

Characterization of Natural Hydrate Bearing Core Samples

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Annual Project Review
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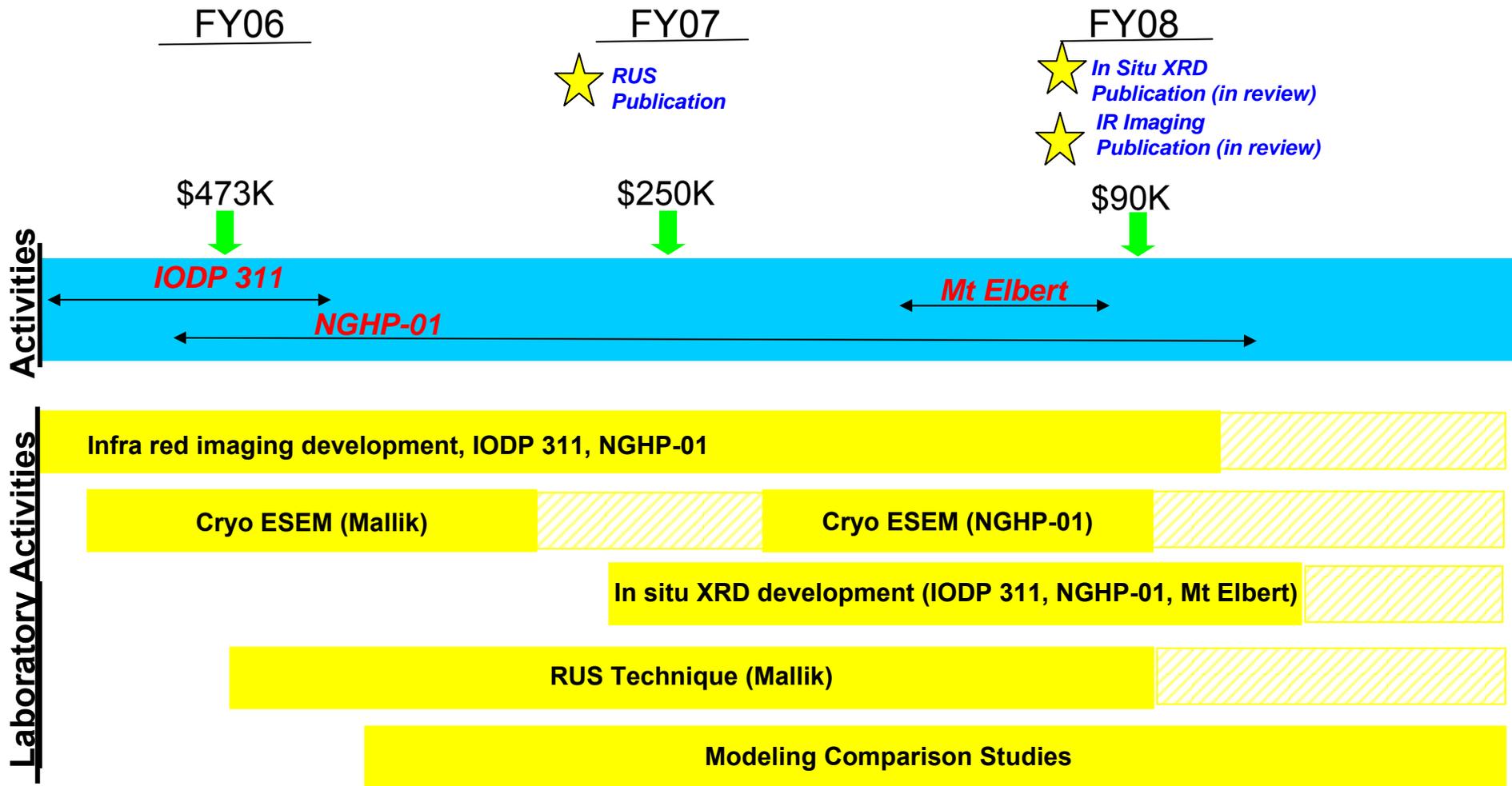
Project Strategy and Objectives

- ▶ Provide a consistent set of measurements on a broad range of natural gas hydrate samples representing both marine and terrestrial sources
 - Link core scale IR with pore scale laboratory measurements
 - Correlate IR data with gas hydrate abundance
 - ◆ Porewater chemistry
 - Reprocess IR data from ODP leg 204, IODP 311, & NGHP-01
 - Laboratory core studies characterizing hydrate equilibrium and dissociation properties
 - Environmental scanning electron microscopy
 - ◆ Imaging gas hydrate texture and dissociation behavior at pore scale
 - Resonant ultrasound spectroscopy
 - ◆ Hydrate abundance
 - In situ XRD
 - ◆ Reservoir conditions
- ▶ Modeling efforts
 - STOMP-HYD
 - Simulator code intercomparison study

Project Timeline

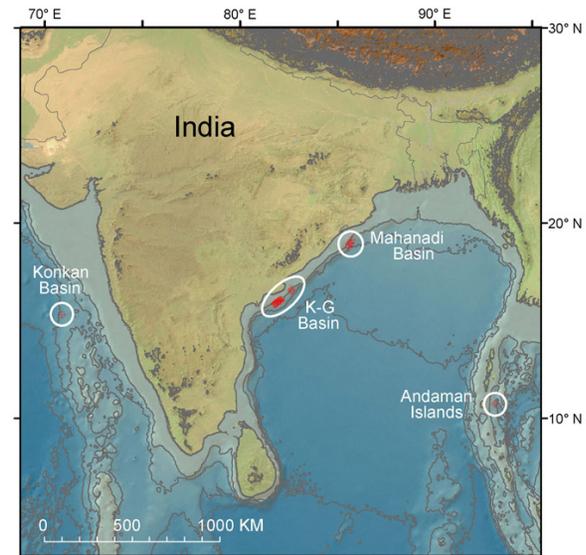
Legend

- ★ Publication
- NETL Activities
- Project Activities

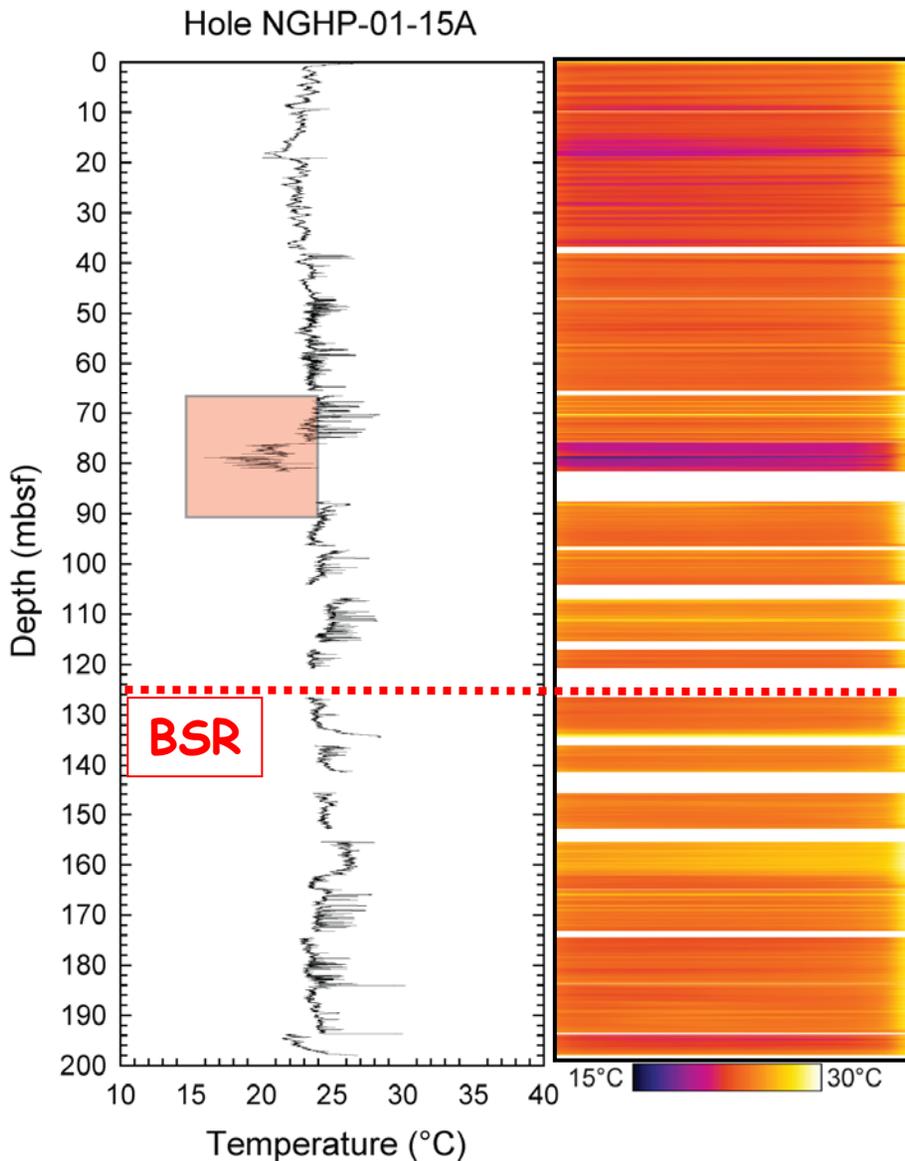


Infrared Imaging Field Application

- ▶ India's Natural Gas Hydrate Program (NGHP)
 - PNNL participated in Expedition 01 (NGHP-01)
 - Infrared core imaging
 - ◆ 2 staff shipboard
 - Supported by Department of Energy (DOE)
- ▶ Shore Based Studies
 - IR imaging data
 - Reprocessing
 - HXRD
 - Attended NGHP-01 conference
 - Held in Delhi, India February 2008
 - Two staff presented results

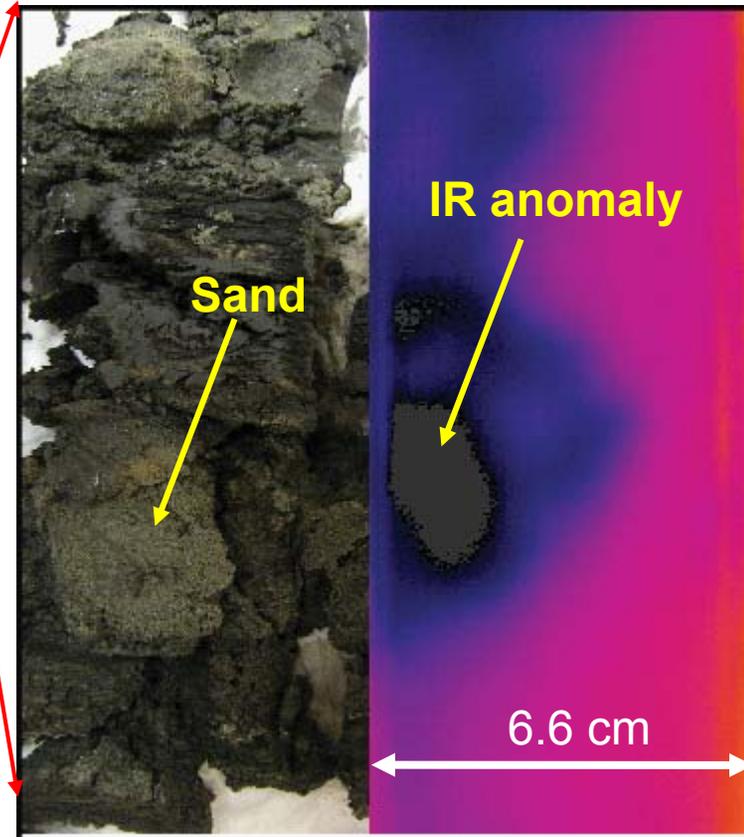


Infrared Imaging Field Application



Krishna-Godawari Basin

Core NGHP-01-15A-09X-2



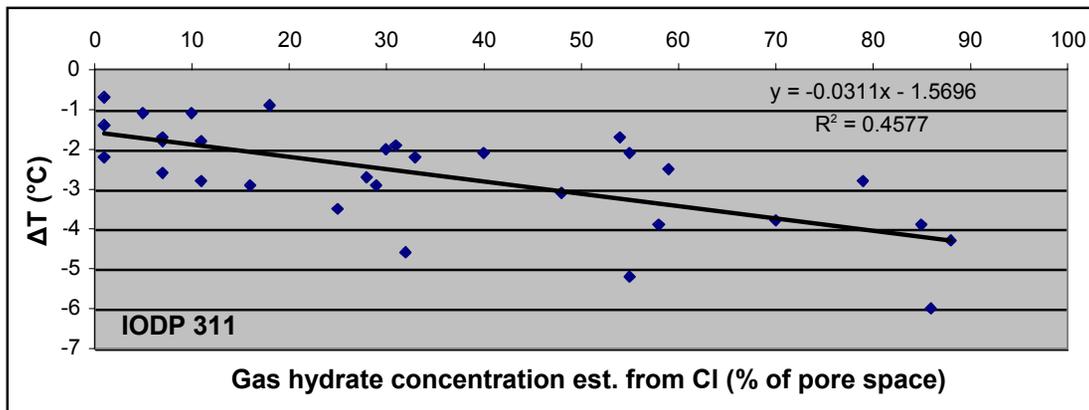
Infrared Imaging Based Technologies

▶ Shore based IR data processing

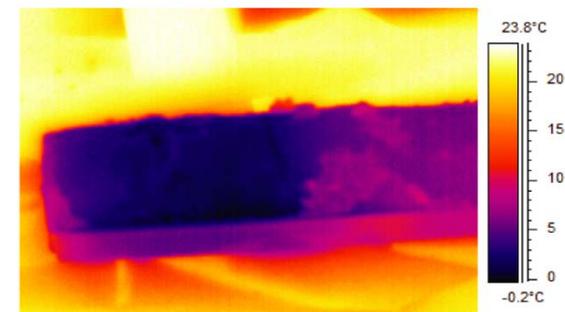
- Proxy for hydrate abundance on cores lacking geochemistry?
 - Chlorinity classical method for estimating hydrate abundance
- IODP 311 Expedition IR data set
 - Correlation between ΔT and pore water chlorinity
 - Publication “Torres, ME; Trehu, AM; Cespedes, N; Kastner, M; Wortmann, UG; Kim, JH; Long, P; Malinverno, A; Pohlman JW; Riedel, M; Collett, T. 2008. Methane hydrate formation in turbidite sediments of northern Cascadia, IODP Expedition 311. Earth and Planetary Science Letters 271 (1-4) p.170-180”

▶ Refinement of NGHP-01 IR data set

- Core history
- Modeling application

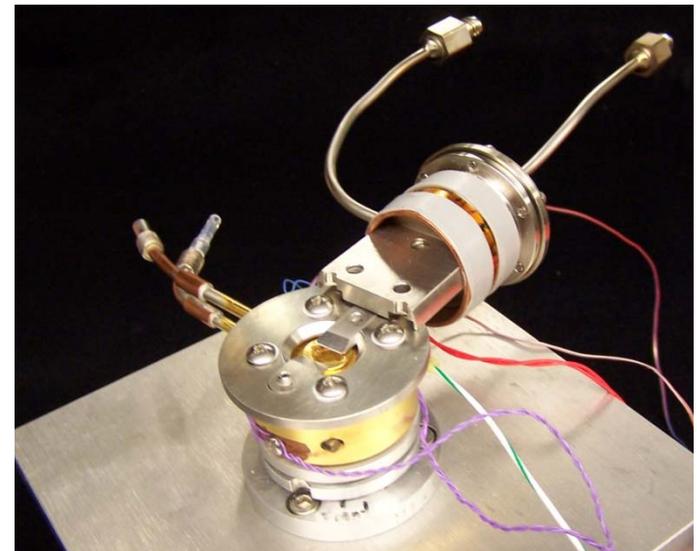
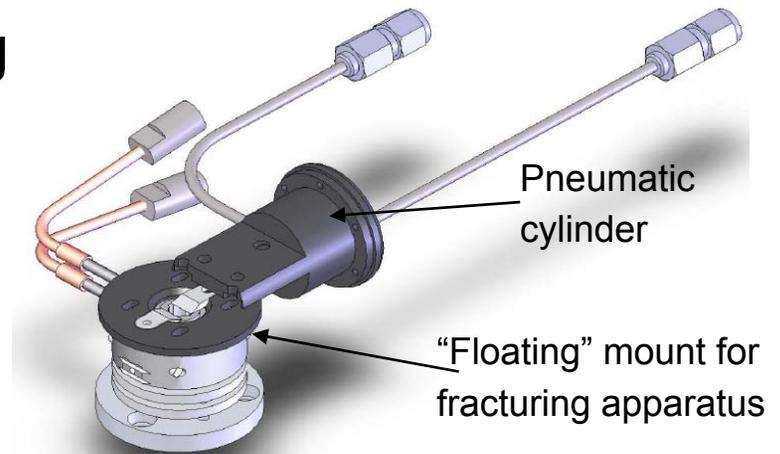


NGHP-01 Core 17



ESEM Gas Hydrate Research

- ▶ Detailed survey of hydrate-bearing samples without high vacuum
 - Image in N_2 , CO_2 , CH_4 , and C_3H_8 atmospheres (~ 2 mbar)
 - Cold stage ($-170^\circ C$) stabilizes gas hydrate
- ▶ In situ sample fracturing
 - Micromanipulator used to expose fresh surface
- ▶ Video imaging system to capture gas hydrate dissociation processes
- ▶ Gas Chemistry
 - Integrated mass spectrometer system
 - In situ gas monitoring during hydrate dissociation



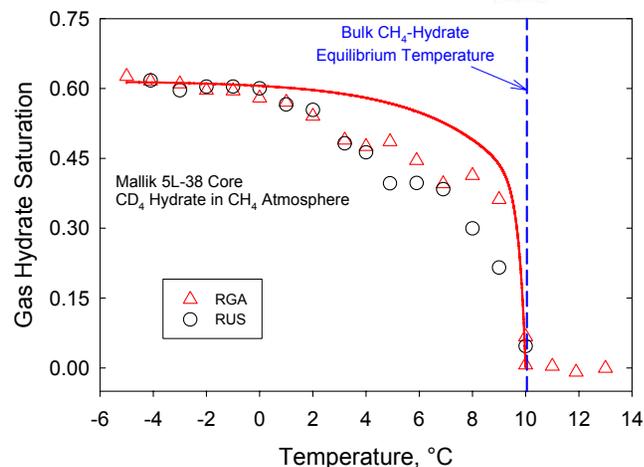
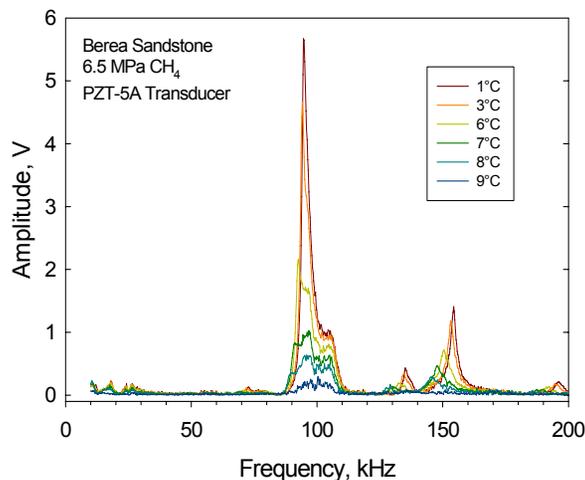
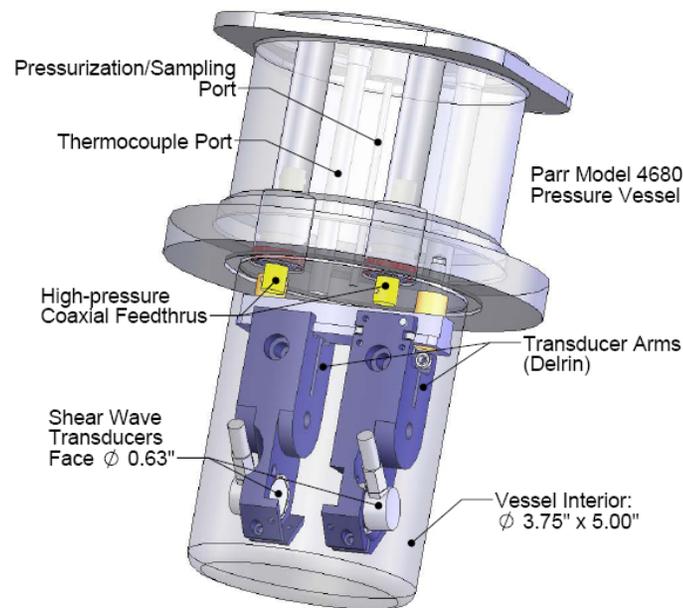
Resonant Ultrasound Spectroscopy

► RUS development

- Resonant peak amplitude correlated with gas hydrate saturation
 - Reservoir conditions
 - ◆ Pressure
 - ◆ Temperature
- Coupled with residual gas analysis
 - Isotopic gas (CD_4)
 - Track hydrate dissociation

► Gas hydrate estimates

- Pore water freezing model
- Pore water chemistry controlling factor



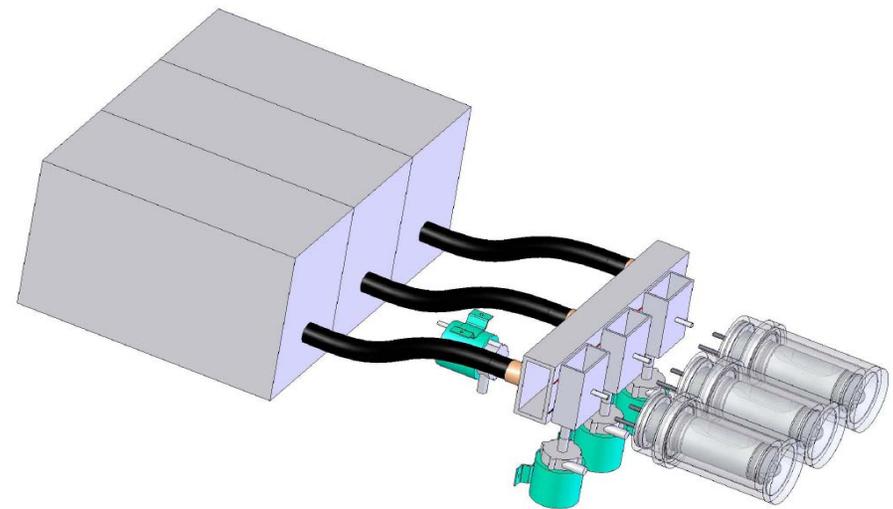
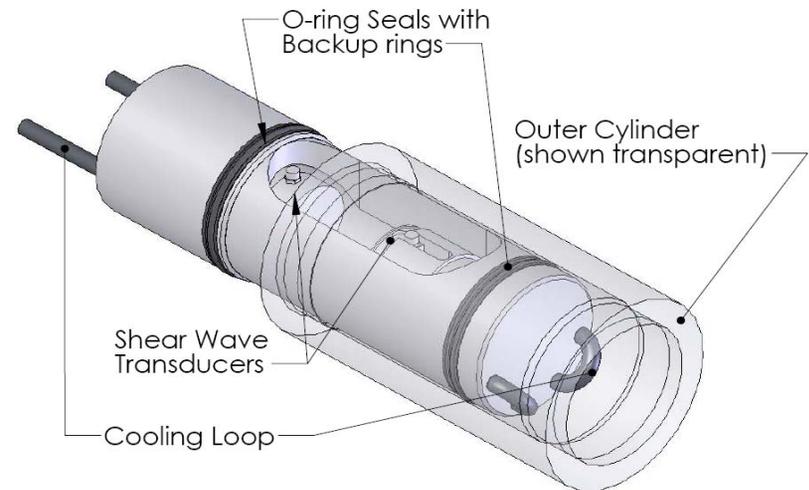
Resonant Ultrasound Spectroscopy

Field Application

- Portable system 75% complete
 - Smaller pressure vessels
 - Shipboard or field laboratory
- Multiple sample analysis
 - 5 core samples

Couple with Residual Gas Analysis

- Track gas chemistry



In Situ High Pressure X-Ray Diffraction

▶ X-Ray Photon Source

- Rotating Anode
 - 18 kW
 - Transmission
- Variable spot size

▶ High Precision Goniometer

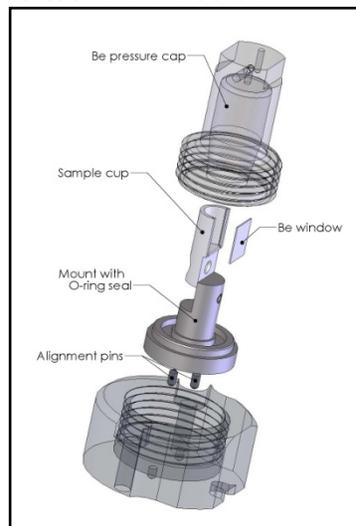
- Vertical & lateral movement
- GADDS Detector
 - True photon counter
 - 100 micron spatial resolution
 - 70° of data collected in seconds

▶ Sample Stage

- -100 to +227°C
- Computer mapping

▶ Be Pressure Cell

- X-ray transparent
- 20 MPa
- 1cm³



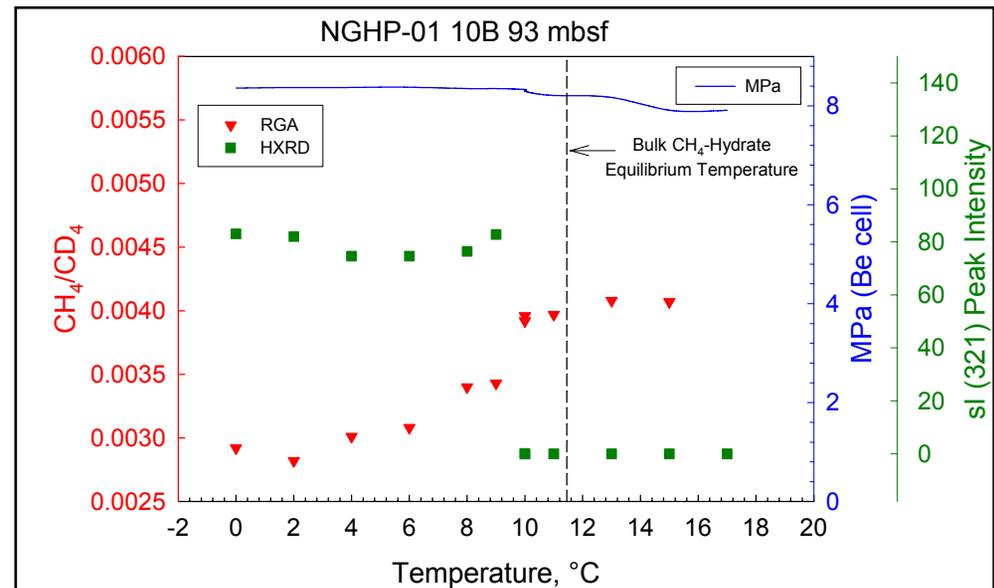
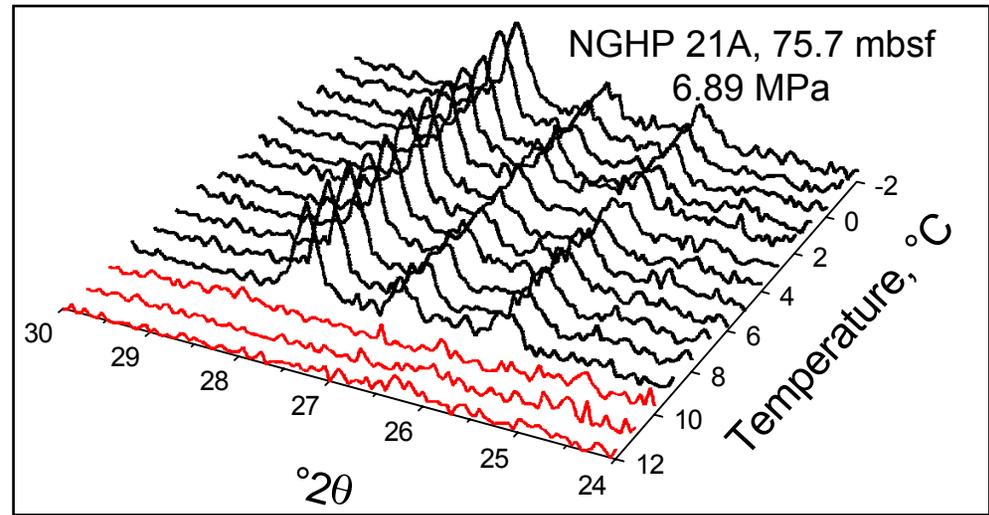
In Situ High Pressure X-Ray Diffraction

► In Situ XRD

- Technique developed for gas hydrate samples
 - Reservoir conditions
- Identify and confirm presence of gas hydrate
 - sl, sll, H, or water ice (1h)

► Gas Hydrate Rich Sediments

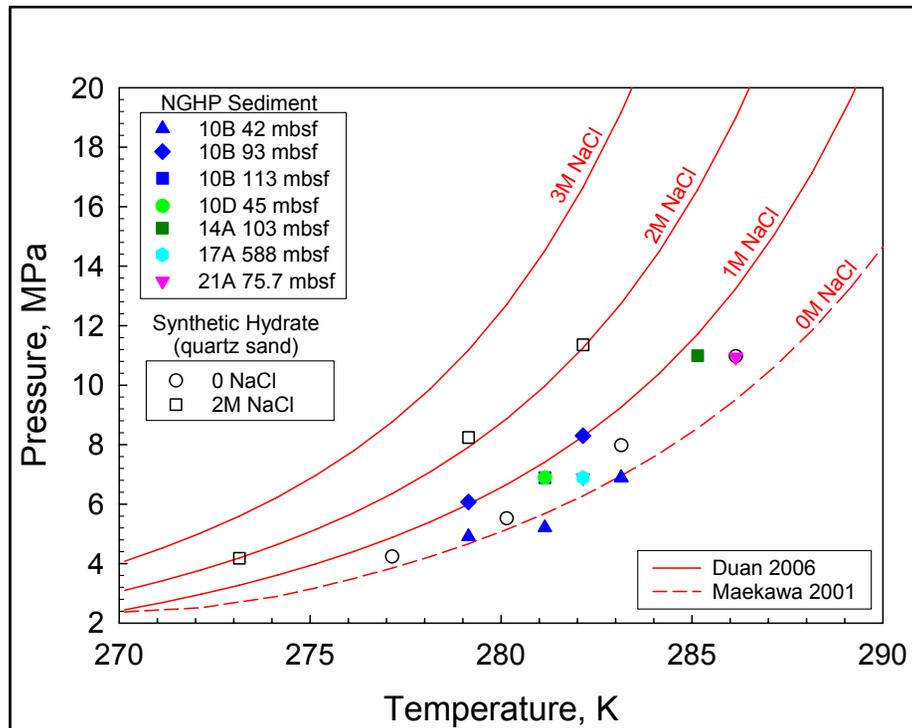
- Dissociation parameters
 - Observe dissociation of gas hydrate in sediment
- Gas Chemistry
 - Coupled with RGA
 - ◆ Direct gas sampling
 - Continuous gas hydrate dissociation



In Situ High Pressure X-Ray Diffraction

► Core Sediment Characterization

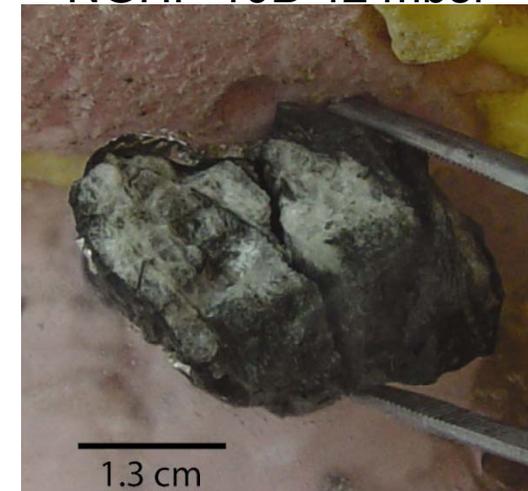
- Mt. Elbert cores (2)
 - sl hydrate detected by in situ XRD
- NGHP-01 core (11)
 - Variation in gas hydrate stability
 - ◆ Natural vs synthetic
 - Gas chemistry



Mt Elbert Core

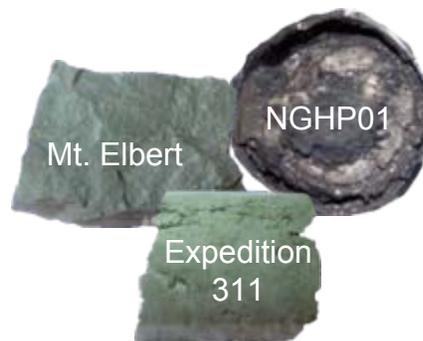
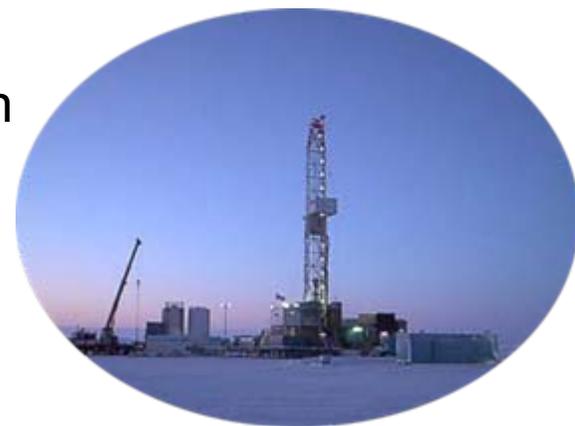


NGHP 10B 42 mbsf



Summary

- ▶ Supporting the National Gas Hydrate Research Program by better understanding gas hydrate properties in natural sediments
 - IR imaging extended beyond core collection
 - Correlate to core properties
 - ◆ Porewater chemistry
 - ◆ Microbial populations
 - Develop IR imaging applications
 - ◆ Use existing IR data for correlation factors
 - Marine and terrestrial core characterization
 - Controlling factors
 - ◆ Physical
 - ◆ Chemical
 - Portable techniques
- ▶ Modeling efforts
 - STOMP-HYD
 - Code comparison



Publications

- B. P. McGrail, S. Ahmed, H. T. Schaef, A. T. Owen, P. F. Martin, and T. Zhu. 2007 “Gas Hydrate Property Measurements in Porous Sediments With Resonant Ultrasound Spectroscopy” *Journal of Geophysical Research*, VOL. 112, B0520.
- M. E. Torres, A. M. Tréhu, N. Cespedes, M. Kastner, U.G. Wortmann, J. H. Kim, P. E. Long, A. Malinverno, J. W. Pohlman, M. Riedel, T. Collett. 2008. “Methane hydrate formation in turbidite sediments of northern Cascadia, IODP Expedition 311”, *Earth and Planetary Science Letters* 271 (1-4) p.170-180.
- P. E. Long, M. Holland, P. Schultheiss, M. Riedel, J. Weinberger, A.M. Trehu, and H.T. Schaef. “Infrared (IR) Imaging of Gas Hydrate-Bearing Cores: State-of-the-Art and Future Prospects” *Soc. Expl. Geophy.*, (in review).
- H. T. Schaef, B. P. McGrail, A. T. Owen, and P. E. Long. “Characterization of NGHP-01 Hydrate Samples by *In Situ* High-Pressure X-Ray Diffraction Coupled with Residual Gas Analysis”, *Marine Geology*, (in review).