinburgh Cell

- room $T$, 2 - 20 GPa (encapsulated gasket ensures isostatic to 10 GPa)
- with micro-furnace, $P_{\text{max}}$ 7 GPa at 1200K
- with WC anvils 2.0 to 20 GPa
- with sintered diamond anvils to 30 GPa

100 mm$^3$ sample volume

Paris-Edinburgh 20 GPa Pressure cell

Encapsulated gasket

Standard gasket

2.8 MN Press

100 mm
SNAP Paris Edinburgh Pressure Cells

VX1: 4 GPa
VX3: 15 GPa
VX5: 10 GPa
10 GPa Paris-Edinburgh Pressure cell in a dedicated liquid $\text{N}_2$/CCR cooler

26 K