Characterization and Decomposition Kinetic Studies

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Peer Review
National Labs and Inter-Agency Efforts
DOE-NETL Methane Hydrate Program
NETL Pittsburgh, PA

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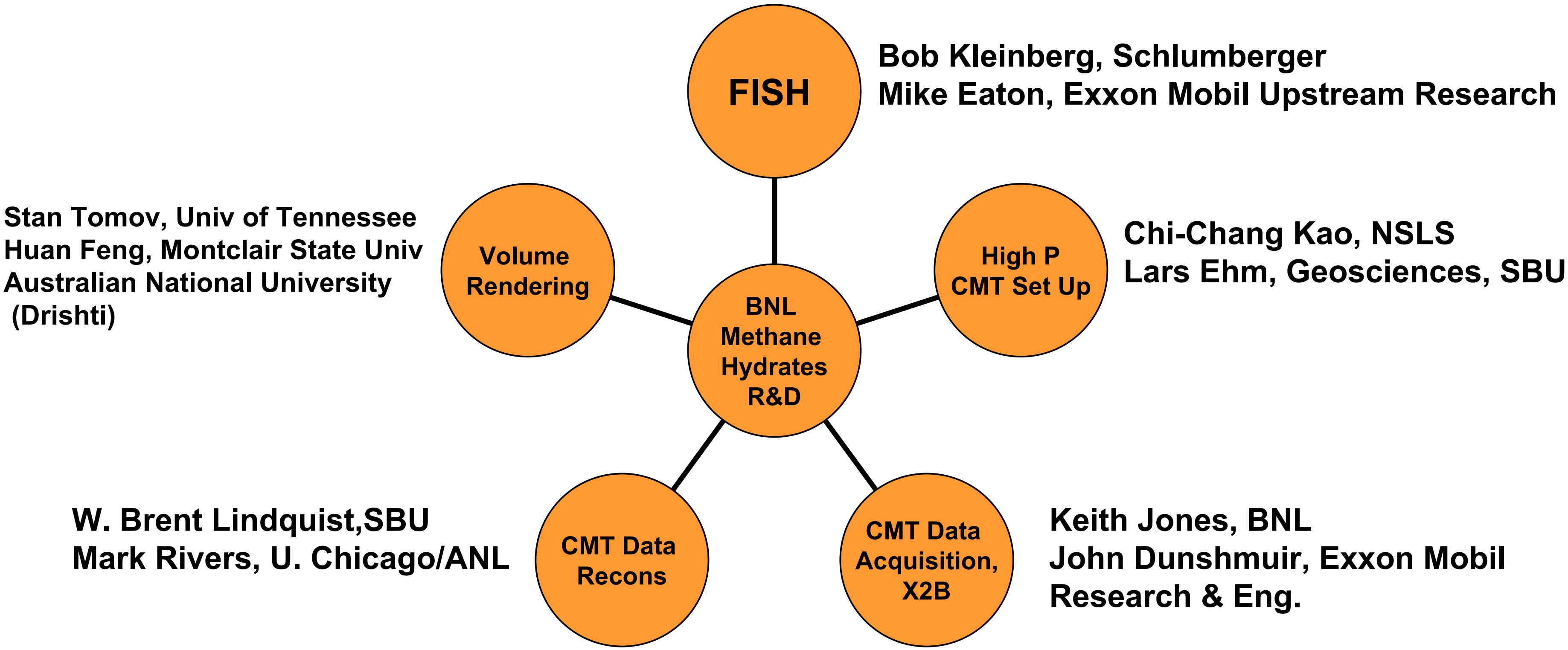
Acknowledgements



<u>Collaborators</u>

R. Kleinberg, Schlumberger Doll Research, Boston, MA
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W. Winters, USGS, Woods Hole, MA
Richard Coffin, NRL, Washington, DC

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- U.S. DOE, Office of Science, Summer Undergraduate Laboratory Internship (SULI) Program ($8K/student)
- SBU: Office of Vice President for Research ($30K)

BNL Project Output

Publications/Abstracts
Total: 23
Since 2006: 14

Education
Mike Eaton, Ph.D., 2007 (Exxon Mobil, Houston)
Prasad Kerkar, Ph.D. student
Christine Horvat (2008), Undergrad, ChemE
Xaie Shi (2007), Undergrad, ChemE

Award
2007 Office of Science Mentor Awards by the Secretary of Energy .

Methane Hydrate Areas of Interest

- Methane Hydrate Advisory Committee Report to the U.S. Congress (2007). 4 Recommended areas:

  - Permafrost hydrate production testing
  - Marine hydrate viability assessment
  - **Climate effect of hydrates**
  - International cooperation

- DOE Methane Hydrate R&D Roadmap (2006)

BNL R&D Focus: Sediment Hosted Hydrates

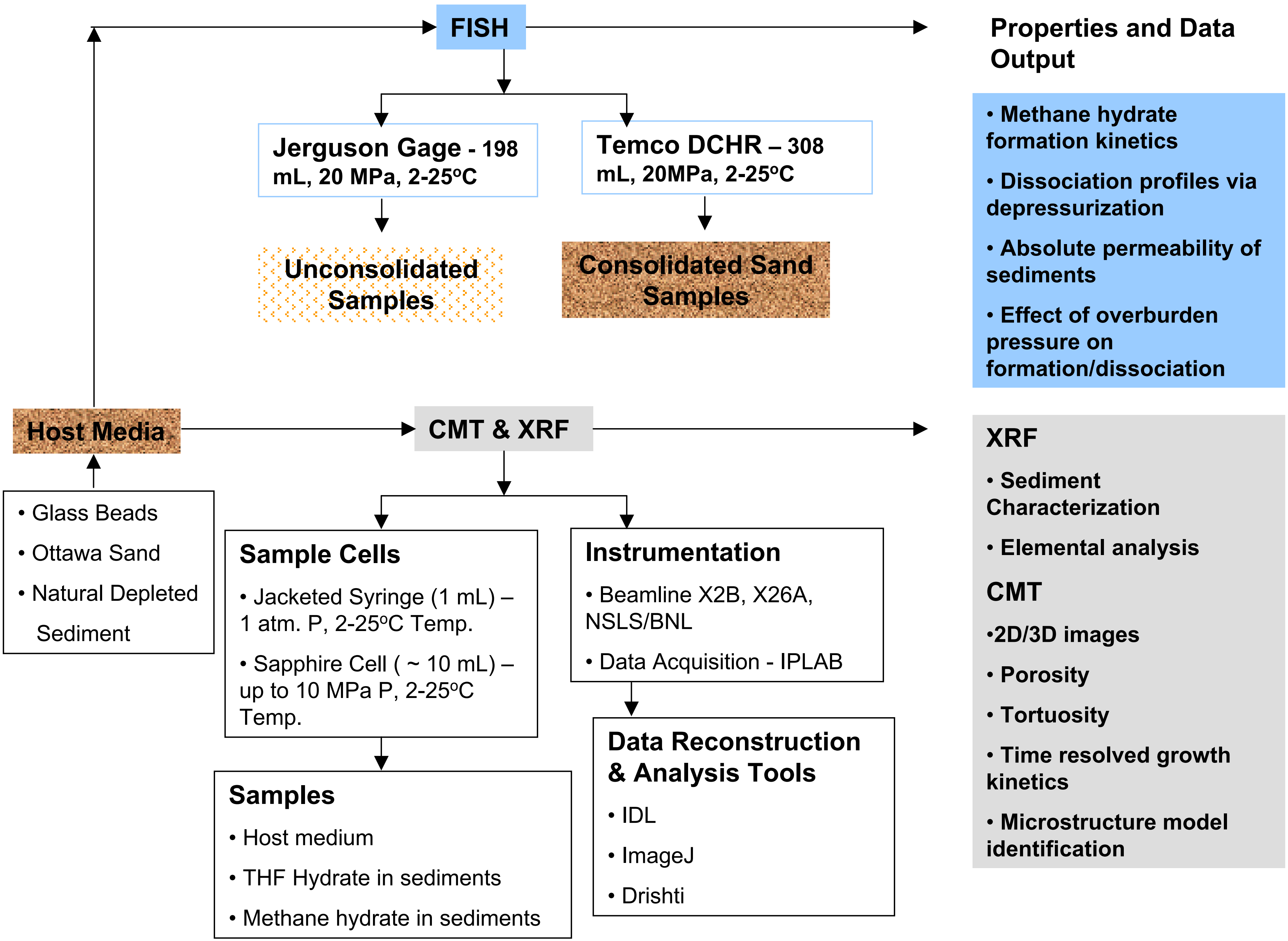
Goal:

• To understand sediment hosted gas hydrate systems through laboratory mimics with emphasis on natural fine-grained sediments for relevance to climate change.

BNL Approach

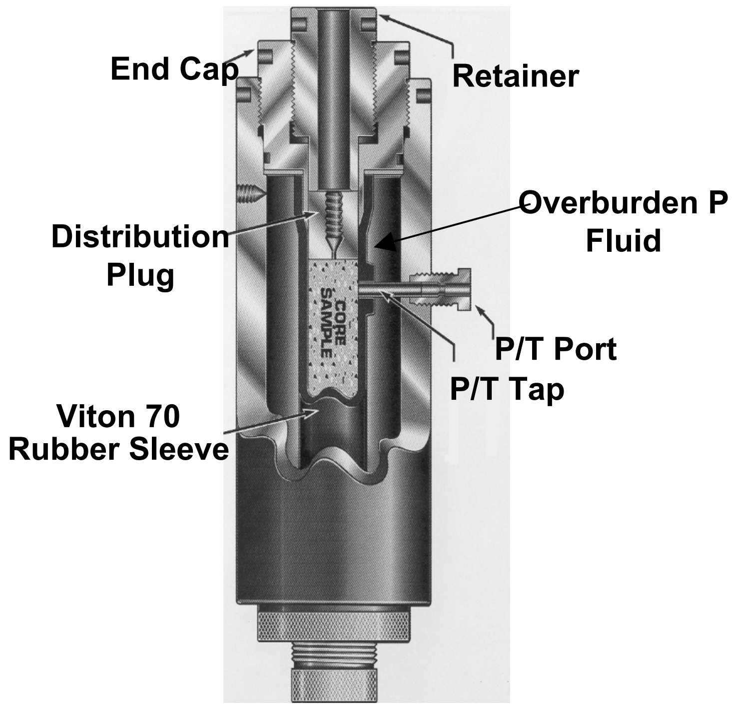
• Establish changes in sediment lithology.
• Decomposition kinetics at **Macro** scale [FISH* unit]
• In situ hydrate growth behavior at **Micro** scale [CMT**]
• Establish a correlation between Micro and Macro data and its relevance to the well log data.

*FISH: Flexible Integrated Study of Hydrates
**CMT: Computed Microtomography

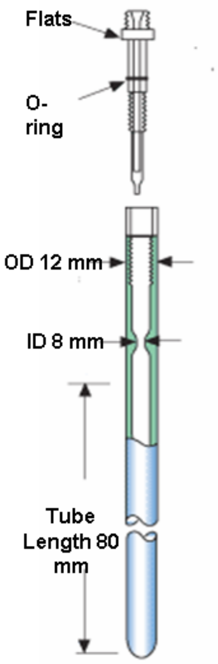

FISH
Properties and Data Output
Jerguson Gage - 198 mL, 20 MPa, 2-25°C
Temco DCHR – 308 mL, 20MPa, 2-25°C
Unconsolidated Samples
Consolidated Sand Samples
• Methane hydrate formation kinetics
• Dissociation profiles via depressurization
• Absolute permeability of sediments
• Effect of overburden pressure on formation/dissociation
Host Media
CMT & XRF
• Glass Beads
• Ottawa Sand
• Natural Depleted Sediment
Sample Cells
• Jacketed Syringe (1 mL) – 1 atm. P, 2-25°C Temp.
• Sapphire Cell (~ 10 mL) – up to 10 MPa P, 2-25°C Temp.
Instrumentation
• Beamline X2B, X26A, NSLS/BNL
• Data Acquisition - IPLAB
Data Reconstruction & Analysis Tools
• IDL
• ImageJ
• Drishti
Samples
• Host medium
• THF Hydrate in sediments
• Methane hydrate in sediments
XRF
• Sediment Characterization
• Elemental analysis
CMT
•2D/3D images
• Porosity
• Tortuosity
• Time resolved growth kinetics
• Microstructure model identification

Developed/Available Facilities

FISH
Jerguson Gage
V = 198 mL



FISH
Temco DCHR
V = 309 mL

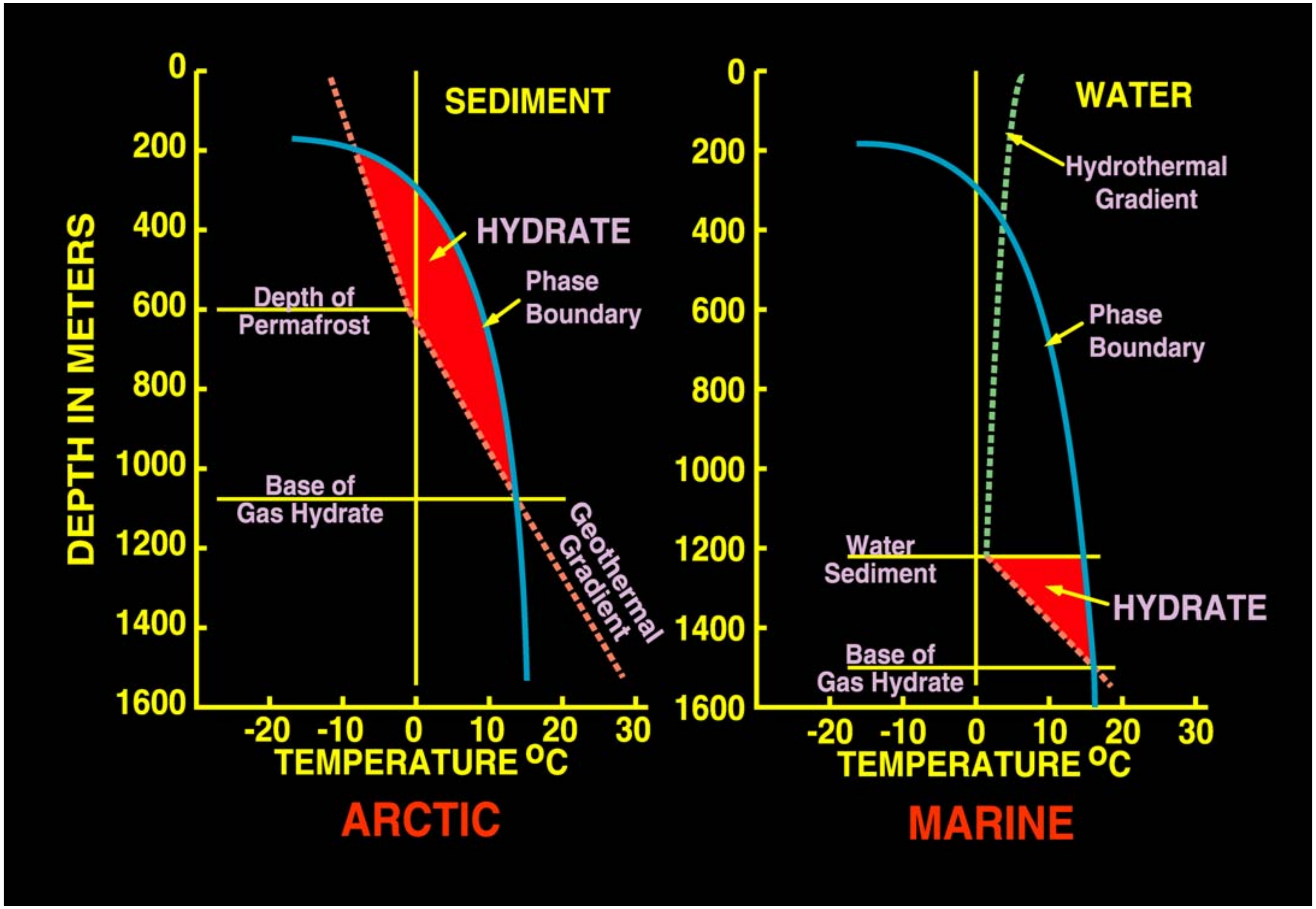


CMT
Sapphire Cell
High P = 8 MPa

Other

- Beamline X-2B, NSLS/BNL: CMT work
- Neutron diffraction high P cell (Developed at SBU)

Methane Hydrate Stability

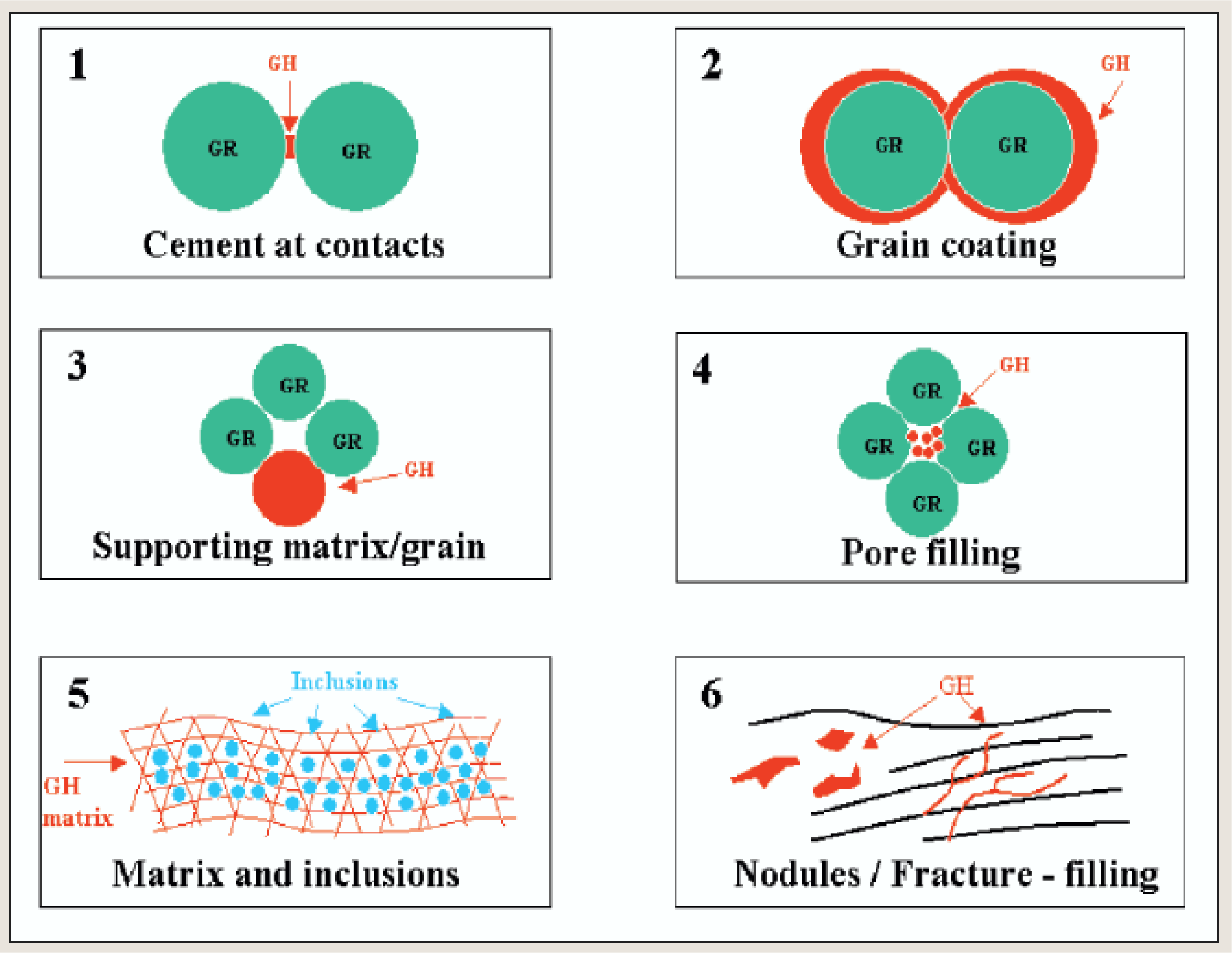


Natural Hydrates in Sediments

Gas hydrates dissociating from sea-floor mounds

Gas hydrates can occur as nodules, laminae,
or veins within sediments

Known Hydrate-in-Sediment Models



Dai et al., 2004

Sediments-hosted hydrates at the MACRO Scale

FISH Unit

Natural Sediments
Blake Ridge (BLR)
Gulf of Mexico (GoM)

Task 1: Unit modifications
Task 2: Methane hydrates- unconsolidated
Task 3: Methane hydrates- consolidated cores

Task 1

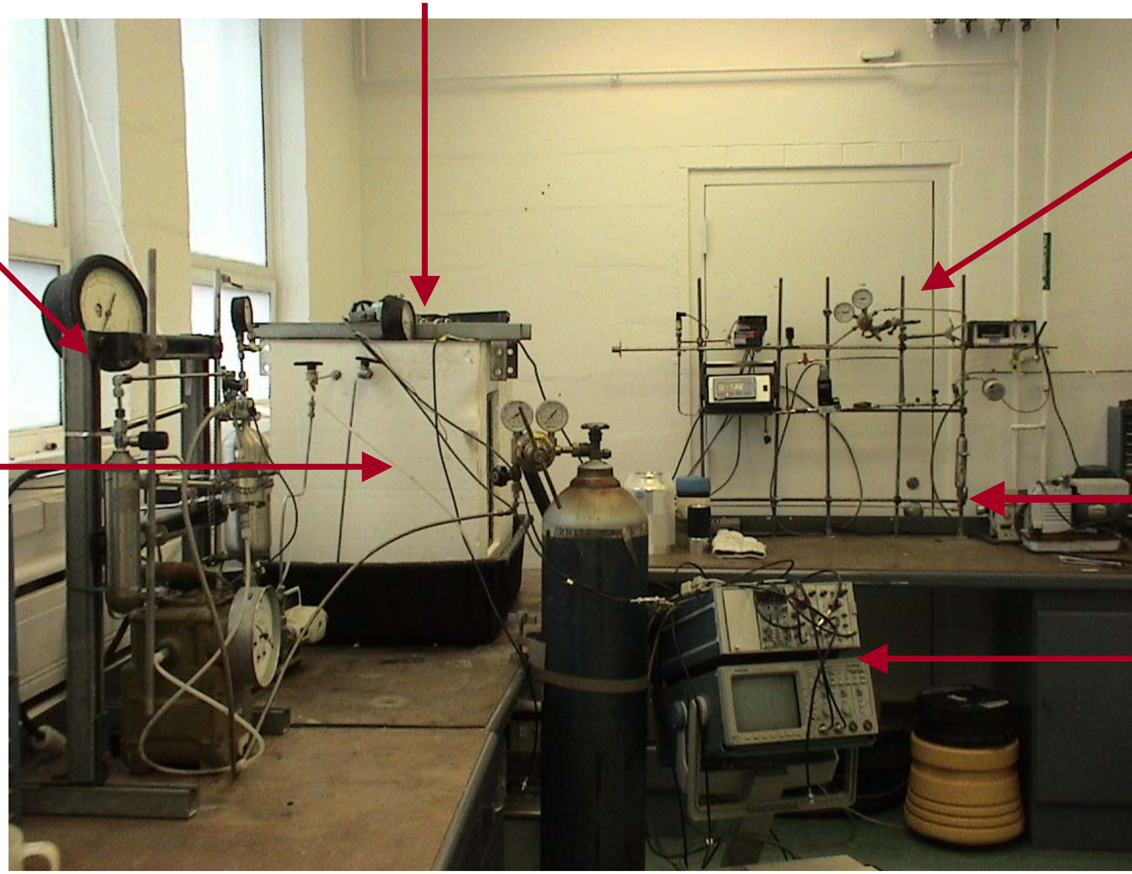
FISH unit modifications

The Original BNL FISH Unit

Pressure vessel
(Interchangeable)

P control
&
Gas
collection
System

Process
conditions
simulator
tank

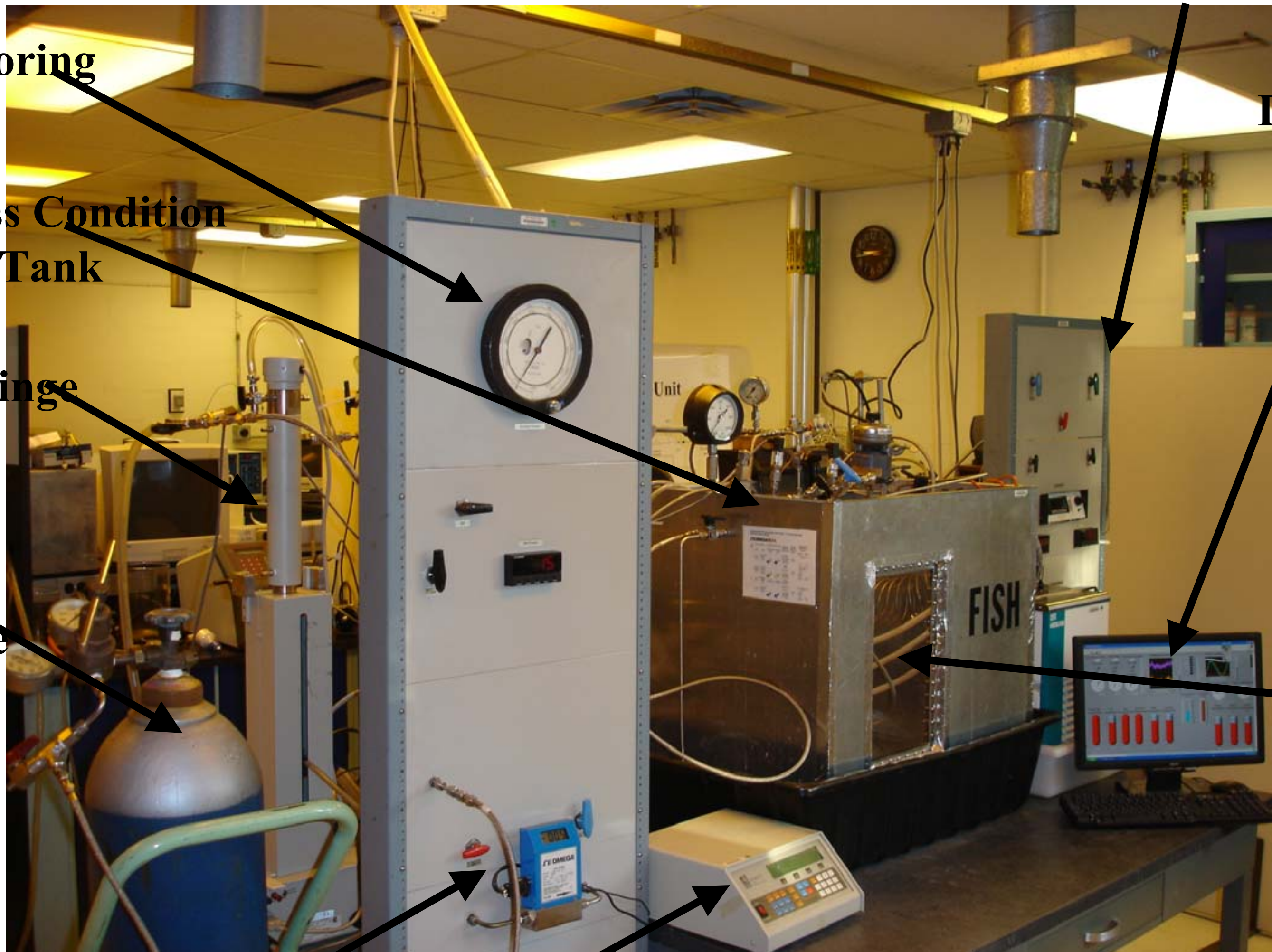


Gas delivery
system

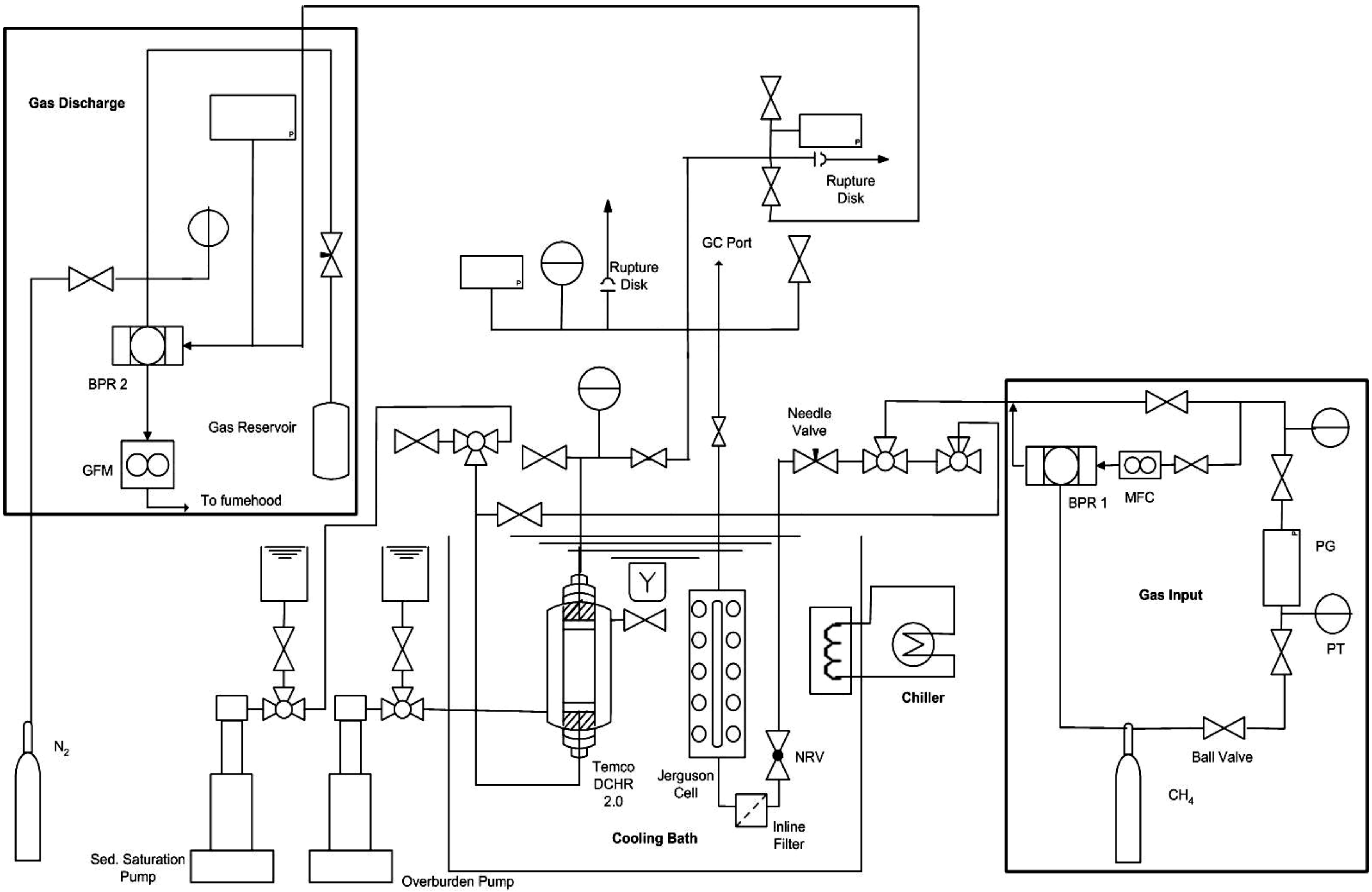
Kinetic data
collection &
analysis

Data collection
(acoustics)

The Modified FISH Unit



The Modified FISH Unit- Schematics

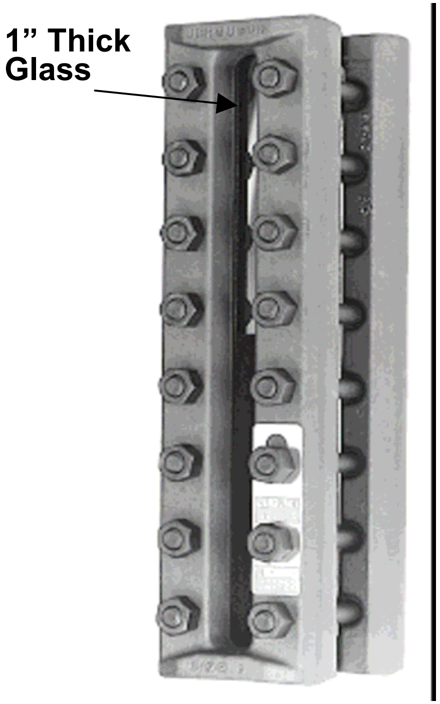


Task 1: FISH Unit Modifications

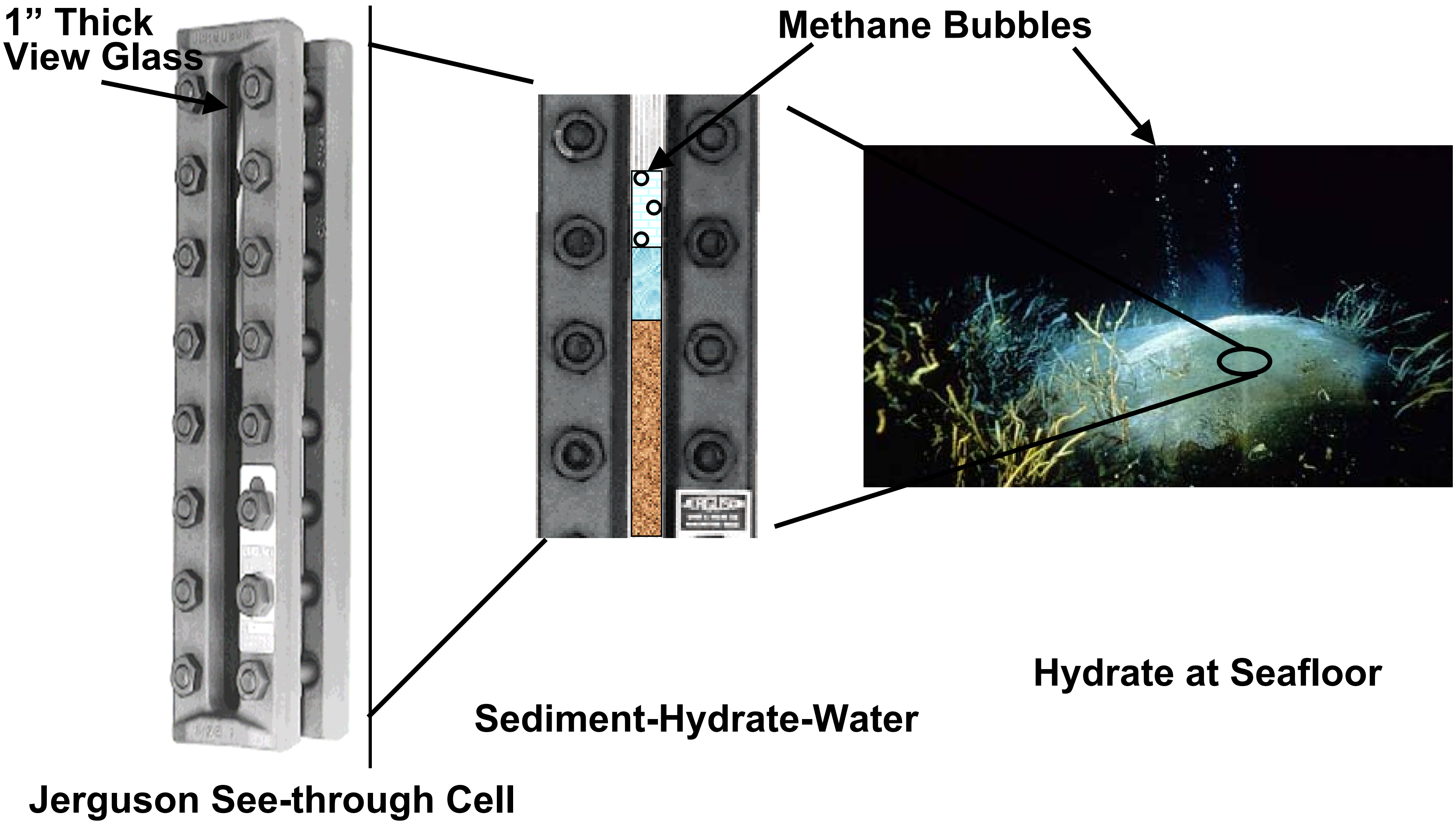
- Labview for data acquisition
- Temco cell addition for confined cores
- Isco pump
- Gore-tex membrane addition
- Precision T controls
- Capability to form both unconsolidated and consolidated cores.

Task 2

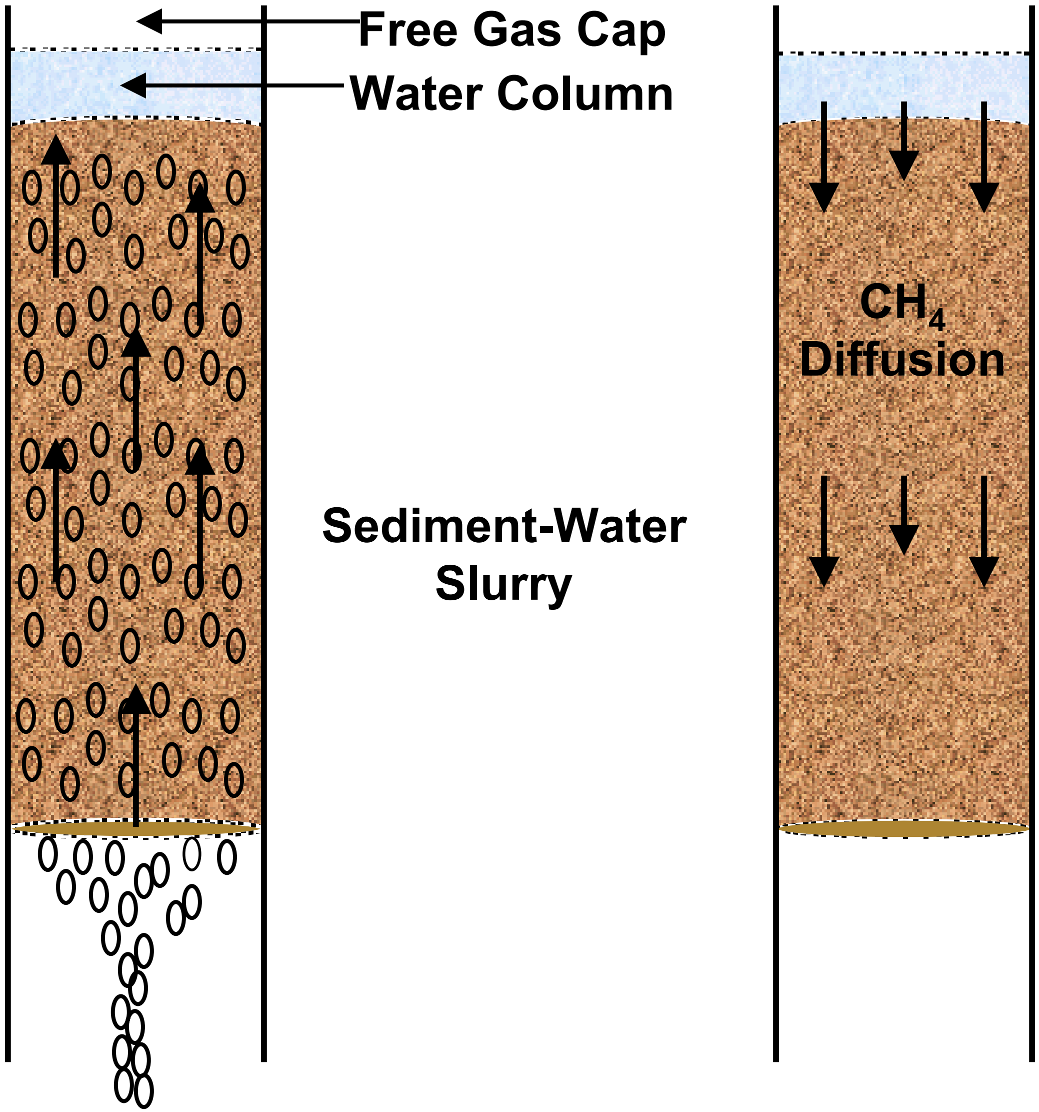
Methane Hydrates- Unconsolidated



Mimicking the Sea-floor



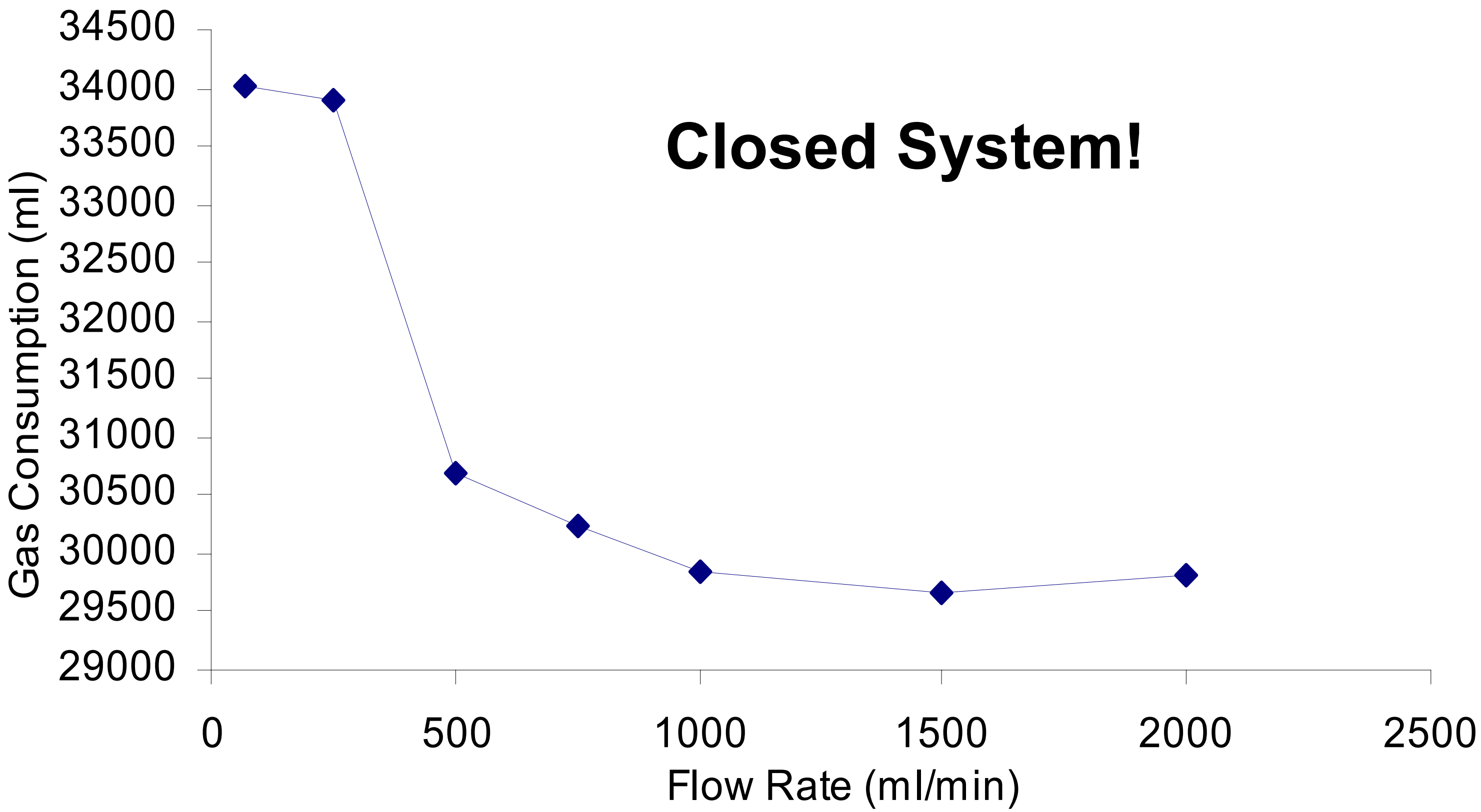
Formation Methods: Dynamic and Static Modes



Gradual charging of Methane (<2000 mL/min)

Rapid charging of Methane (>>2000 mL/min)

Dynamic mode – Effect of Flow rate

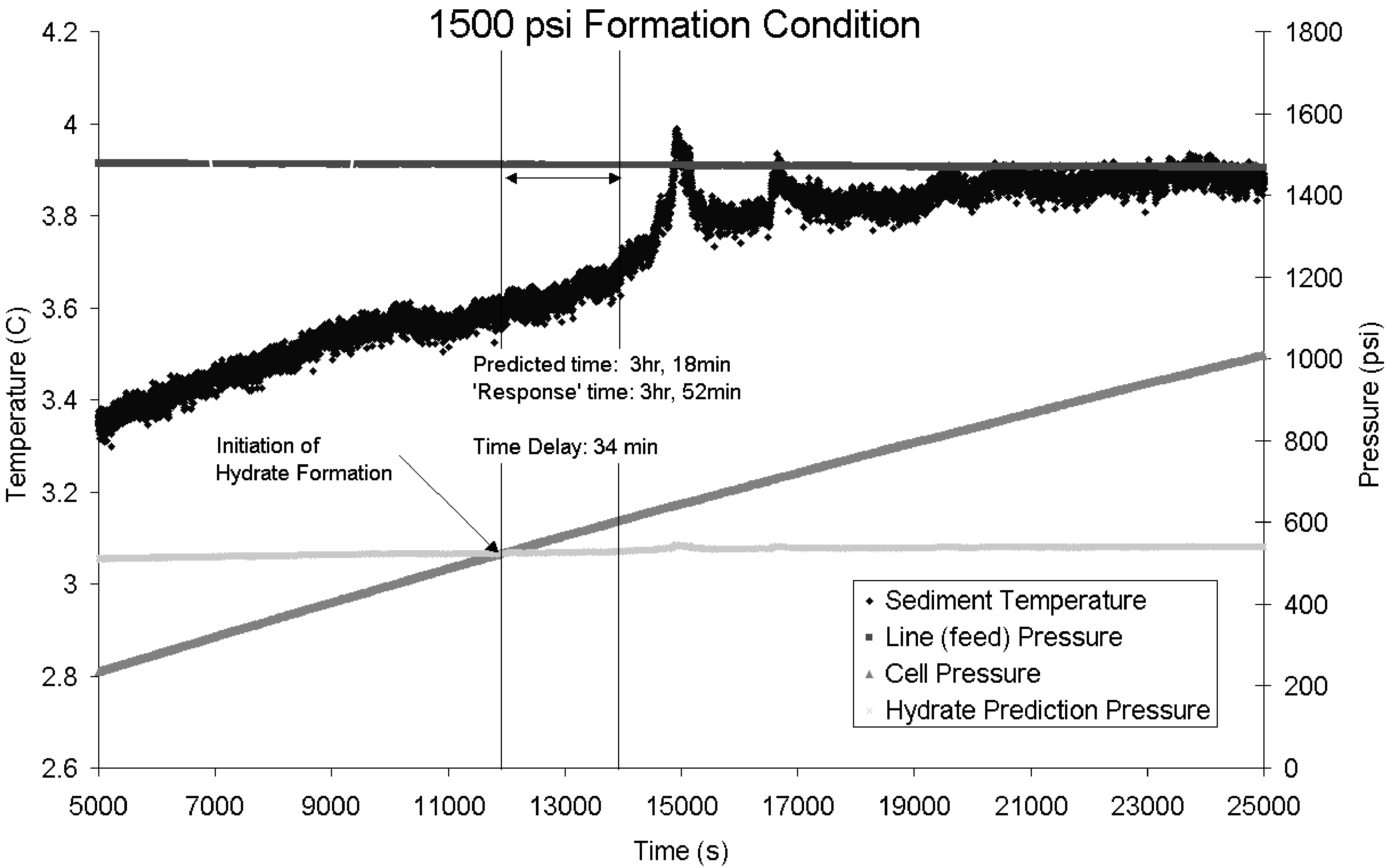


20 mL water + 60 gm BLR sediment

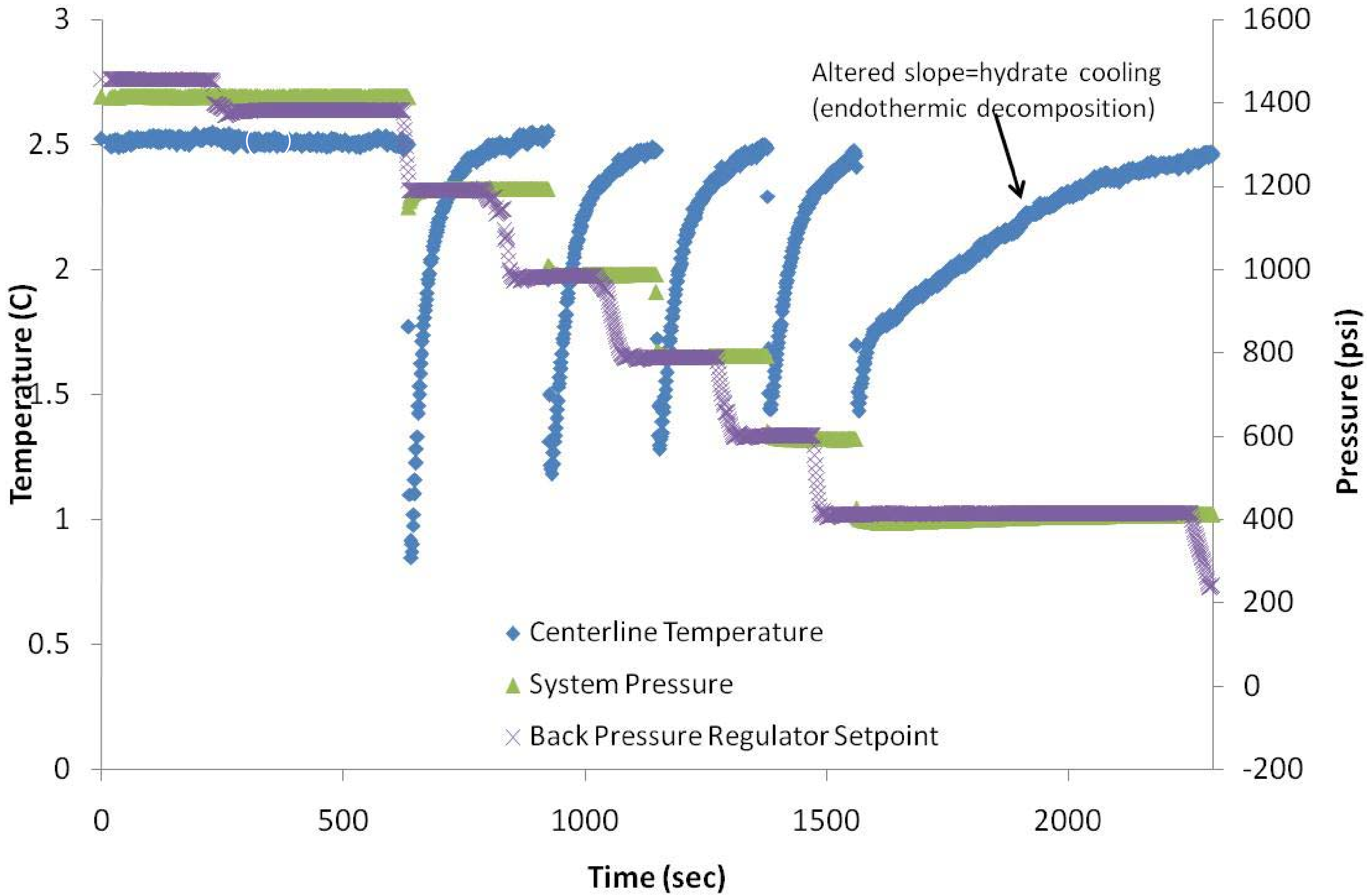
> 1000 mL/min (0.035 m/s)– minimal gas hold up

< 150 mL/min (0.005 m/s)– highest gas hold up

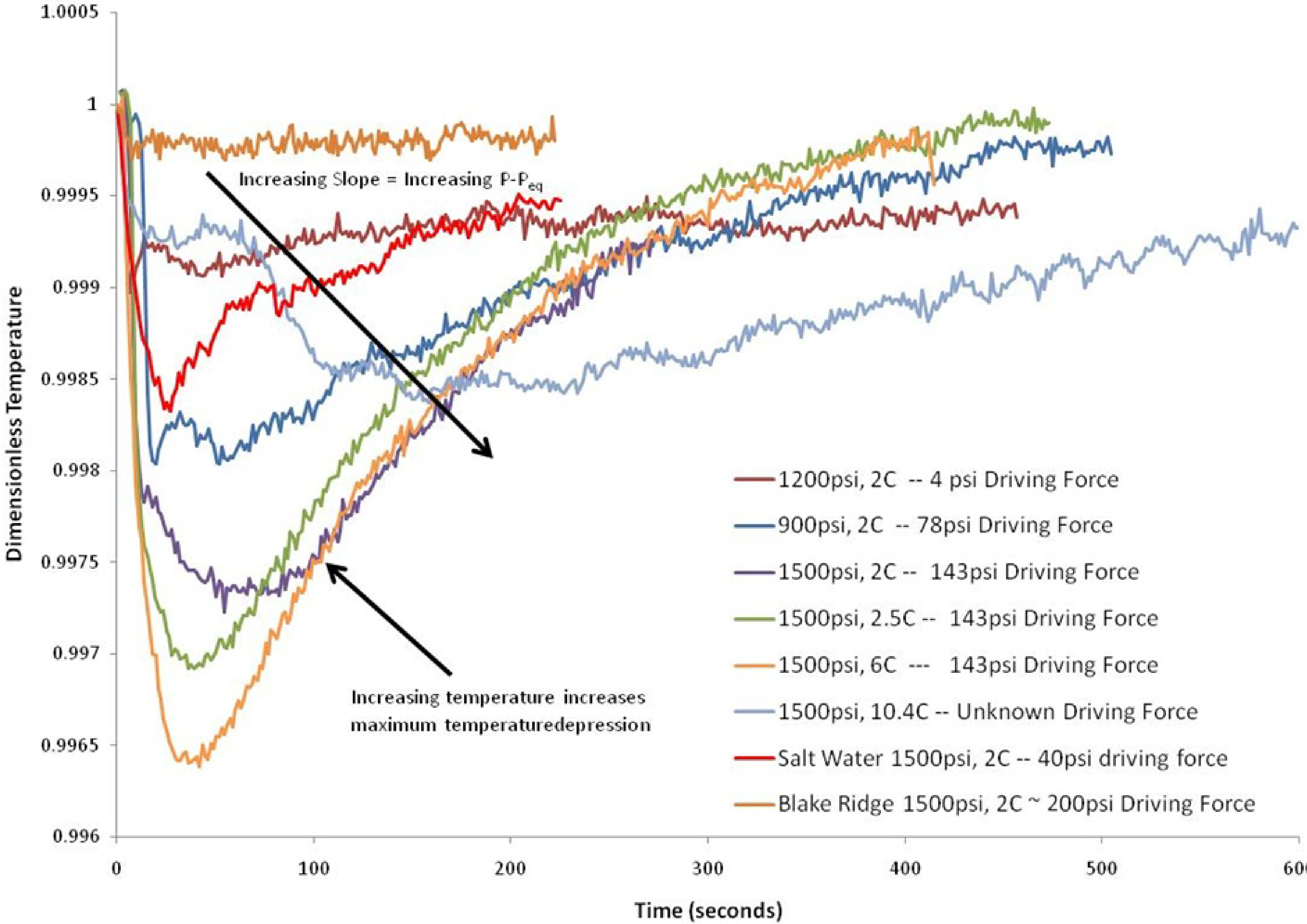
Formation Kinetics (3.5°C, 1500 psig, <2000mL/min, BLR)



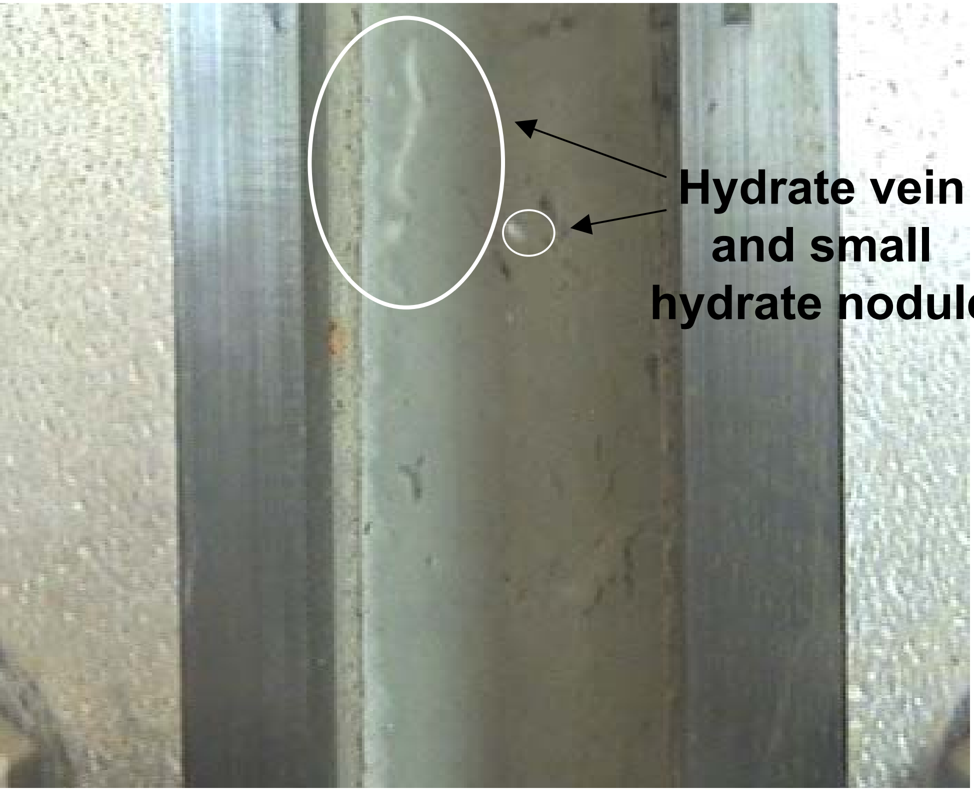
Dissociation Kinetics (T_i=2.5°C, P_i=1500 psig)

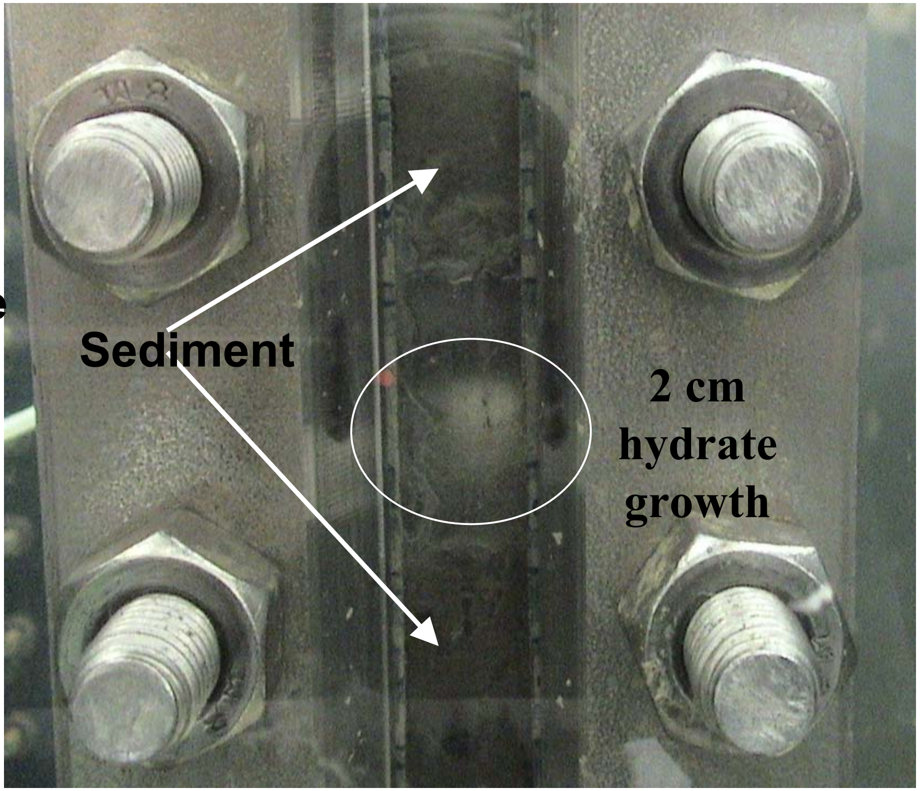


Dissociation Kinetics



Static mode (2°C, 1500 psig, >2000mL/min): GoM vs. BLR

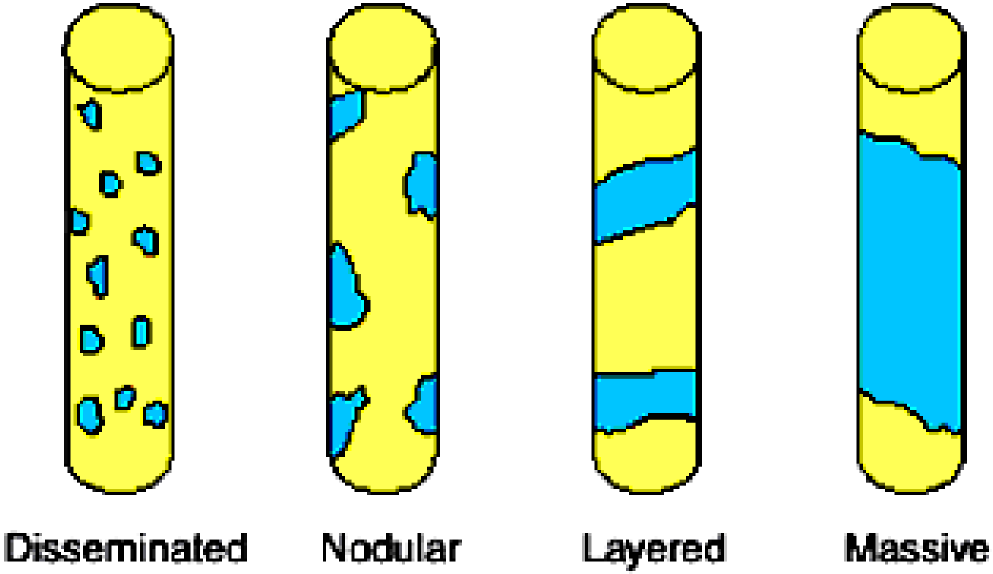




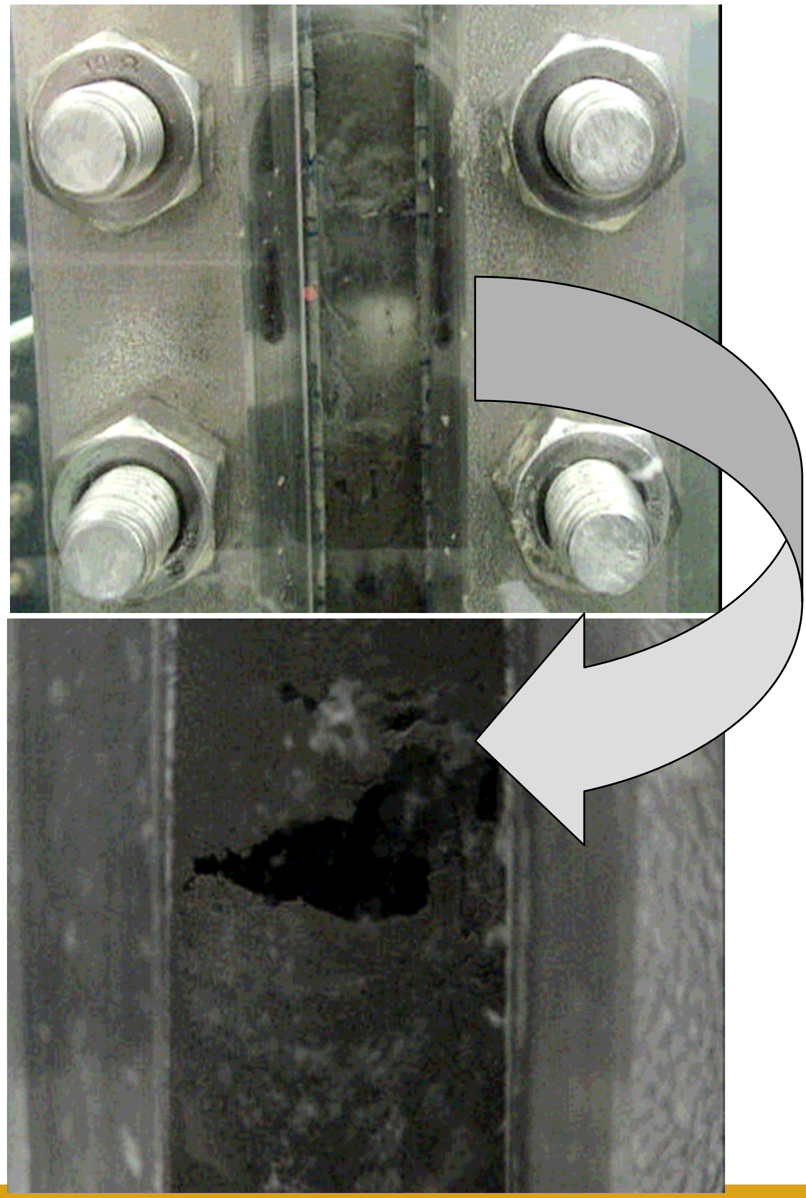
GoM
Particle size: 6 μm
Fine to very fine silt

BLR
Particle size: 21 μm
Medium to coarse silt

Gas Hydrate Configurations – Massive in BLR

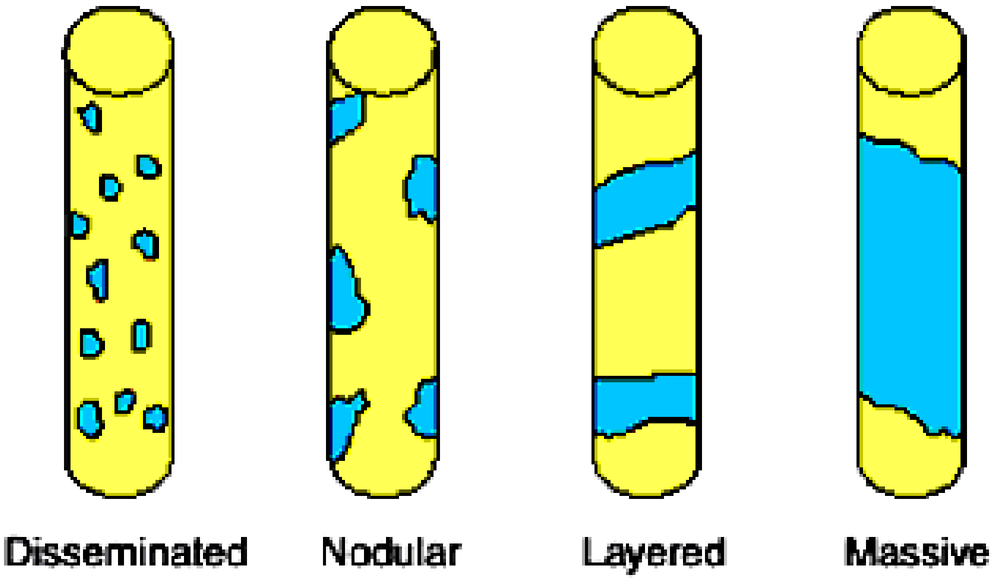


Sloan, 1998; Collett, 2000

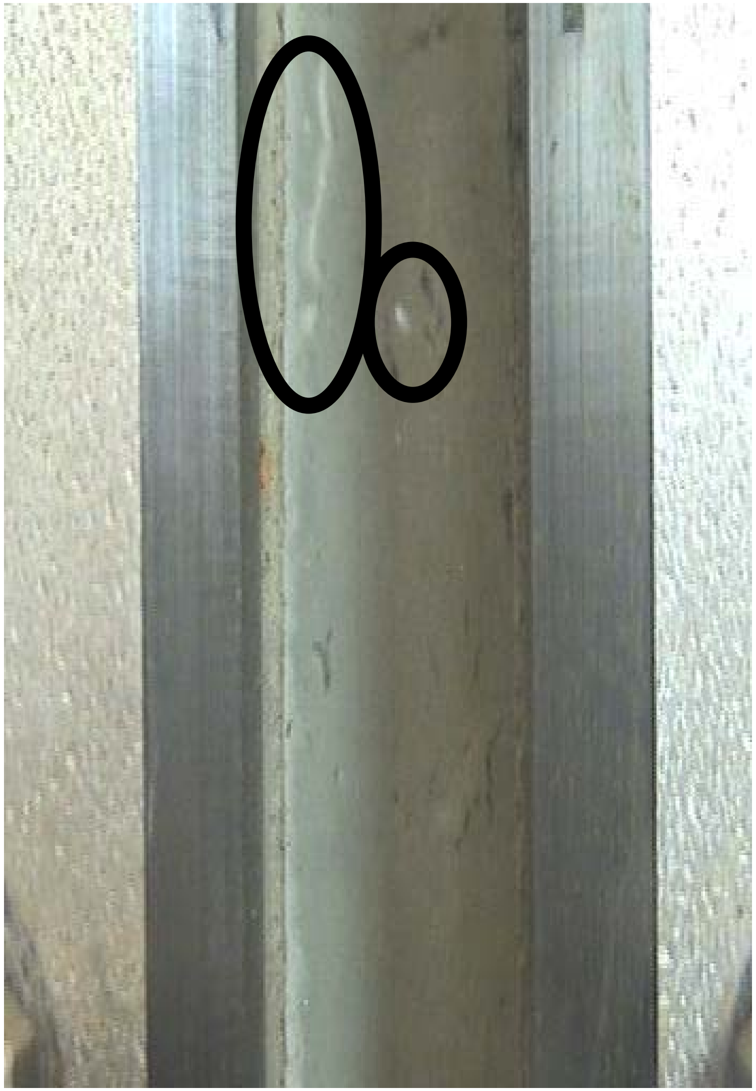


Massive Methane Hydrate in Blake Ridge (BLR) Sediment (2°C, 1500 psi) Formation and Dissociation (*Eaton, 2007*)

Gas Hydrate Configurations – Nodules or Veins in GOM



Sloan, 1998; Collett, 2000



Nodules and Veins of Methane Hydrate in Gulf of Mexico (GOM) Sediment (2°C, 1500 psi) (*Eaton, 2007*)

Conclusions- Unconsolidated Cores

- Total runs: 23
  - Dynamic mode: 10
  - Static mode: 13

- Run Conditions: P: 900-1500 psi; T: 2-10^{o}C; CH_4 flow rate: 70-2000 mL/min.

- At gas flow rate < 200 ml CH_4/min to the cell, a marked increase in gas uptake by hydrates in the BLR sediments (increased gas holdup from the larger grained sediments).

- Static-charge formation method revealed that;

  - hydrate formation rates in fine-grained sediments were mass-transfer-controlled, close agreement to theory (gas uptake time of over 2 weeks).

  - in coarse/more porous sediments (BLR), gas uptake rates were enhanced compared to those in the fine-grained sediments.

- Type of hydrates formed:

  - Coarse BLR sediments: large masses of hydrate which excluded sediments

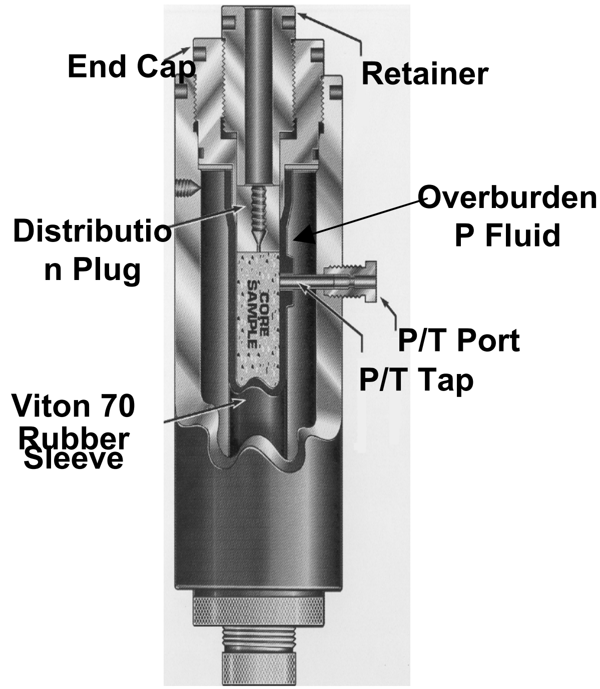
  - Fine-grained GoM sediments: typically formed tiny nodules/veins against the glass of the reactor with remaining gas uptake formed hydrates dispersed within sediment in the column.

Conclusions- Unconsolidated Cores (Contd.)

Dissociation kinetics in natural sediments (GoM and BLR):

- Warmer the temperature of hydrate formation/dissociation, greater the T drop while dissociation
- With increasing pressure drop for hydrate dissociation (Peqm-Psys), the host sediment requires more time for T to warm up after dissociation
- BLR sediments resulted in the quickest warm up after dissociation than those from GOM.

Task 3: Methane Hydrates- Consolidated



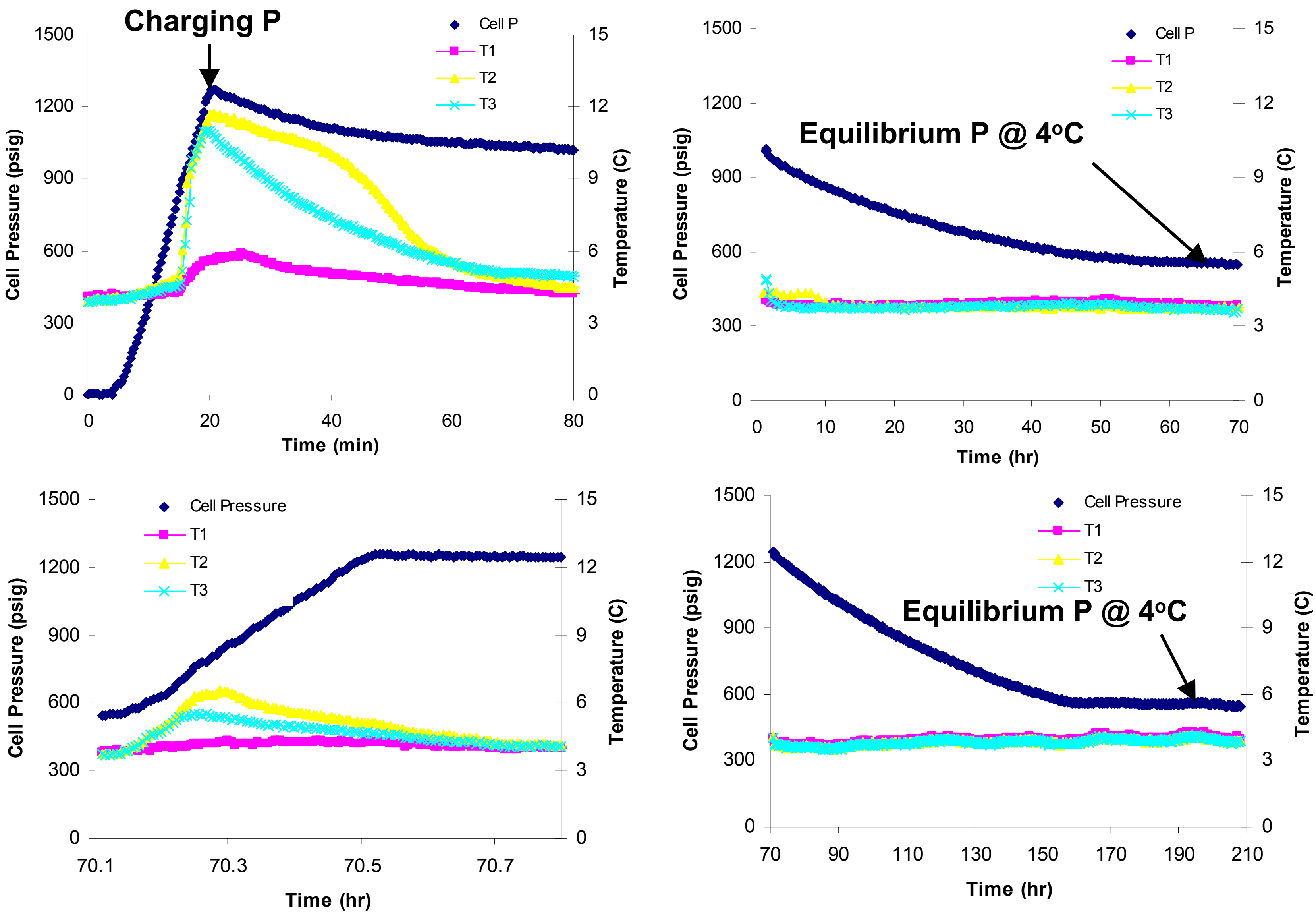
Temco vessel

- **Replace Jerguson vessel with Temco vessel in the FISH unit.**

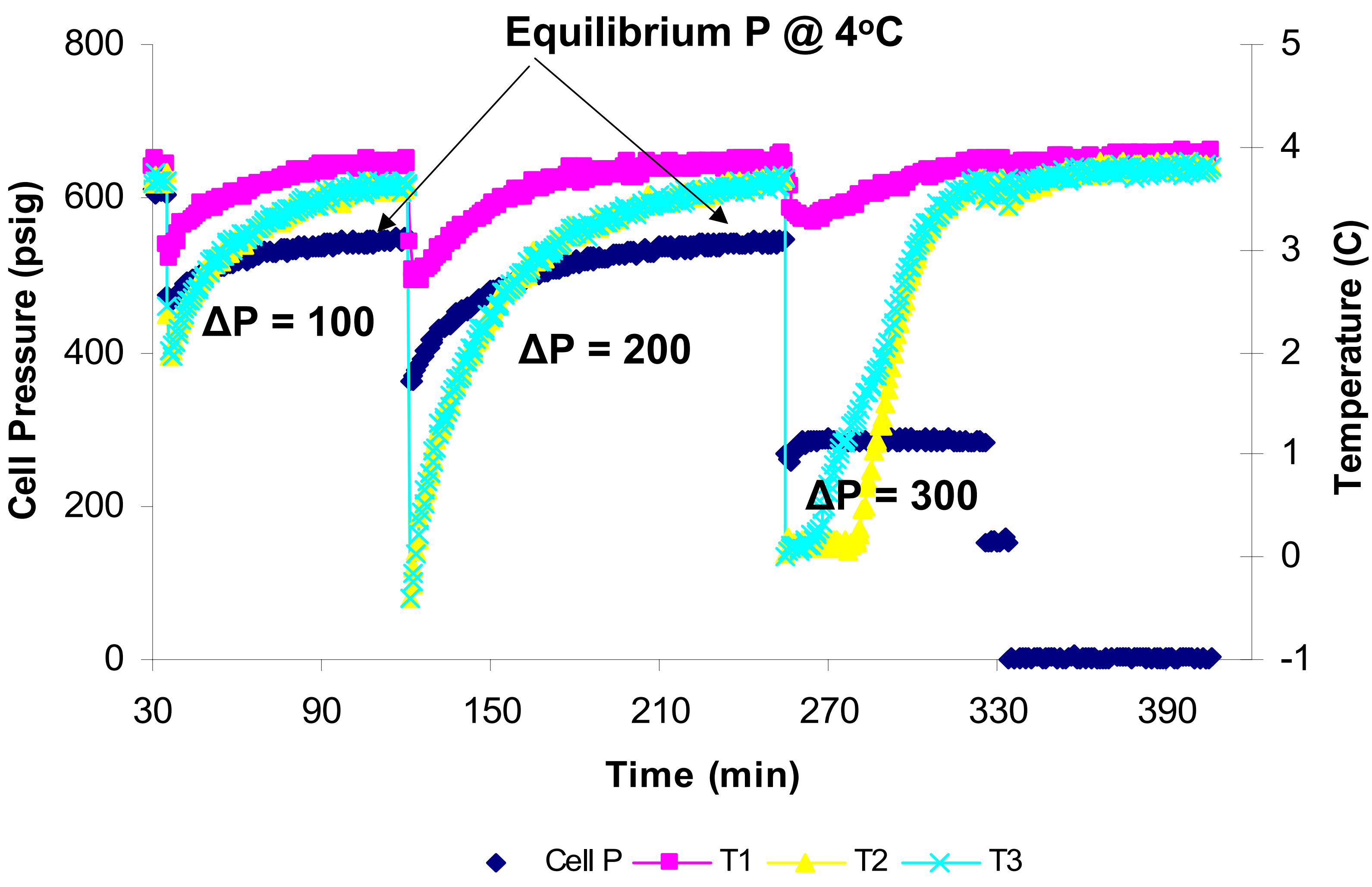
Confined Cores- Experimental Conditions

- Sediment: **Ottawa Sand** (110 μm grain size)
- Sediment bulk density: 1.625 gm/mL
- Core Dimensions: D= 2”, L= ~6”(Volume: ~284.6 mL)
- **Water saturation: 100%**
- **Confining pressure: 1300 psig**
- Core holder: Temco DCHR w/3 pressure ports (1”, 3”, 5”)
- Methane purity: > 99.99%
- Methane charging flow rate: < 2000 mL/min (gradual charge)
- **Methane hydrate formation conditions: ~ 1200 psig, 4^{o}C**
- Methane hydrate dissociation conditions:
    - 100 psi ΔP from equilibrium pressure
    - 200 psi ΔP from equilibrium pressure

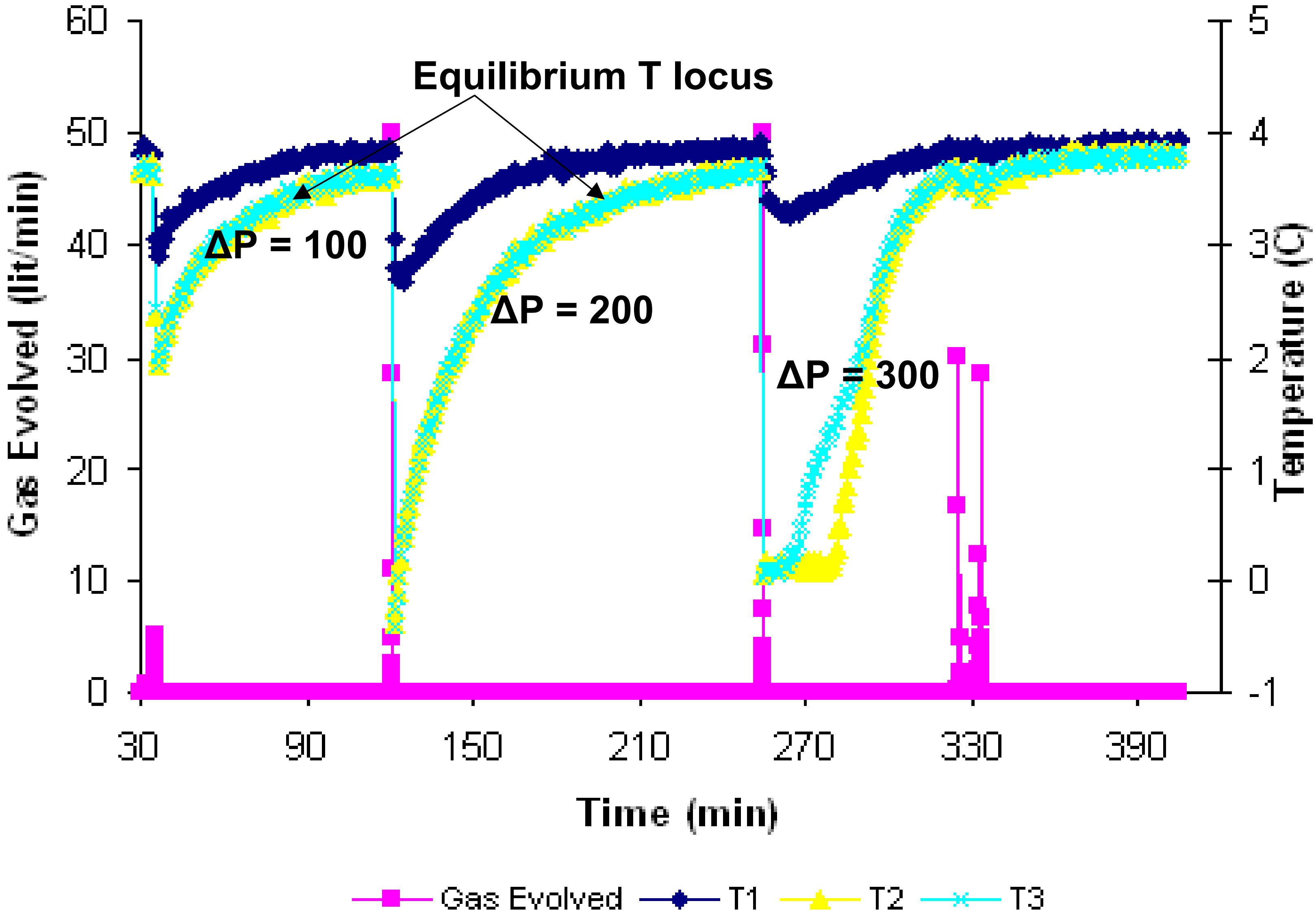
Confined Cores: Formation



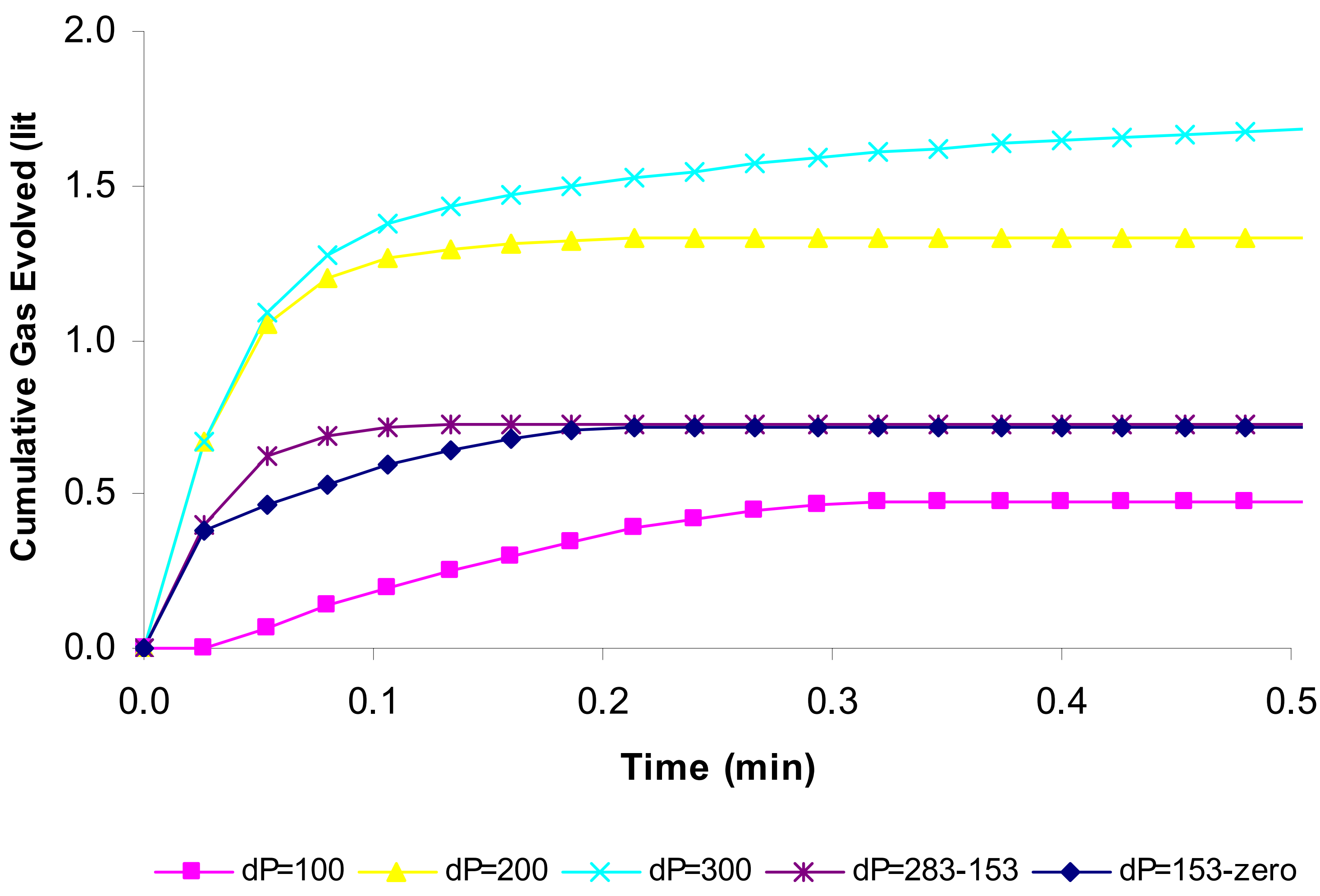
P/T during Dissociation (w/100 psi ΔP)



Gas Evolved during Dissociation (w/100 psi ΔP)

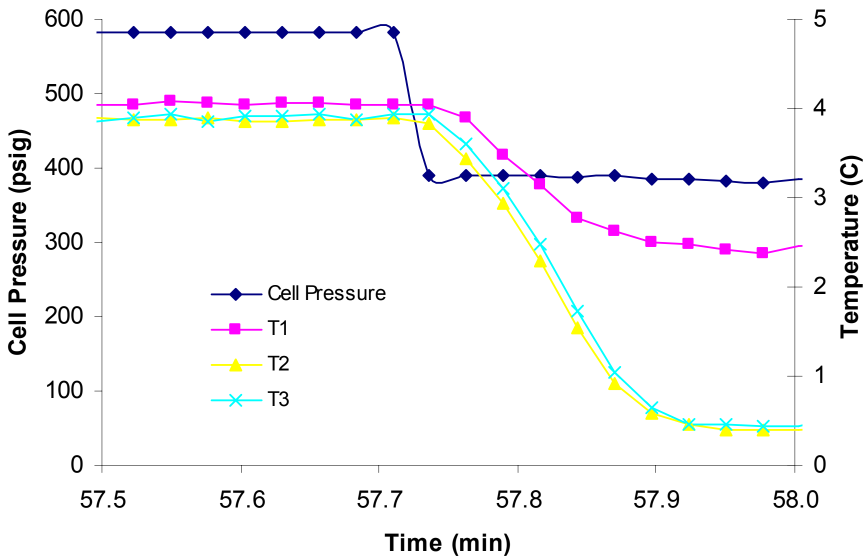


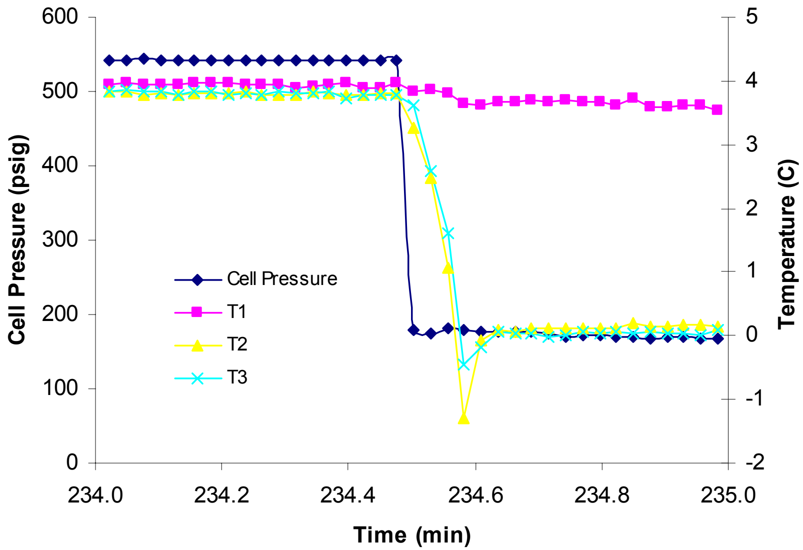
Cumulative Gas Produced during Dissociation



Where do hydrates start to dissociate?

T1 – Core Surface; T2 – Half-radius; T3 – Core center





- **Dissociation front moves from the center towards the wall.**
- **Methane hydrate saturation = 73.3%.**

Conclusions: Consolidated cores

Host: Ottawa sand (110 μm)

Hydrate formation (at 1200 psig / 4ºC/108 mL pore water):

- Slow (60 hrs) for the pore pressure to asymptote to the equilibrium pressure.
- Upon recharging, t = 90 hr to equilibrate as more pore water is consumed over time.

Hydrate dissociation with the depressurization technique

- Instantaneous gas output as high as 50 L/min for both 100 and 200 psi pressure drop below the equilibrium pressure.
- The greater the pressure drop during dissociation, the higher the degree of cooling.
- A longer time period was observed for sediments to reach initial in-situ T.
- Enthalpy of dissociation = 59.1 kJ/mol (from Clausius-Clapeyron equation).
- The pressure drop of 200 psi was enough to completely dissociate methane hydrates formed in confined sediments in all the runs.
- Methane hydrate saturation = 73.3%.

Conclusions: Consolidated cores (Contd.)

- During the endothermic methane hydrate dissociation, T of the core followed the order: Center (T3) < half-radius (T2) < wall (T1).

  - Hydrate front started to dissociate from the center towards the wall.

- Hydrate formation threshold:

  - Unconsolidated (~ 30 min. lag) vs Consolidated (none)

Sediments-hosted hydrates at MICRO Scale

Goal: Establish hydrate growth behavior

Computed Microtomography (CMT)

Beamline X-2B
Brookhaven National Laboratory (BNL)
National Synchrotron Light Source (NSLS)

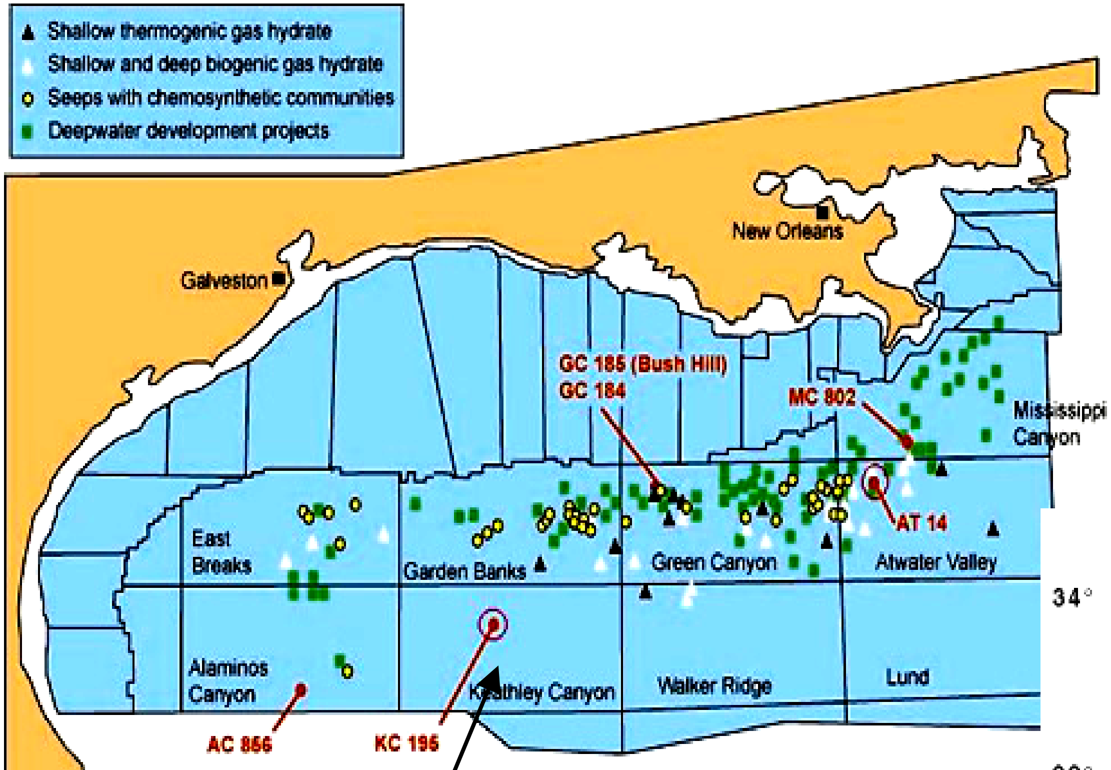
Task 4. Sediment Characterization
Task 5. In Situ Hydrate formation/dissociation

Task 4

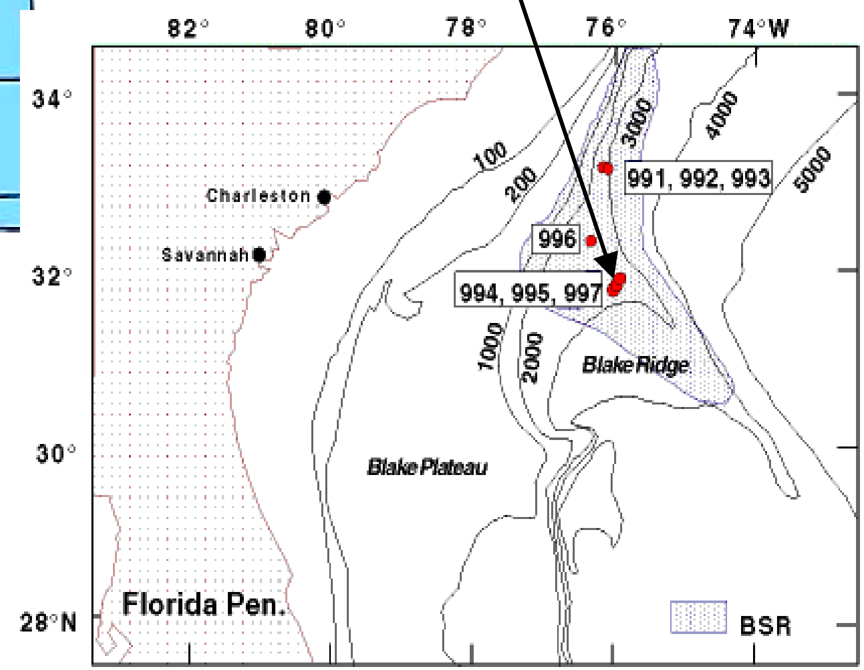
Sediment Characterization

- **Blake Ridge (BLR)**
- **Gulf of Mexico (GoM)**

Host Sediments: BLR



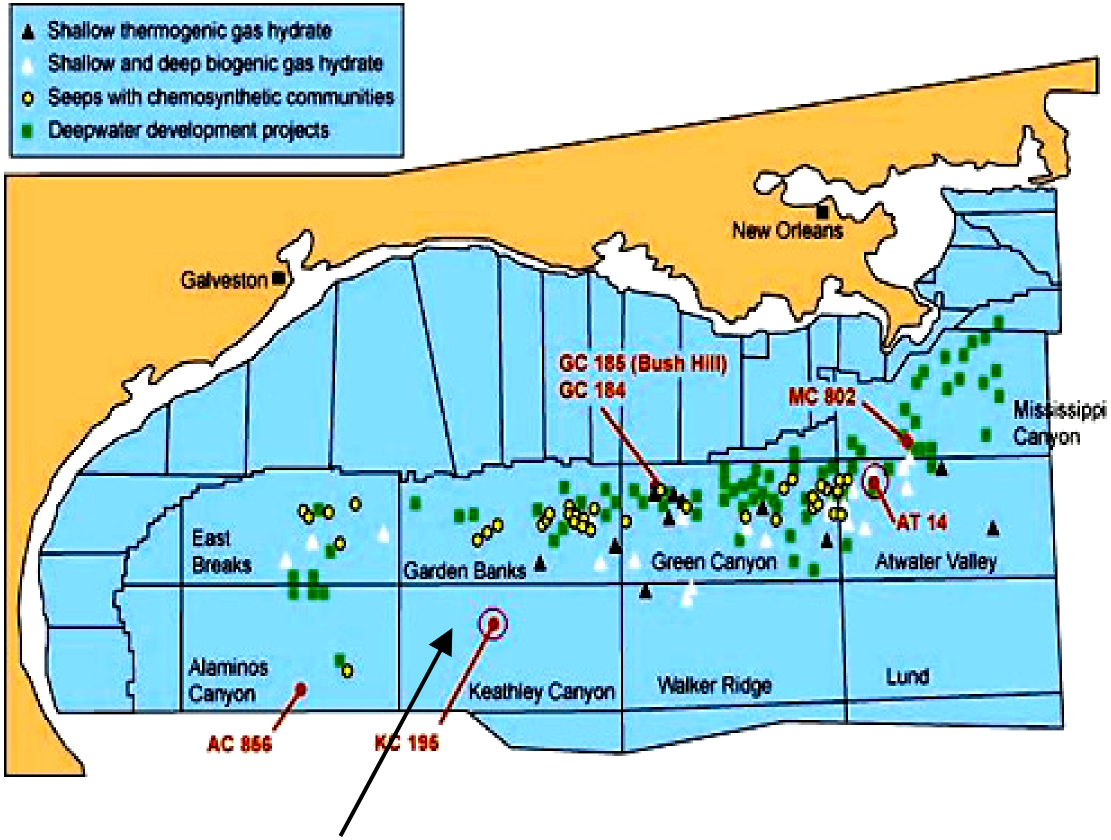
ODP Leg164, Site 995A, **667.85 mbsf, WD=2278.5 m, Bulk porosity = 51%, Average depth mbsf – 200-425**



KC151, Hole#3, **1 mbsf, WD=1311 m, well depth: 440 mbsf.**

NETL; Collett, 2004

Host Sediment: GoM



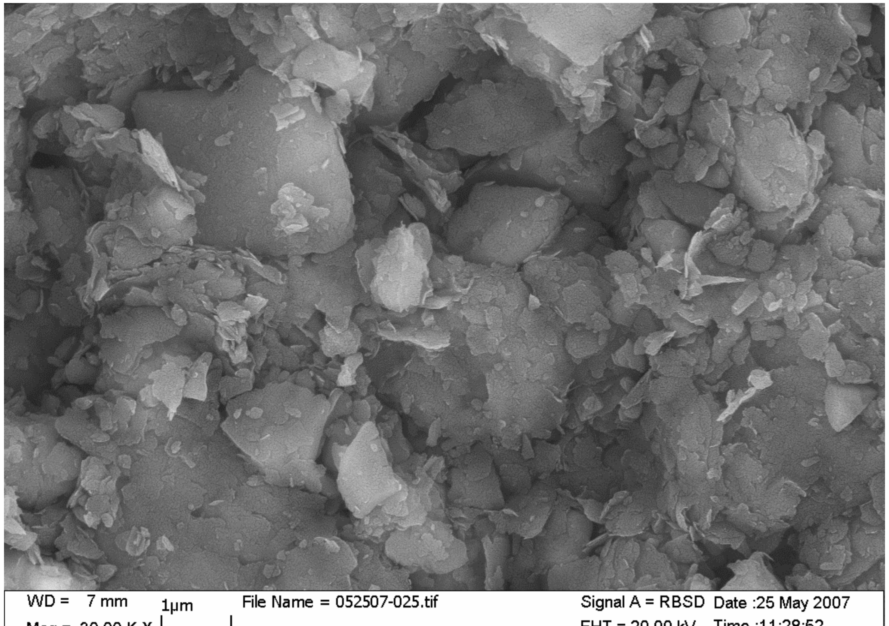
KC151, Hole#3, **1 mbsf, WD=1311 m**

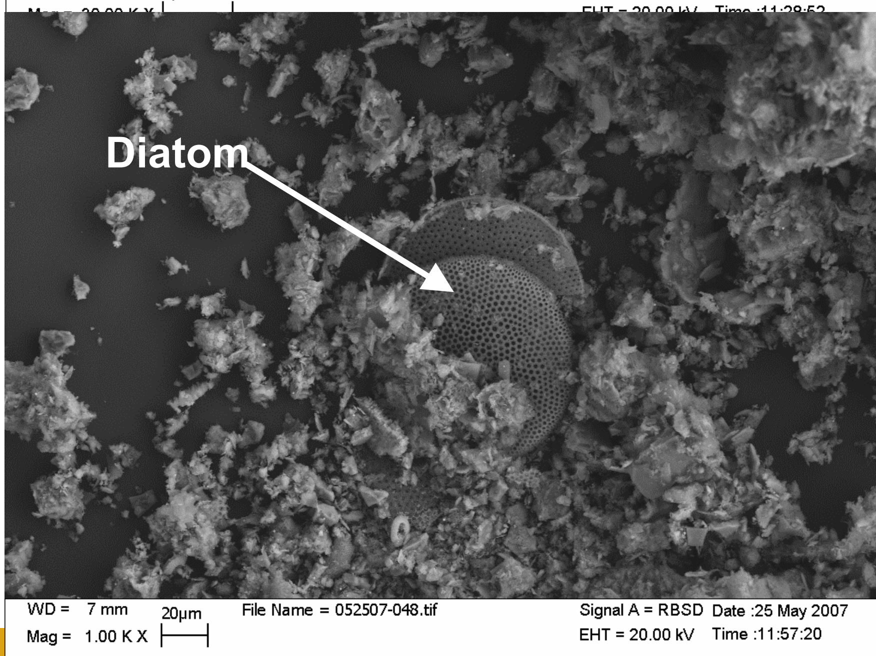
KC151-3 (0-10mbsf)	
Salinity (ppt)	35.775
Water content (solids %)	87.15
Grain density (kg/m³)	2715.75
Bulk density (kg/m³)	1541
Void ratio	2.305
Sediment	Clay
% Sand	1.12
% Silt	14.62
% Clay size	84.27

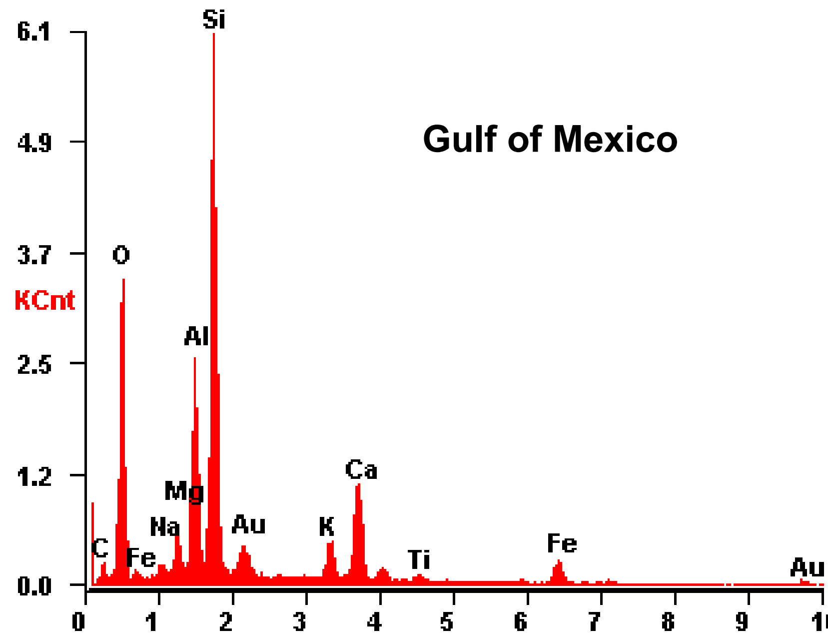
(Winters et al., 2008)

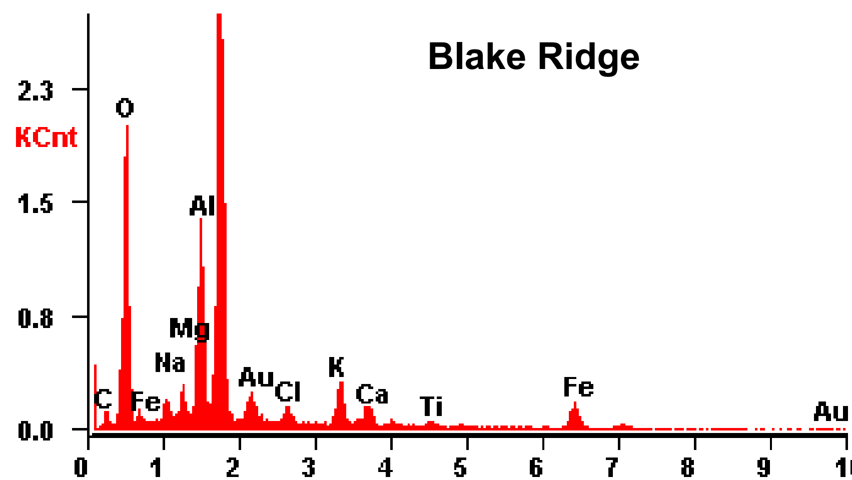
NETL; Collett, 2004

SEM/EDX Analysis– GoM and BLR



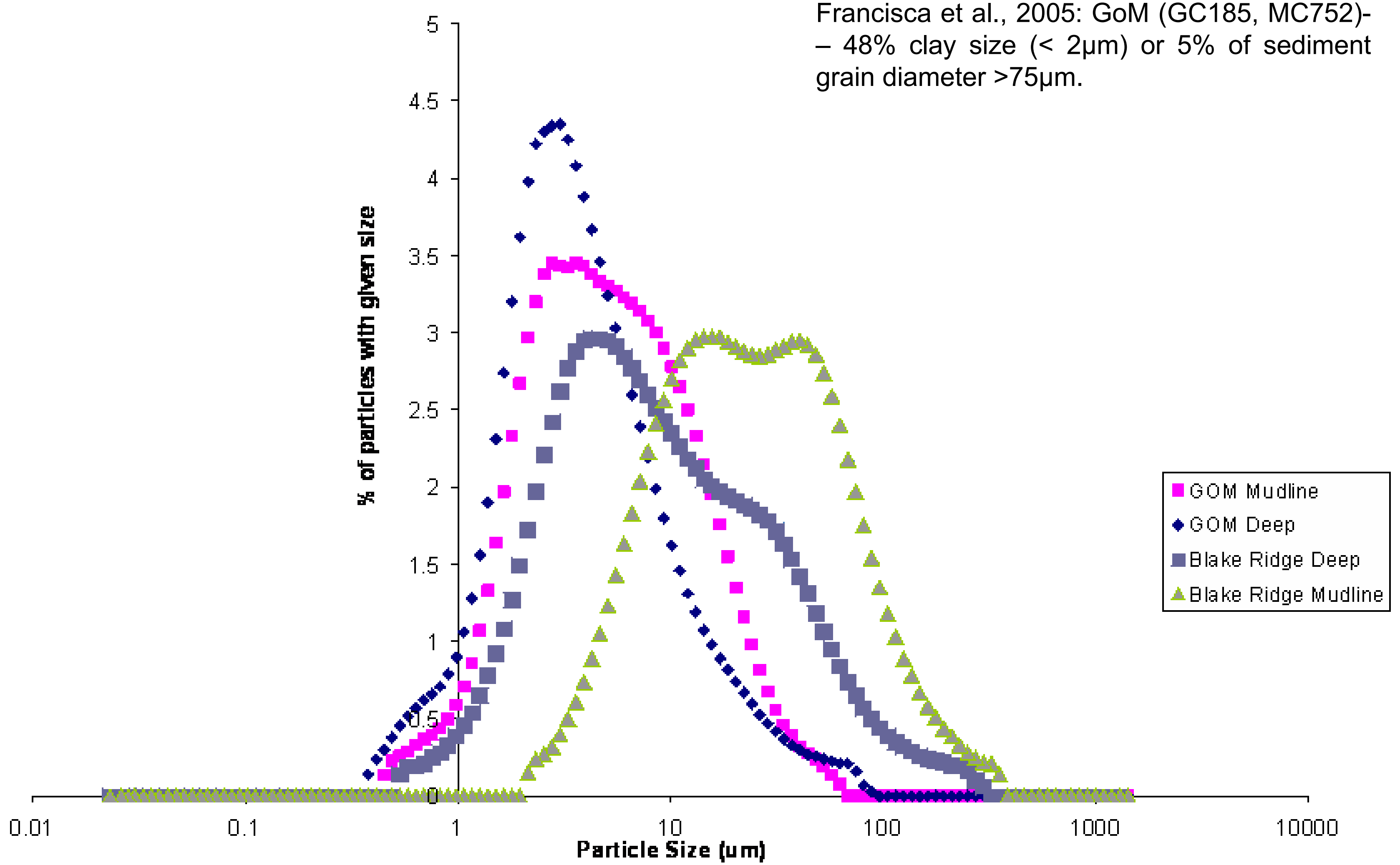




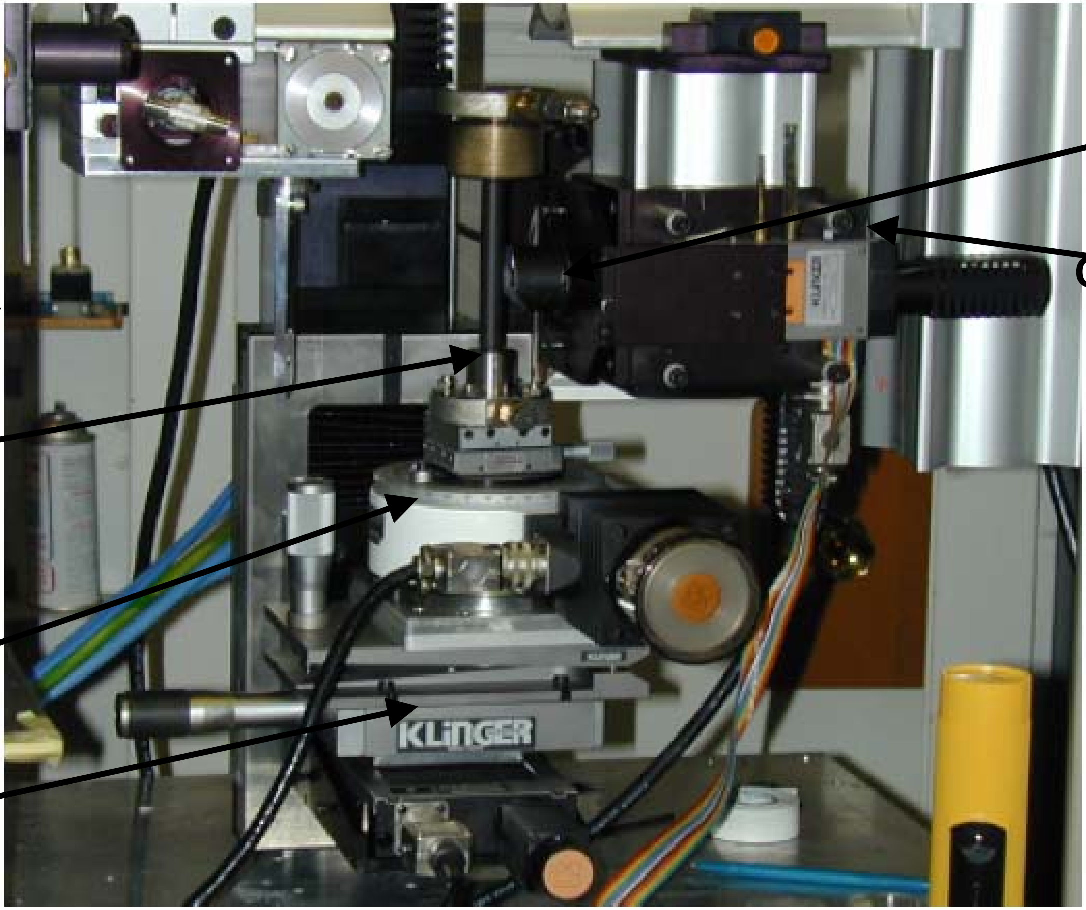


Particle Size Distribution: GoM vs. BLR

Francisca et al., 2005: GoM (GC185, MC752)-– 48% clay size (< 2µm) or 5% of sediment grain diameter >75µm.



Set up of X2B at NSLS/BNL



- Source type: Bending magnet
- Energy range: **8-35 keV**
- Mono crystal/ grating: Si(111)
- Angular scan: **180 deg.** (maximum 1800 views)

- Scan variables: **Beam energy, ROI, angular increment, exposure time etc.**
- Absorption tomographic scanning: *IP Lab, ExxonMobil Res. & Engg*)
- Output file format: **filename.prj** (~ 1GB)

Task 4: Conclusions

- Particle size: BLR > GoM
- BLR- Reported earlier
  - *Porosity (CMT): 68.6%; Tortuosity (CMT): 1.81
  *Bulk porosity: 70.0% (Winters et al.)
- GoM
  - CMT data complete. Analysis nearly complete.

Task 5

In Situ Hydrate Formation/Dissociation

- Optimization of CMT data reconstruction steps
- System: THF/Water/Glass beads

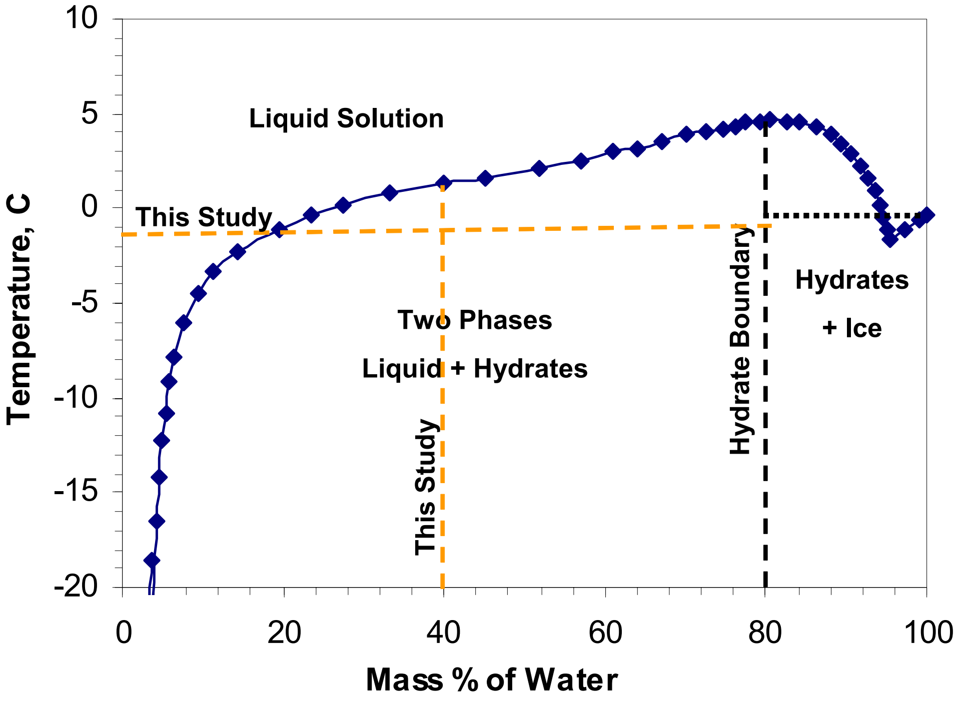
THF Hydrates- Literature

Santamarina and Ruppel (ICGH 2008, Vancouver)

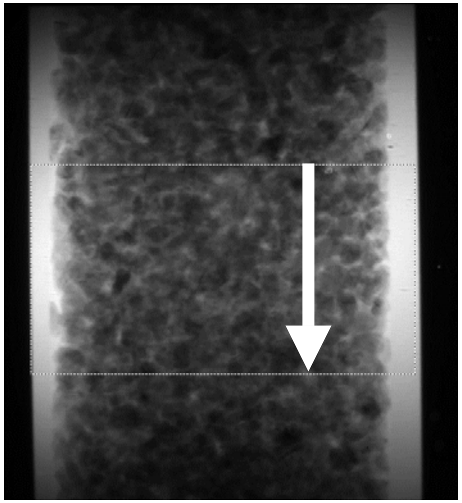
• Based on THF hydrate bearing sediments: Factors controlling mechanical properties:
  - Loci of hydrate formation at the pore scale
  - Soil characteristics
  - Impact of hydrate formation technique.

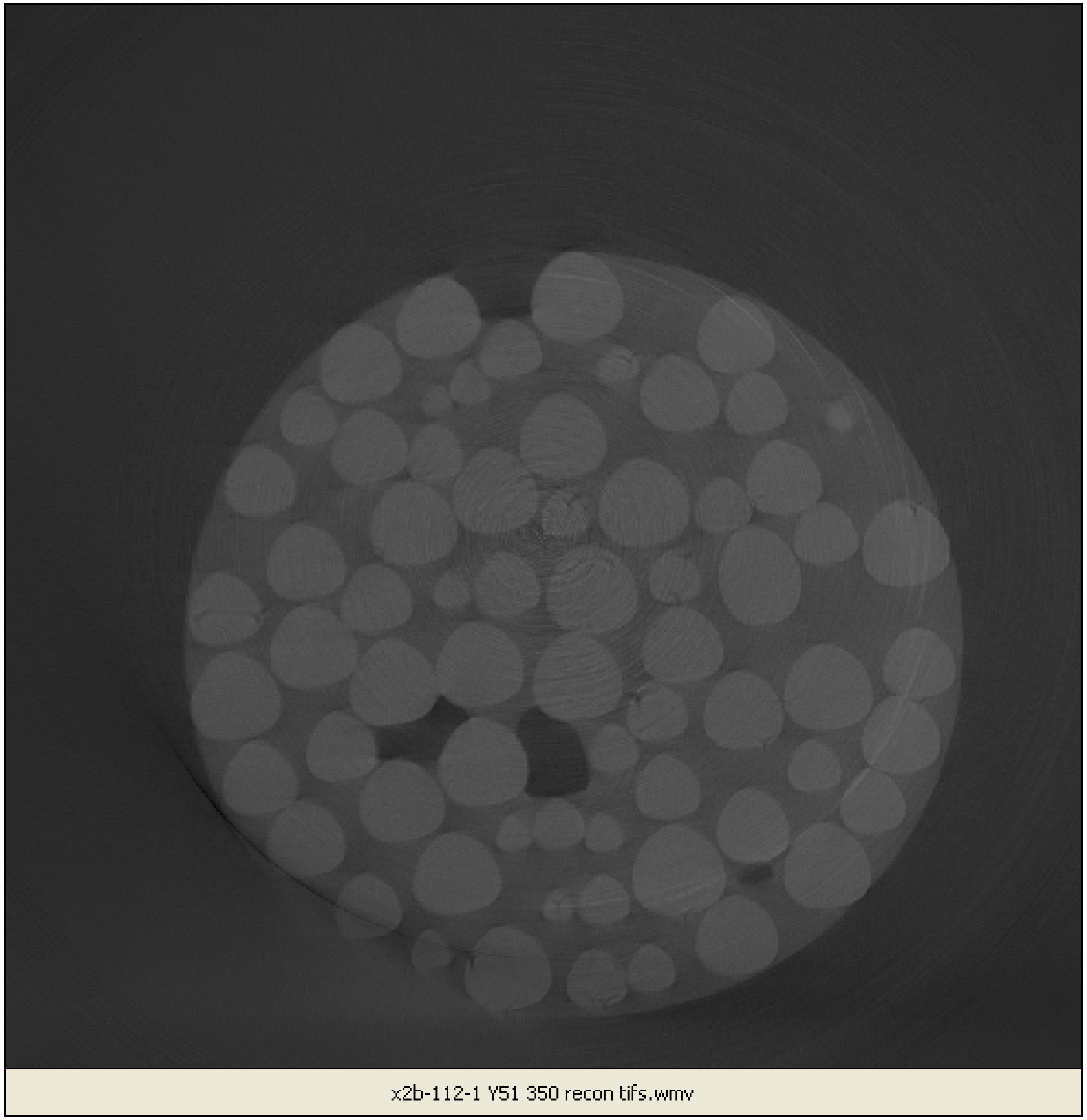
Surrogate for Methane – THF!

- **Solution**: Water-THF (40-60 wt%)
- **Salt**: For density contrast
- **Cell**: 1 cc
- **Porous Media**: 500 micron glass beads
- **T:** < 4^{o}C
- **P:** 1 atm



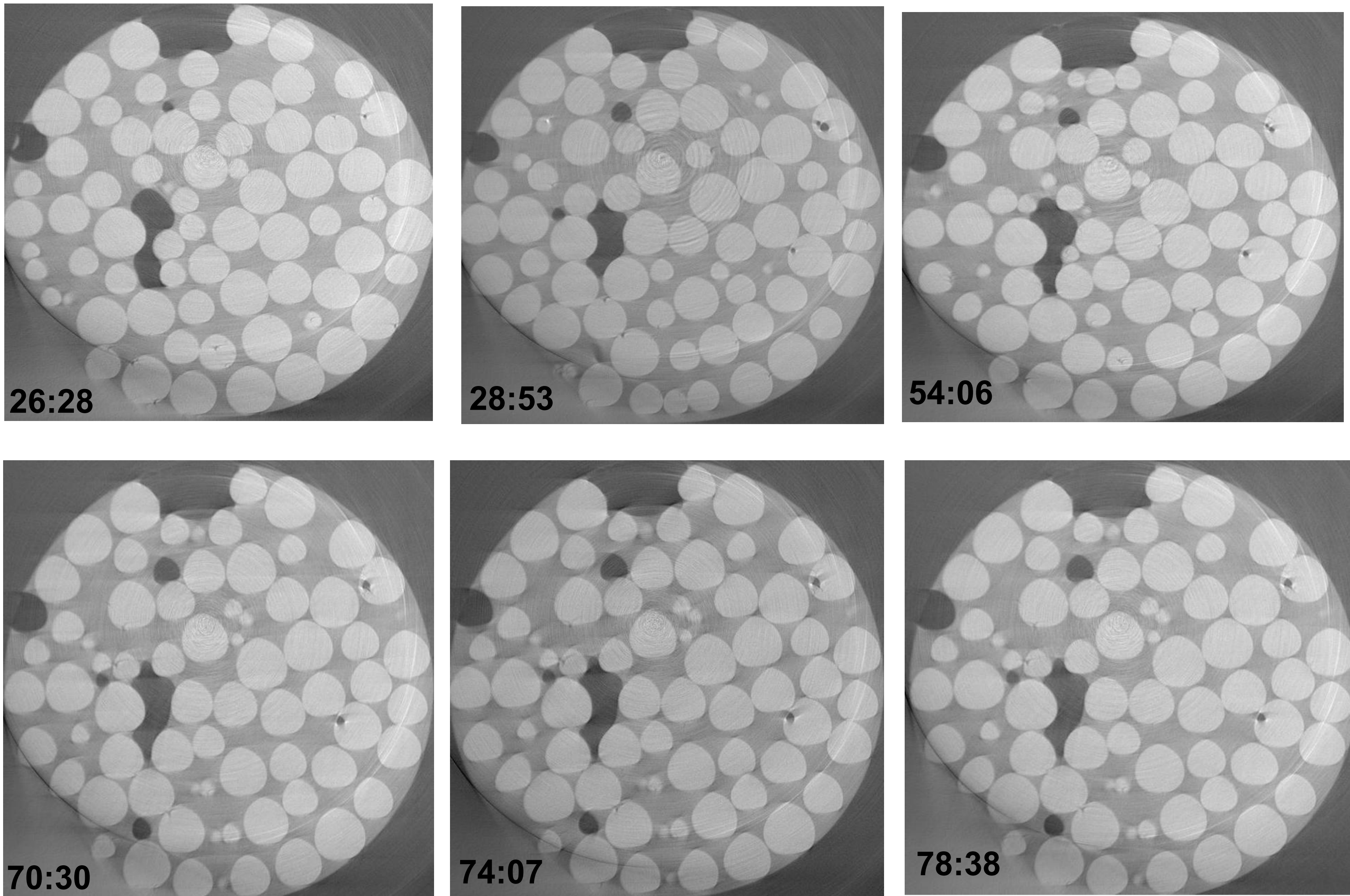
Vertical Stack of 300 Images -Video



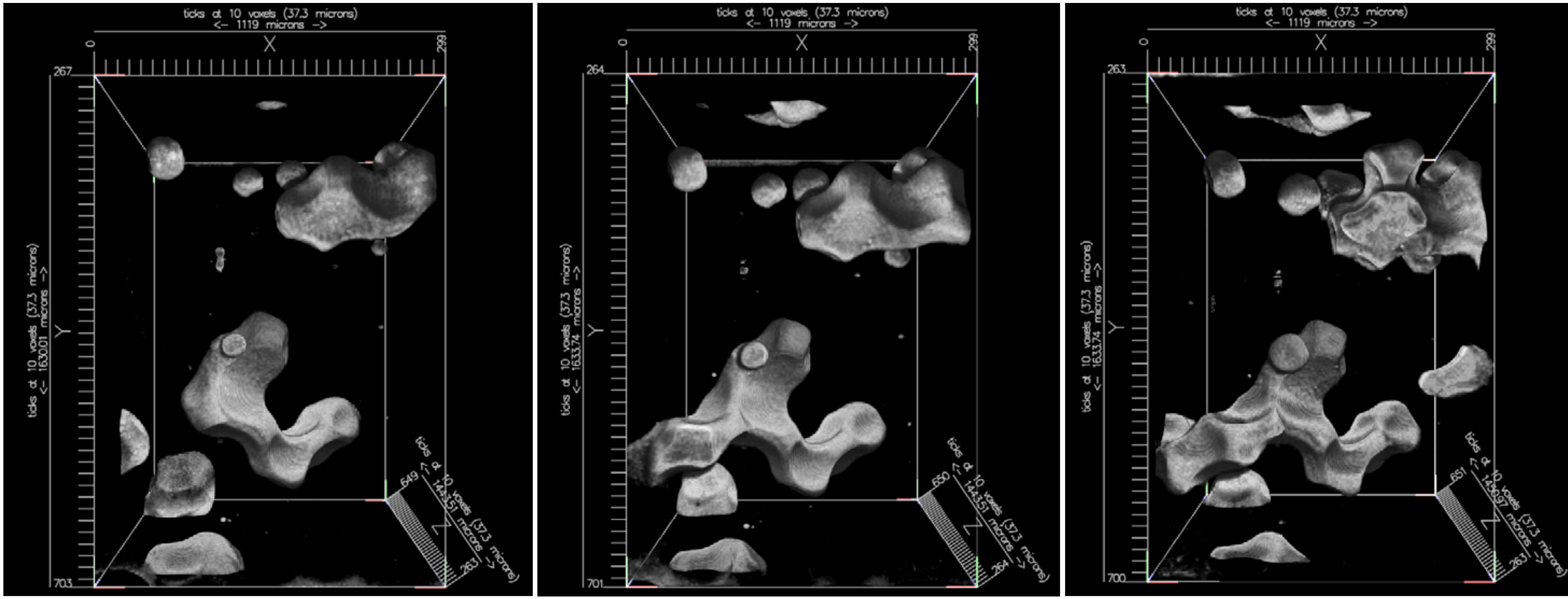


78:39 Hours; X2b-112-1 Ymin51Ymax350

2-D Hydrate Growth with Time



Time Resolved 3-D Hydrate Growth



Time resolved THF hydrate growth in glass beads serving as host. The 3-D structures are rendered from tomography scans at cooling times (a) 29 h, (b) 54 h and (c) 78 h. The glass beads are not shown to allow enhancement of the contrast for distinct observation of THF-hydrate growth (shown in grey scale).

Conclusions- CMT Data

- 2-D images and grain-to-grain match between the specific vertical cross-section images from different tomoscans taken with time indicates the growth of hydrates displaces beads within the unconsolidated pack.

- The 3-D volumes rendered from stack of images from each tomoscan with time show the growth of hydrate patchy and preferentially from already nucleated region.

- Confirms the microstructural model hydrate-water-grain system as “pore filling, i.e. growing in pores” cementation model.

- The Contact angle is being calculated.

Ongoing and Future Work

FISH unit- Macro

- Continue hydrate cores in the Temco cell.
  - With GoM fine grained sediments
  - Sediments from the India cruise
  - In pore water from cruises [R. Coffin]

CMT- Micro

- Finish analysis of the CMT data for the GoM sediment characterization.
- High P cell design for in situ studies.
- Extend the THF work to methane.

Relevance to Climate Change Models

- Compare the hydrate decomposition data hosted in natural sediment from different sites.
- Utilization of hydrate decomposition data in climate change models.