

# Laboratory measurements on THF-hydrate bearing porous media



**ROSE Meeting  
Trondheim, Norway**

Mandy Schindler, Manika Prasad

April 25, 2016

# Introduction

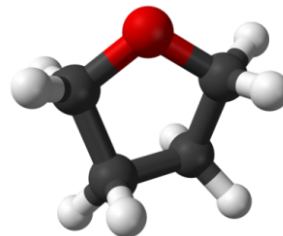
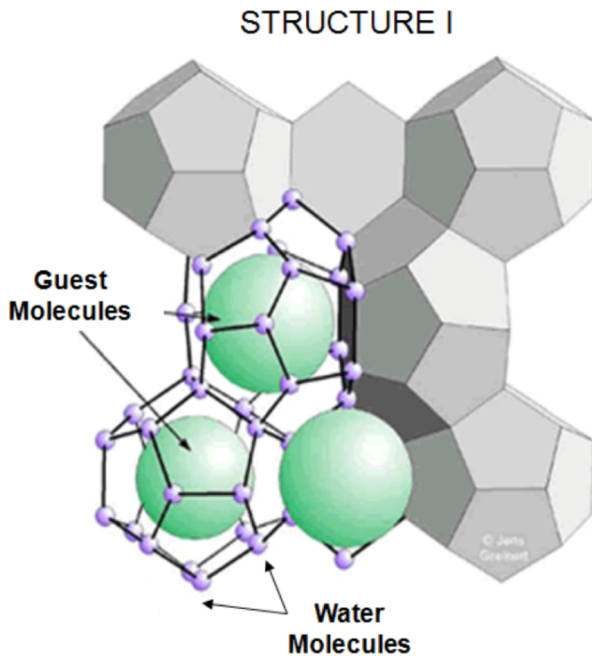
- **Low Temperature, High Pressure**

- Arctic permafrost
- Marine sediments (> 500m deep)

- **Availability of methane and water**

- **Formation: gas dissolved in water or free gas phase**

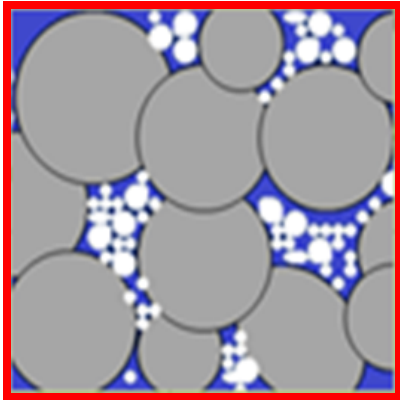
- **For laboratory experiments: tetrahydrofuran hydrate**



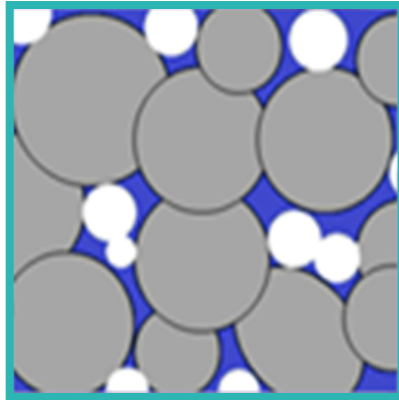
# Pore-Scale Hydrate Distribution

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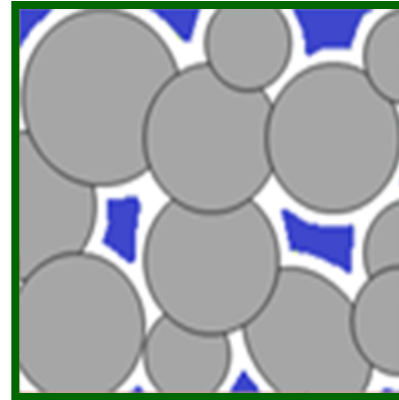
**Pore Filling**



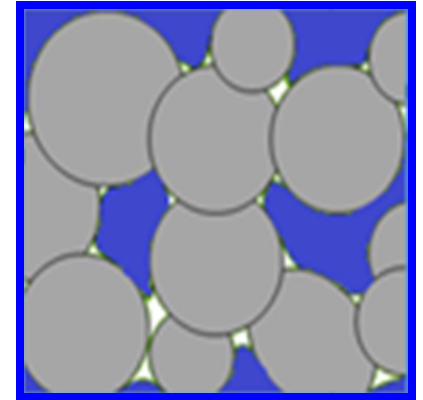
**Sediment Frame**



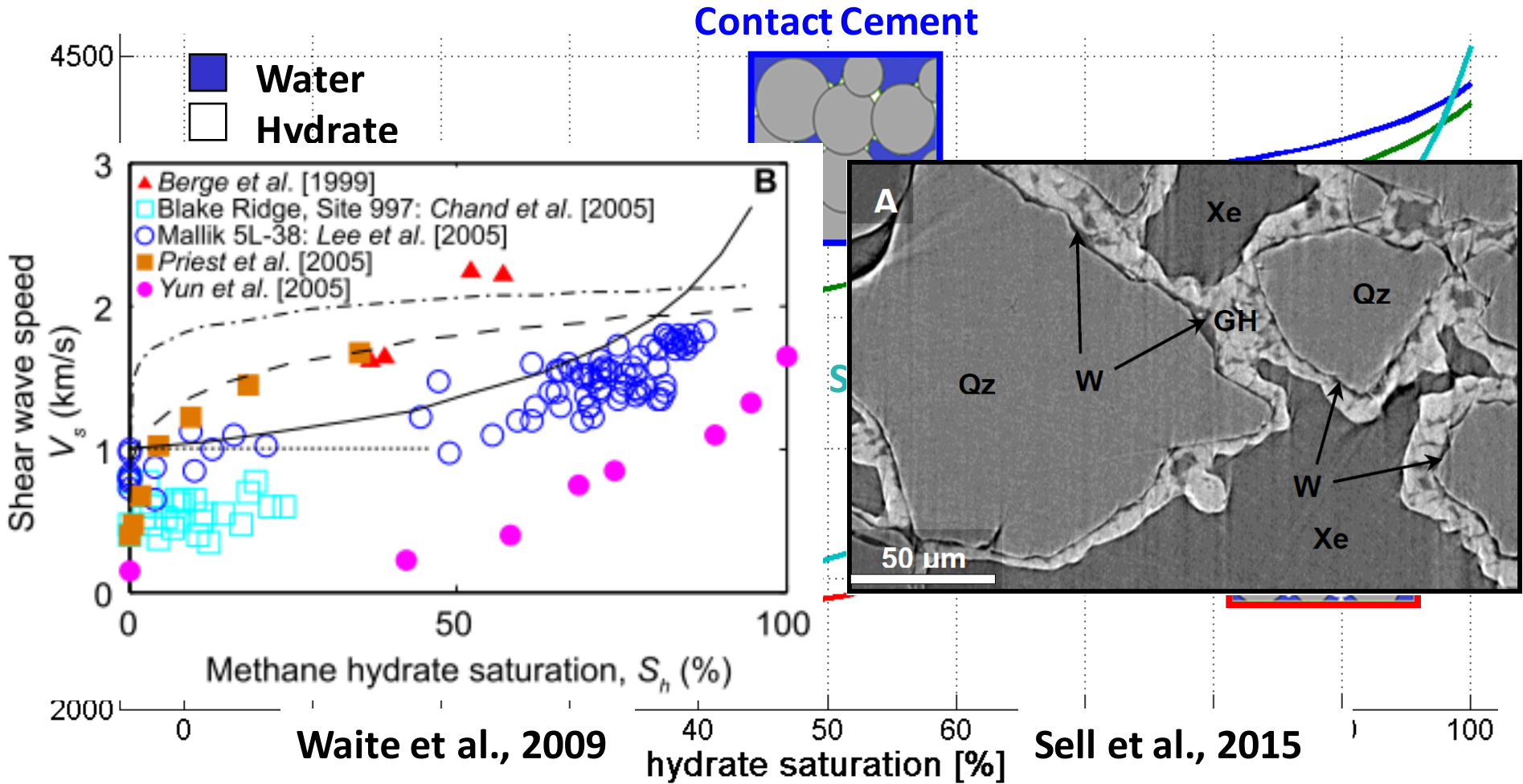
**Envelope Cement**



**Contact Cement**



# Rock Physics Models



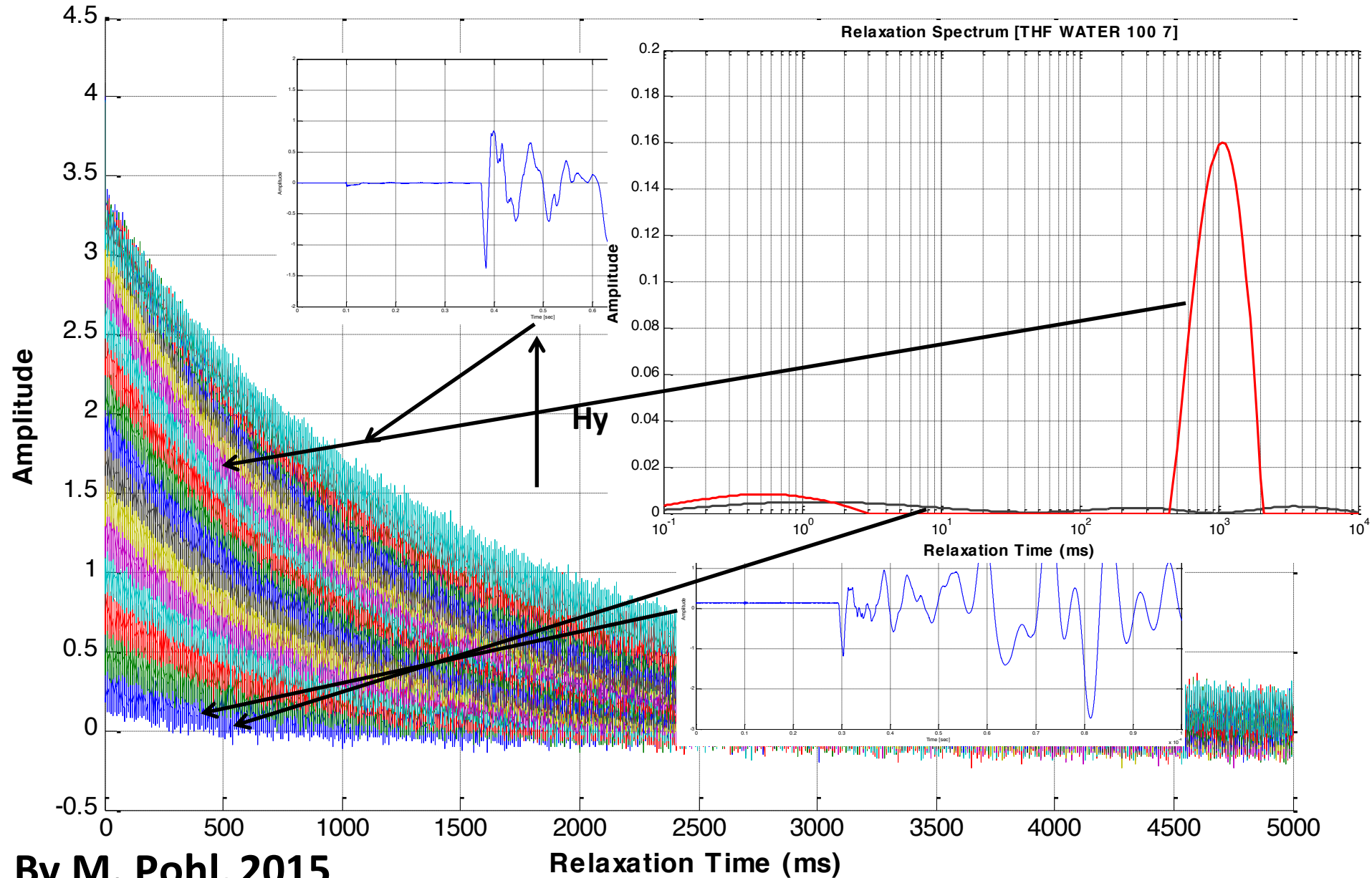
Effective medium model by Ecker et al., 1998, Helgerud et al., 1999  
 based on work by Dvorkin et al., 1994



3<sup>rd</sup> International Workshop  
on Rock Physics, Perth  
April 2015

# Relaxation Time for 100 % THF Hydrate

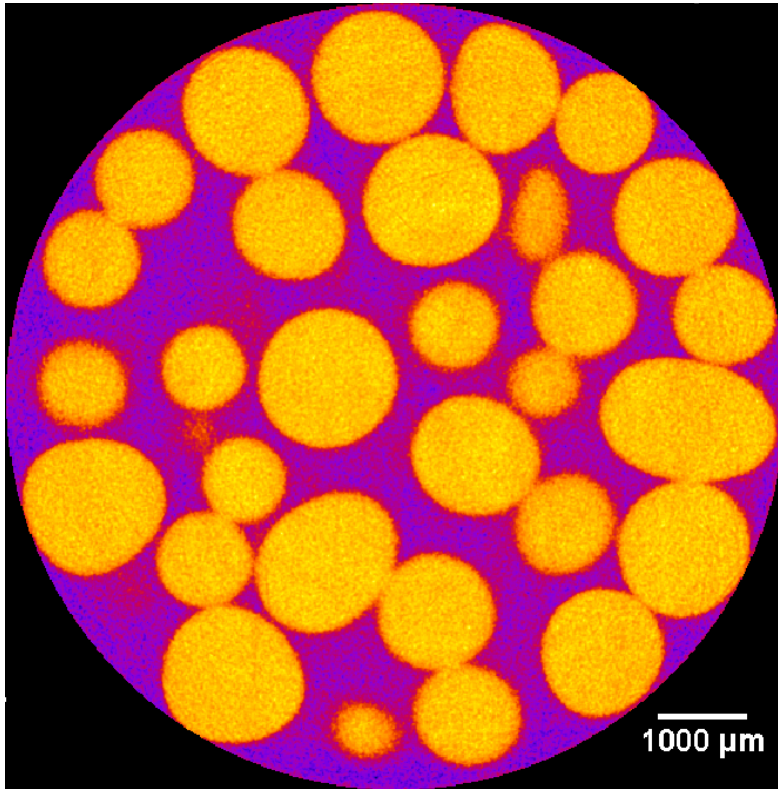
RAW DATA



By M. Pohl, 2015

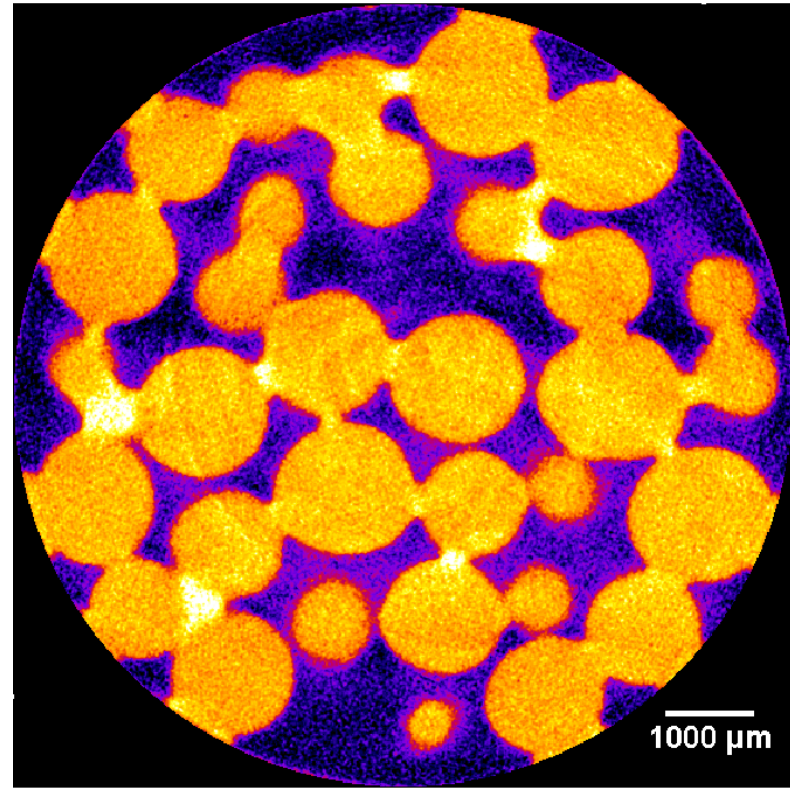
# Micro CT Imaging

**BaCl<sub>2</sub>: 6wt%**



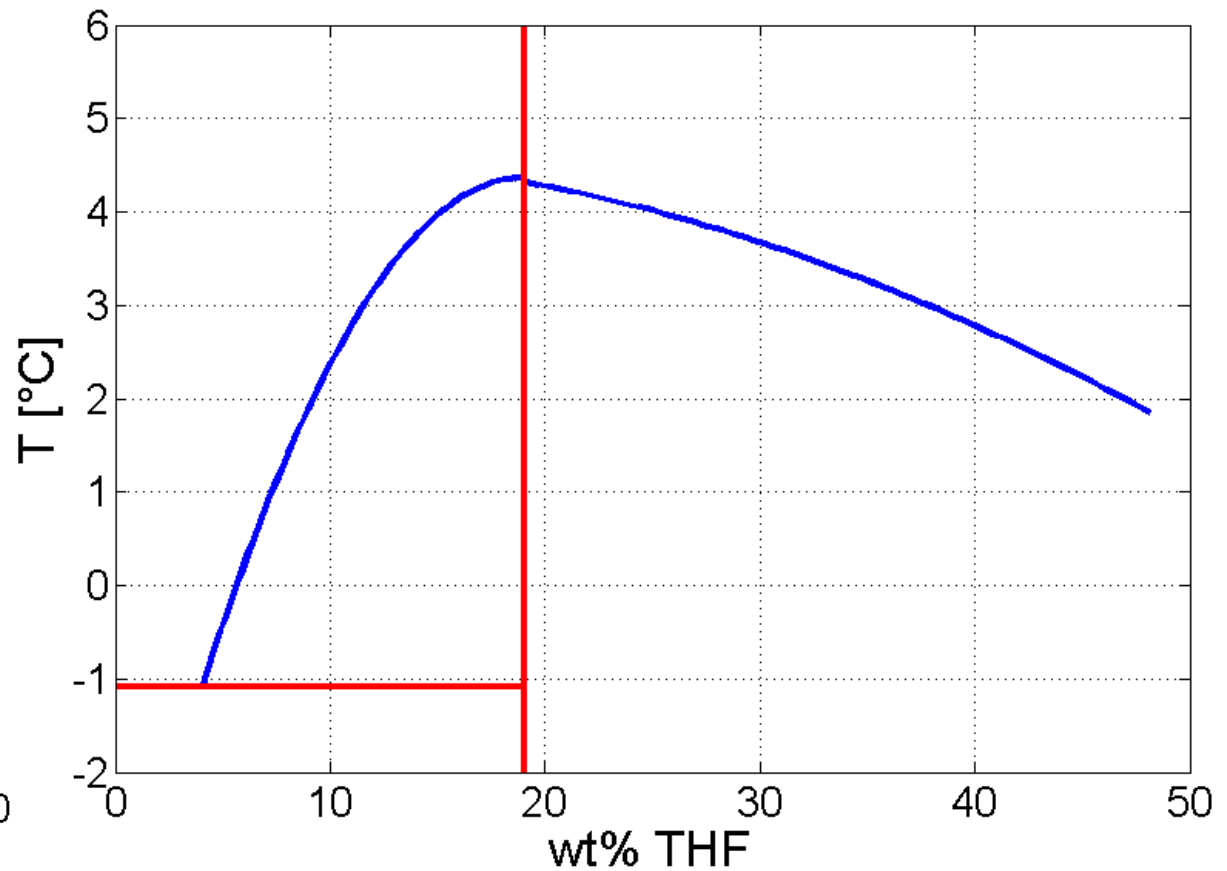
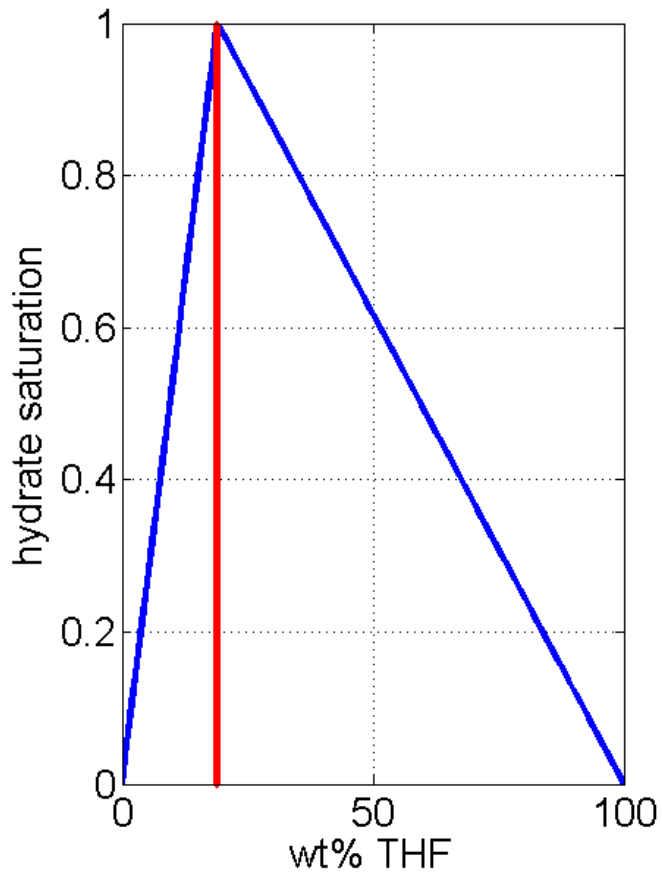
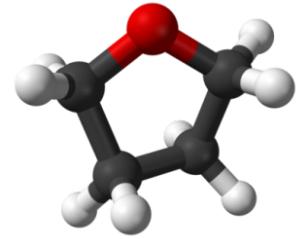
**Room temperature**

**BaCl<sub>2</sub>: 23wt%**



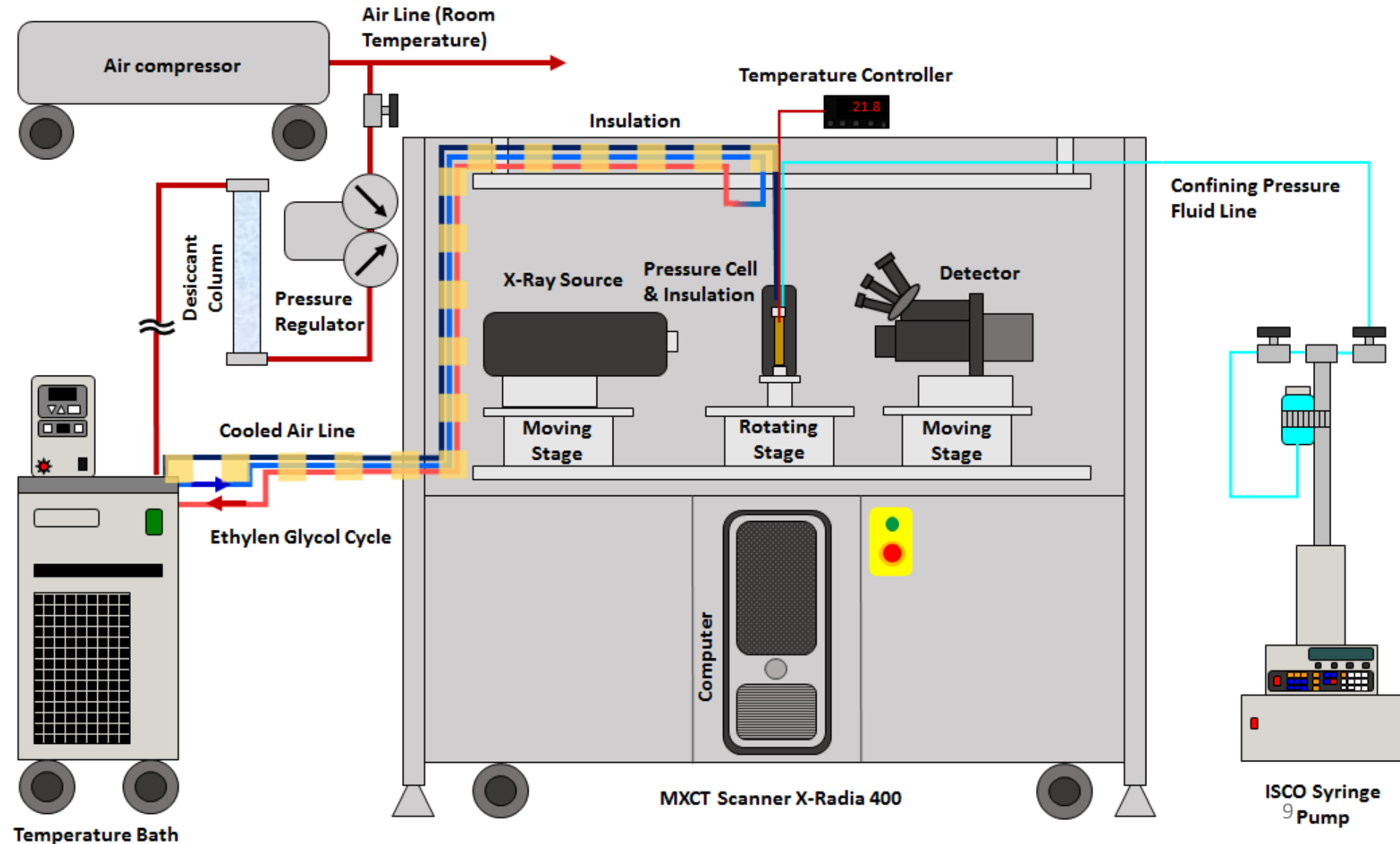
**1°C  
80% THF hydrate saturation**

# Tetrahydrofuran (THF) Hydrate



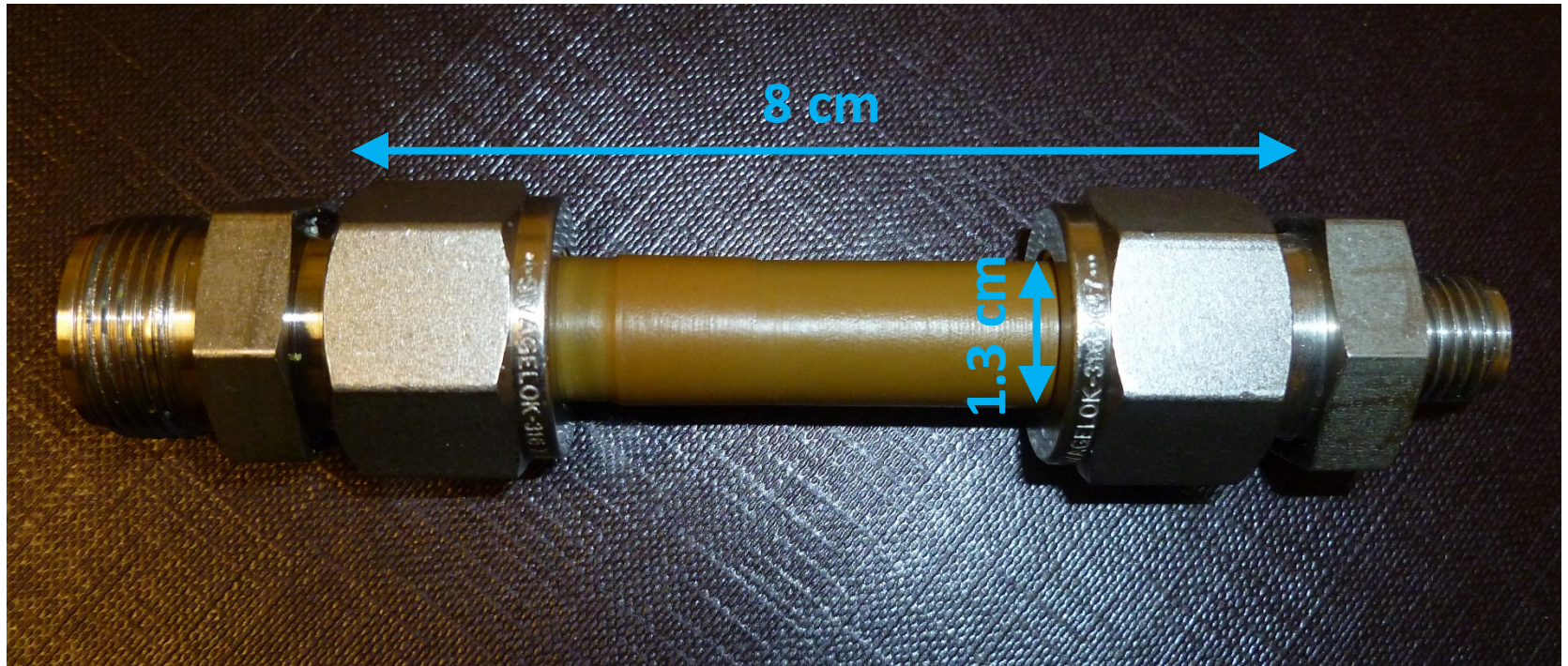
after Makino et al., 2005

# Micro CT Experimental Setup





# Micro CT Pressure Vessel

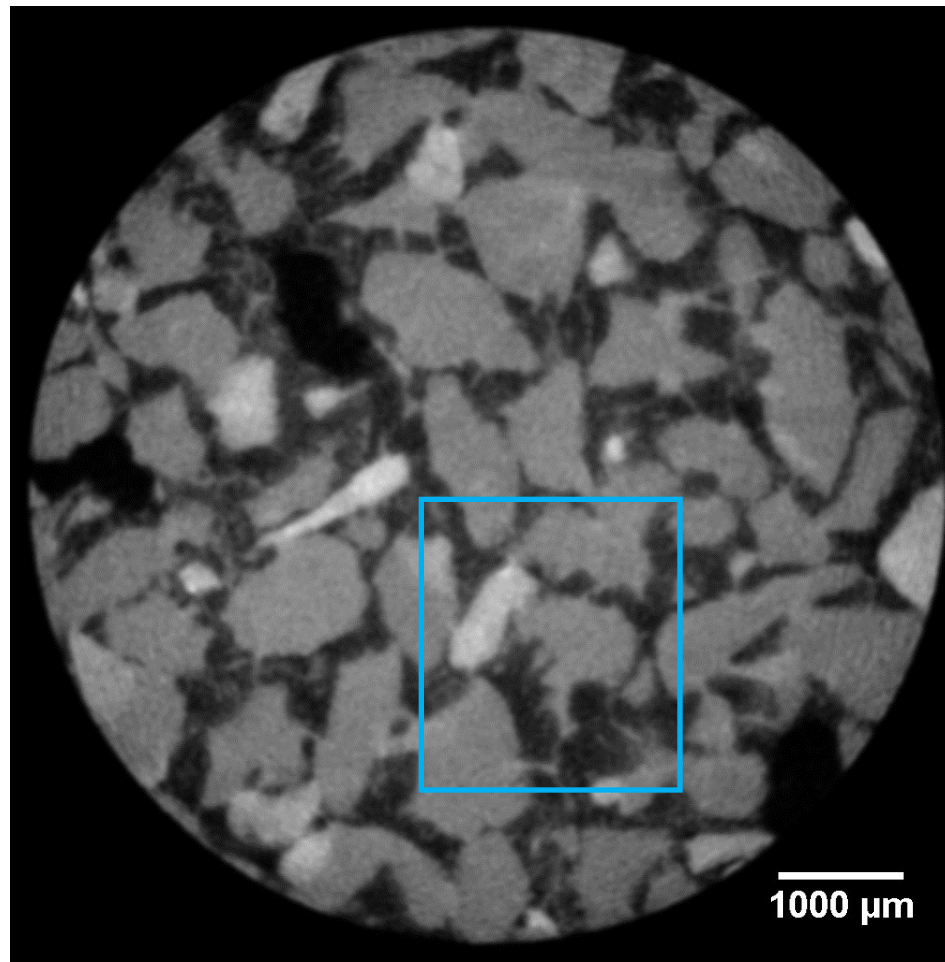


- Torlon pressure vessel (up to 5000 psi – 34.5 MPa)
- inner diameter: 8 mm, outer diameter: 12.7 mm (0.5 inches)
- Quartz sand ( $\phi$  grain size: 1000  $\mu\text{m}$ ) and clay (bentonite) as host sediments
- THF and water as hydrate-forming components
- Barium chloride added for density contrast (~12 wt%)
- Cooling ~ 8 hours
- Resolution: 10 microns

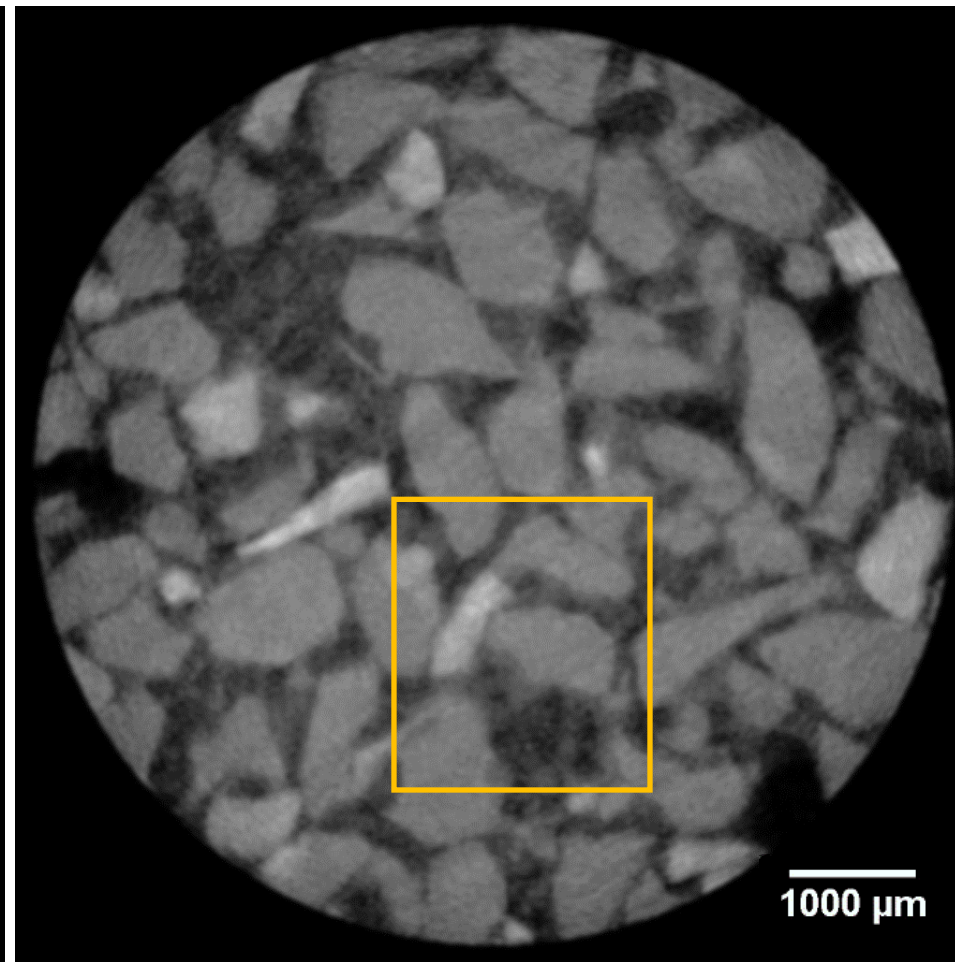
# Quartz With $S_h=80\%$

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With Hydrate



Without Hydrate

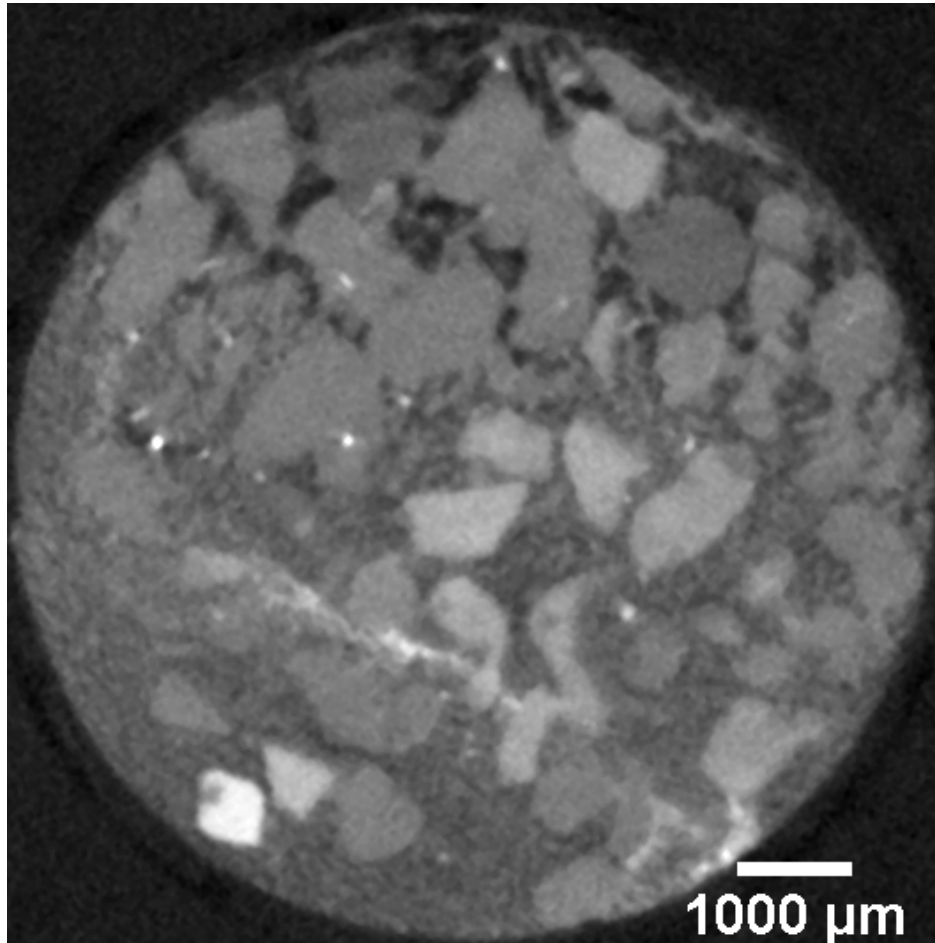




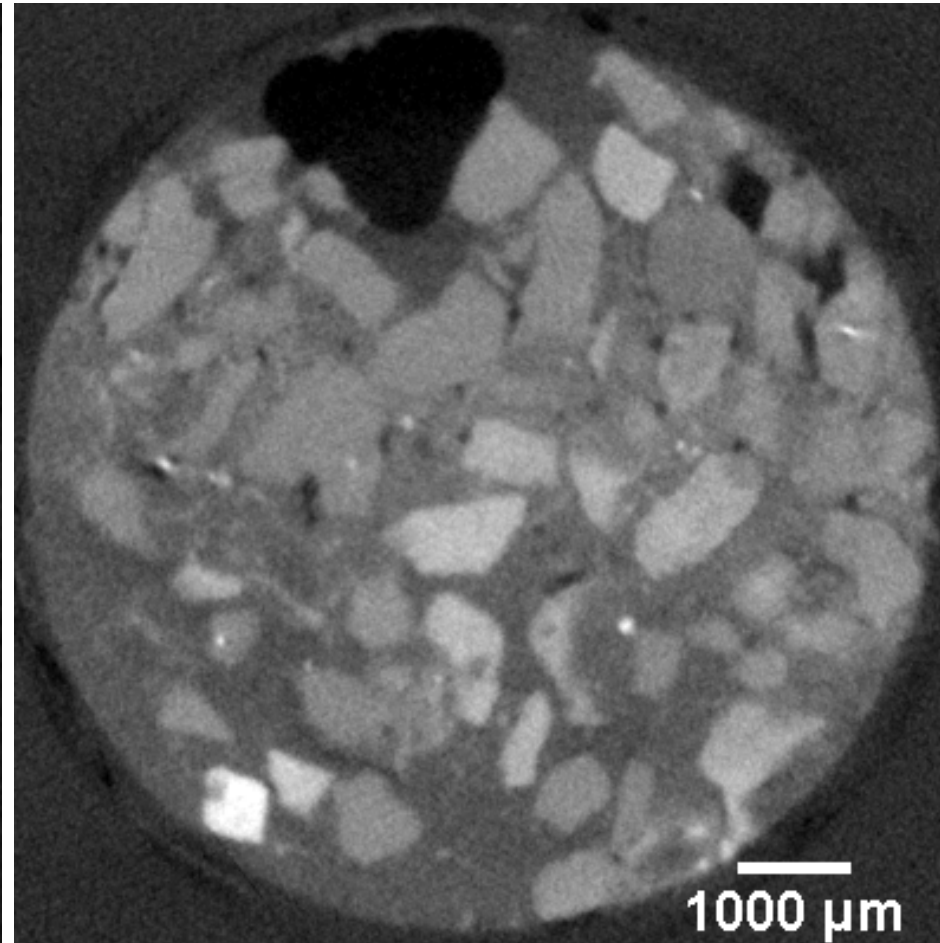
# Quartz and Clay With $S_h=80\%$

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With Hydrate



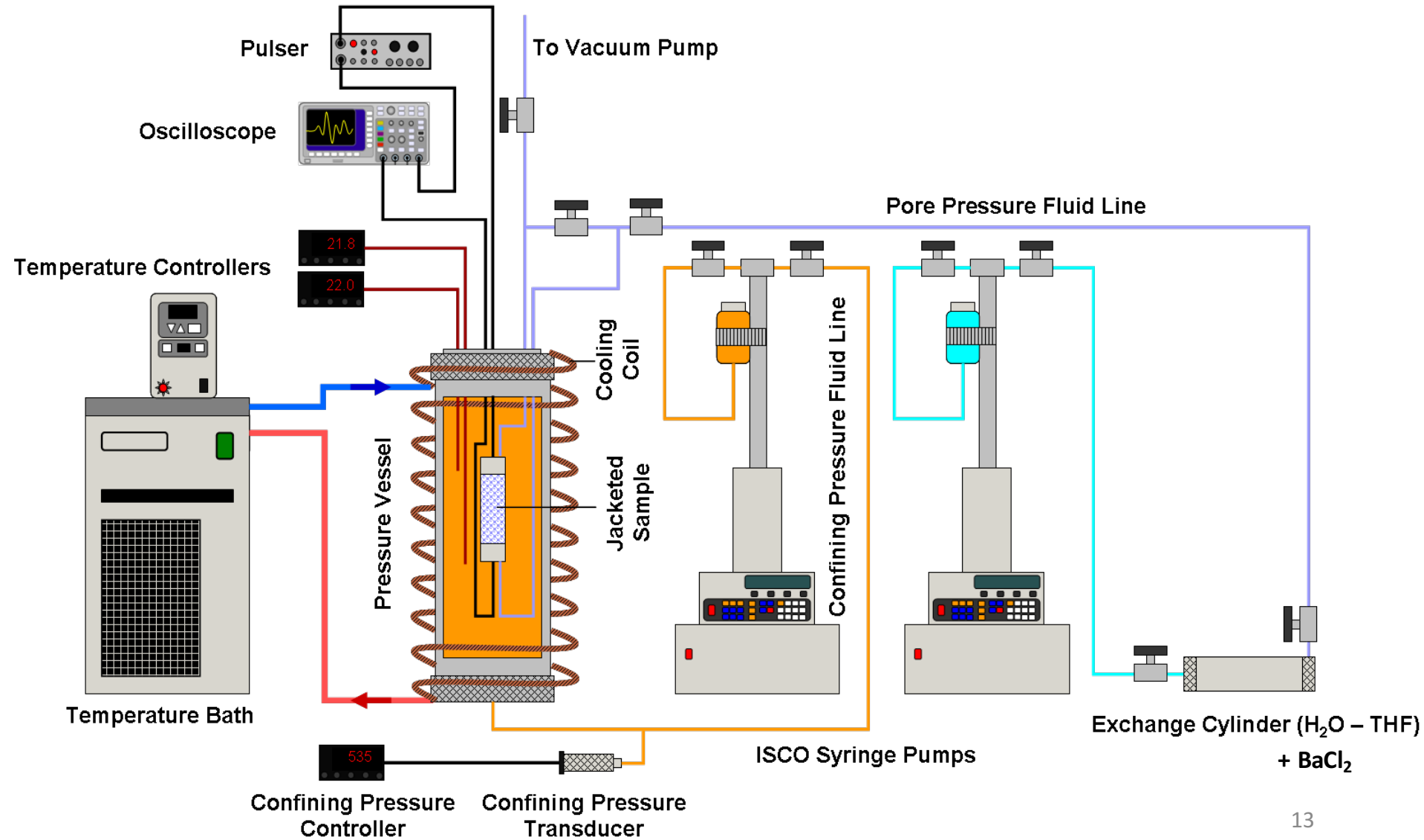
Without Hydrate



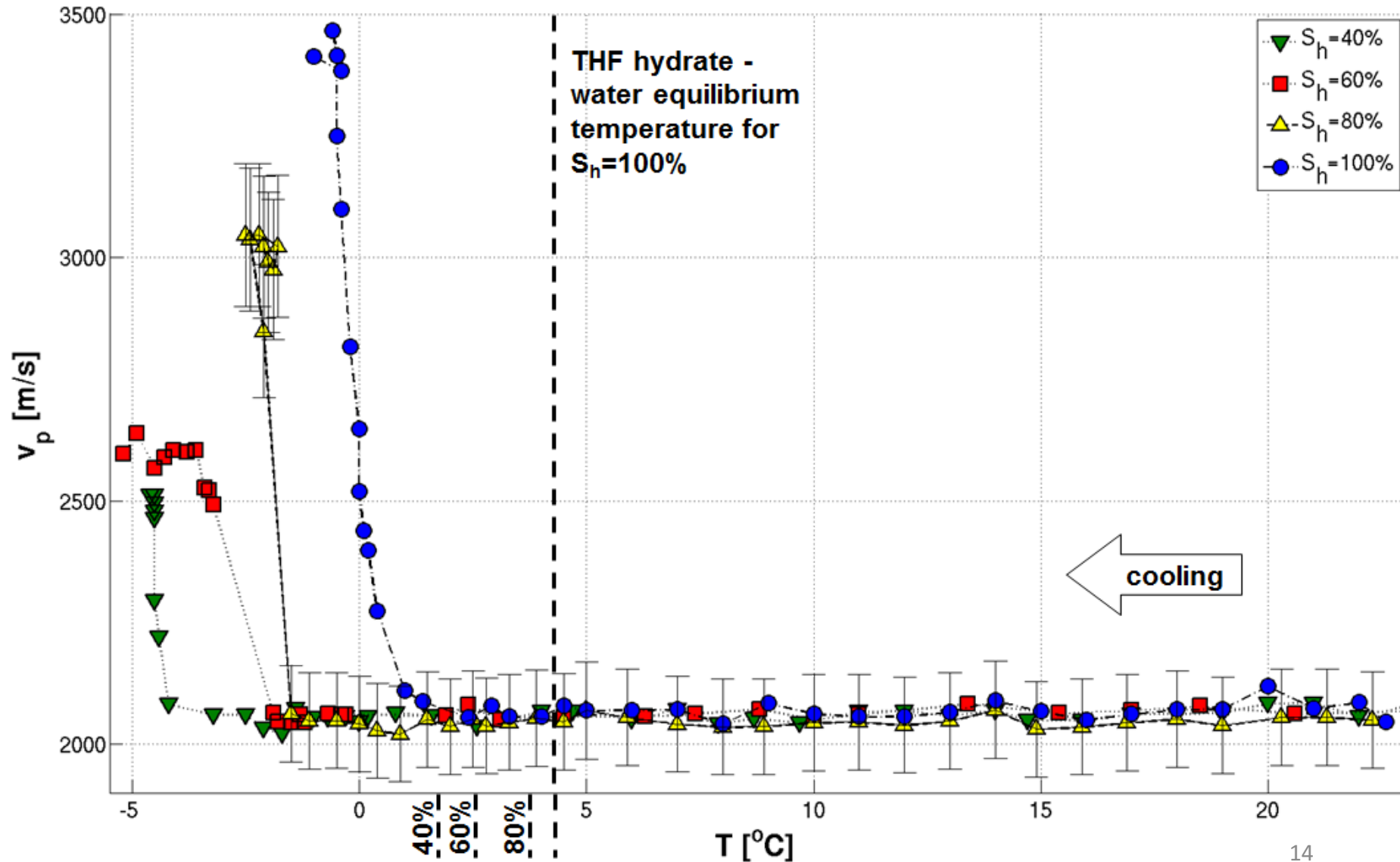
**Heterogeneity in hydrate and clay distribution**  
**Clay moved by hydrate**



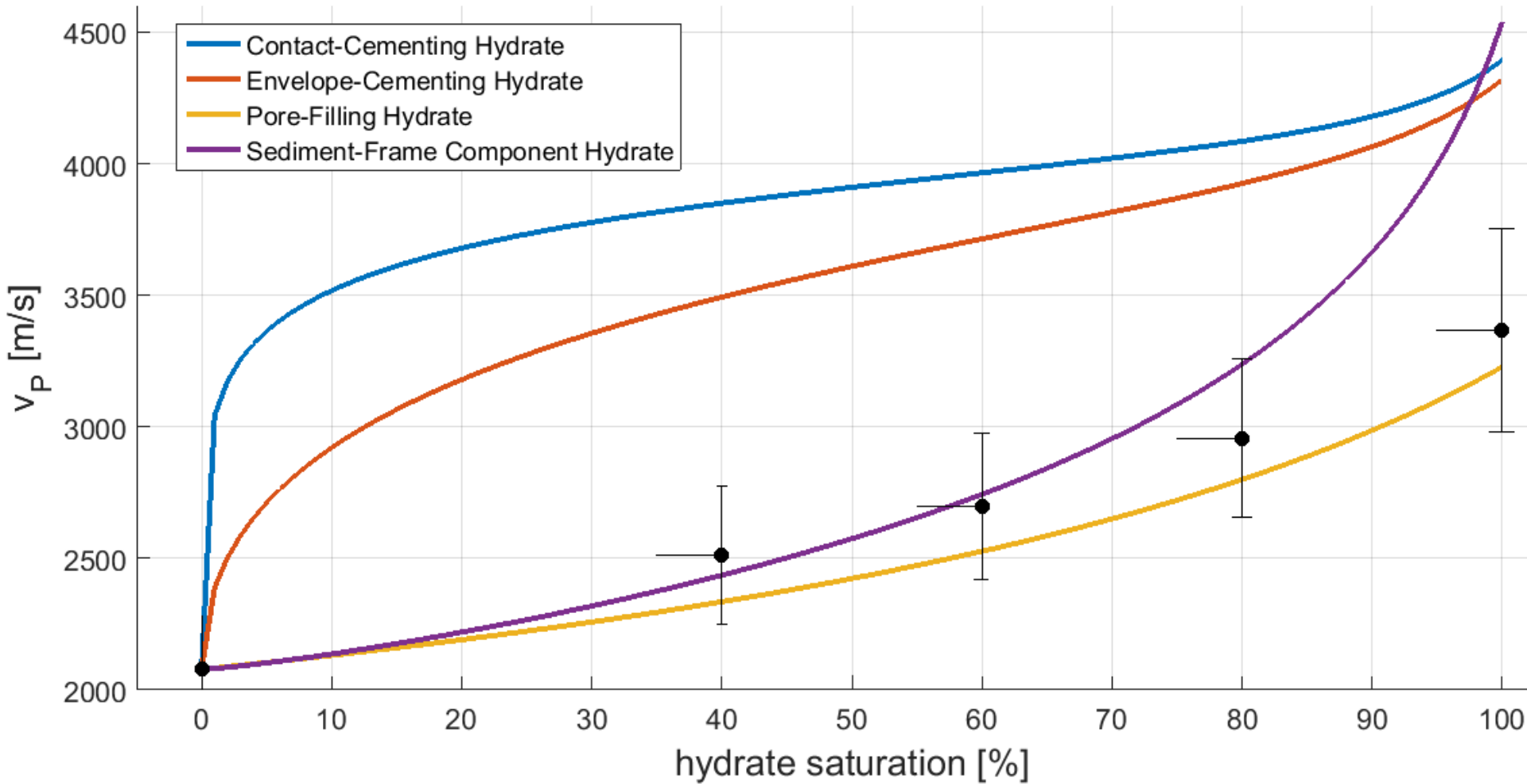
# Ultrasonic Velocity Measurements



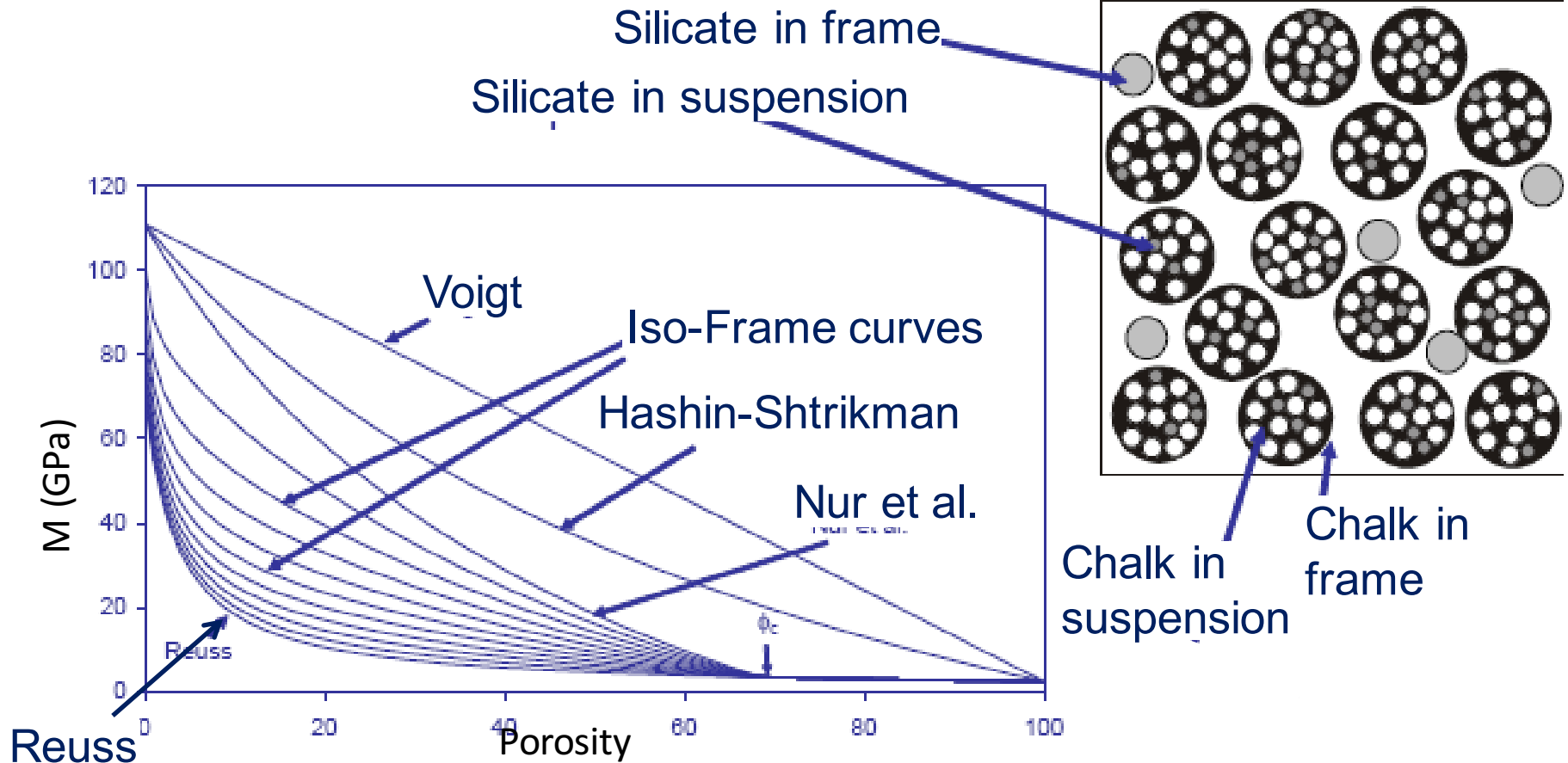
# Velocities for Different Hydrate Saturations



# Effective Medium Models



# Iso-frame Model



Iso-frame fraction  $IF \propto 1/\Phi$   
And affects elastic moduli and velocity

Fabricius et al., 2004

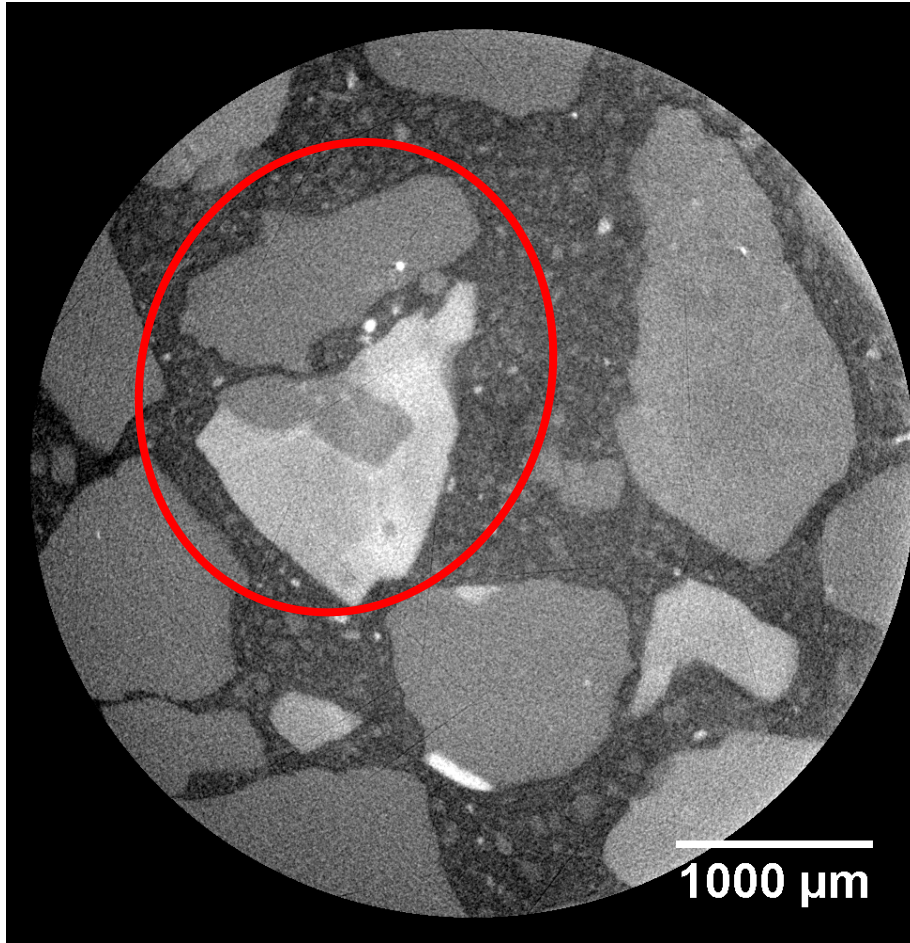
# Conclusions

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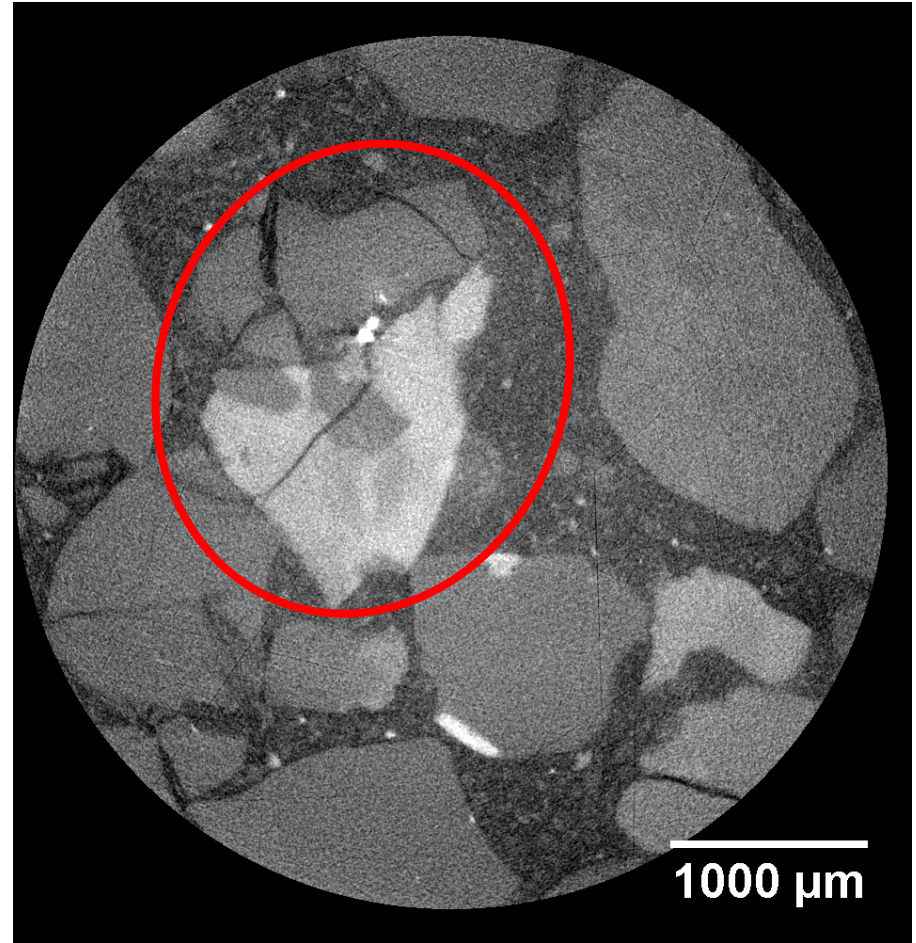
- Significant improvement of  $\mu$ CT image quality and resolution → use different host sediments
- Hydrate distribution does not confirm one model
- Mixing of effective medium models: partially load bearing, partially pore filling
- Clay causes heterogeneous hydrate saturation → clay moved during hydrate formation
  
- Link changes in elastic properties (from US velocities) to their cause on the pore scale (from  $\mu$ CT imaging)

# $\mu$ CT Imaging Under Confining Pressure

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Atmospheric pressure



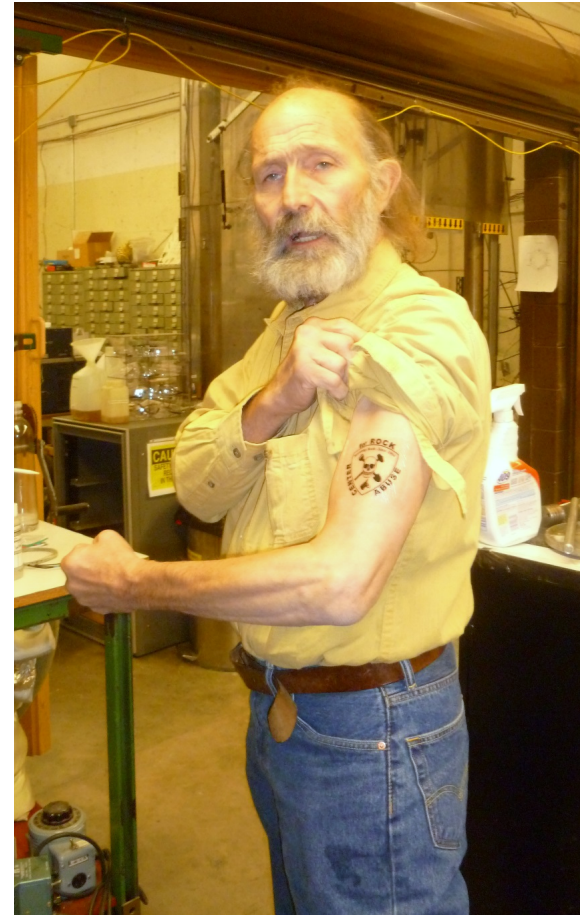
2000 psi (13.8 MPa)



# Acknowledgements

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- Department of Energy  
grant number: DE-FE 0009963
- Fellow rock abusers: Azar Hasanov,  
Hanna Flamme, Kurt Livo
- Dr. Mike Batzle



# References

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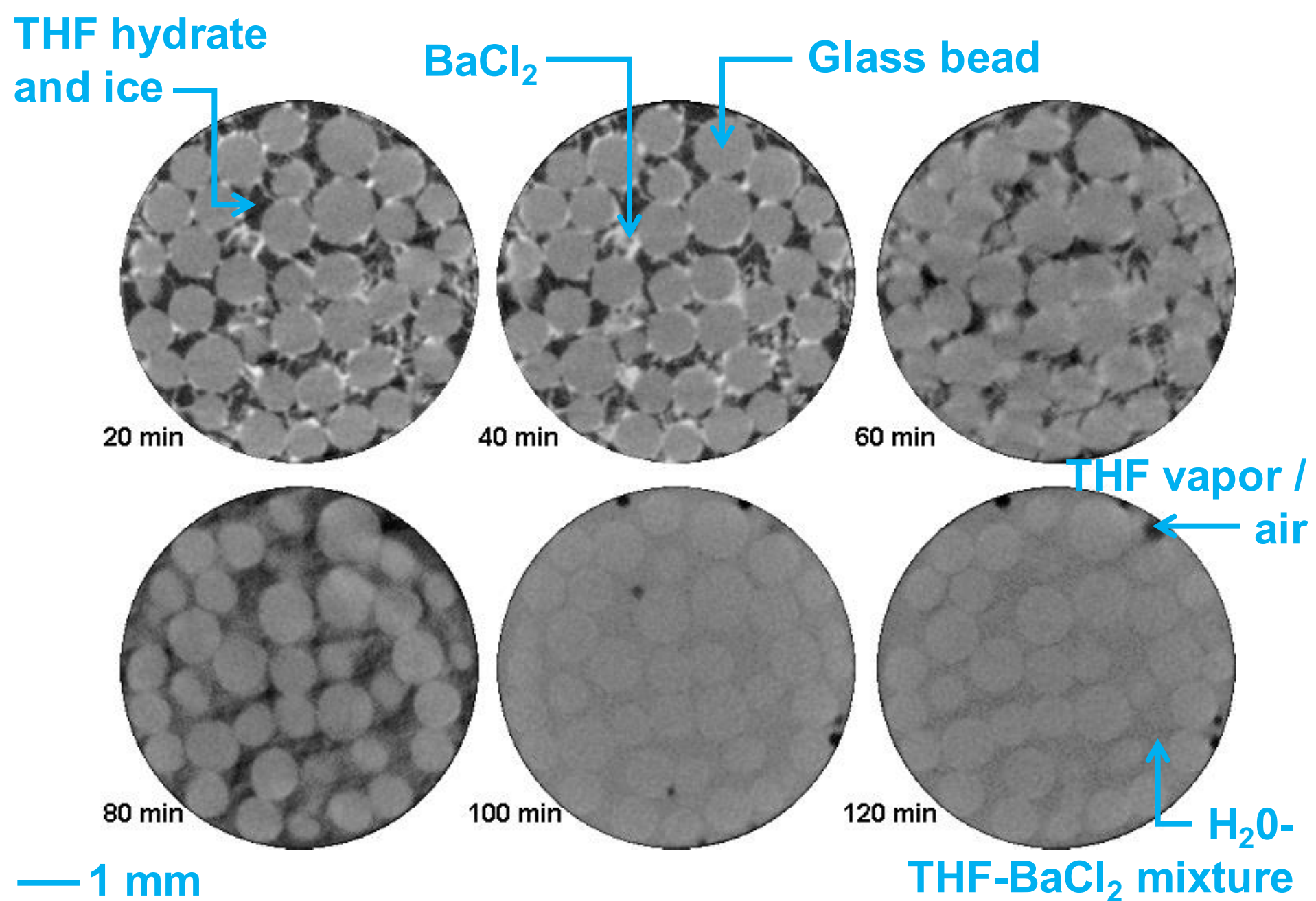
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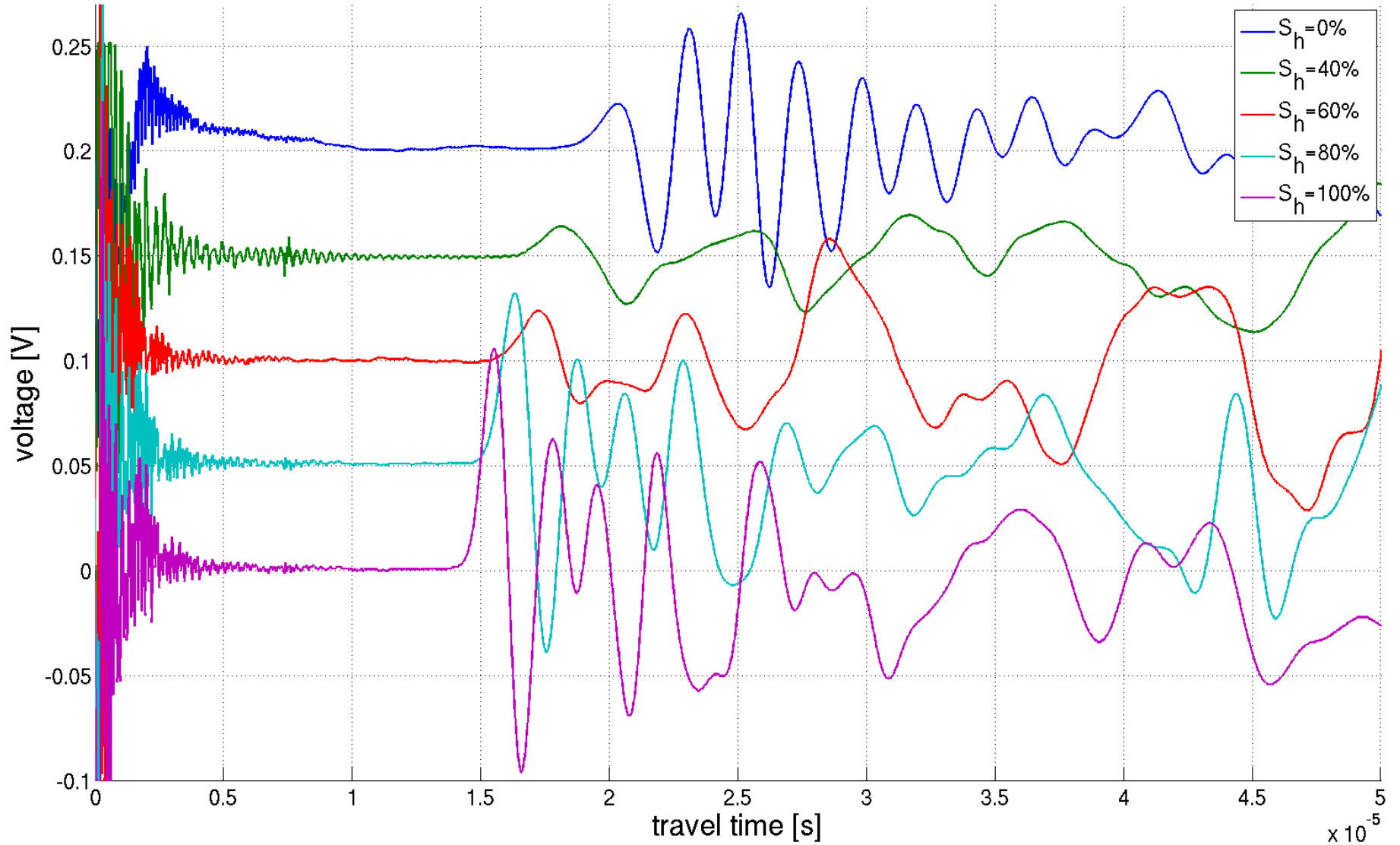
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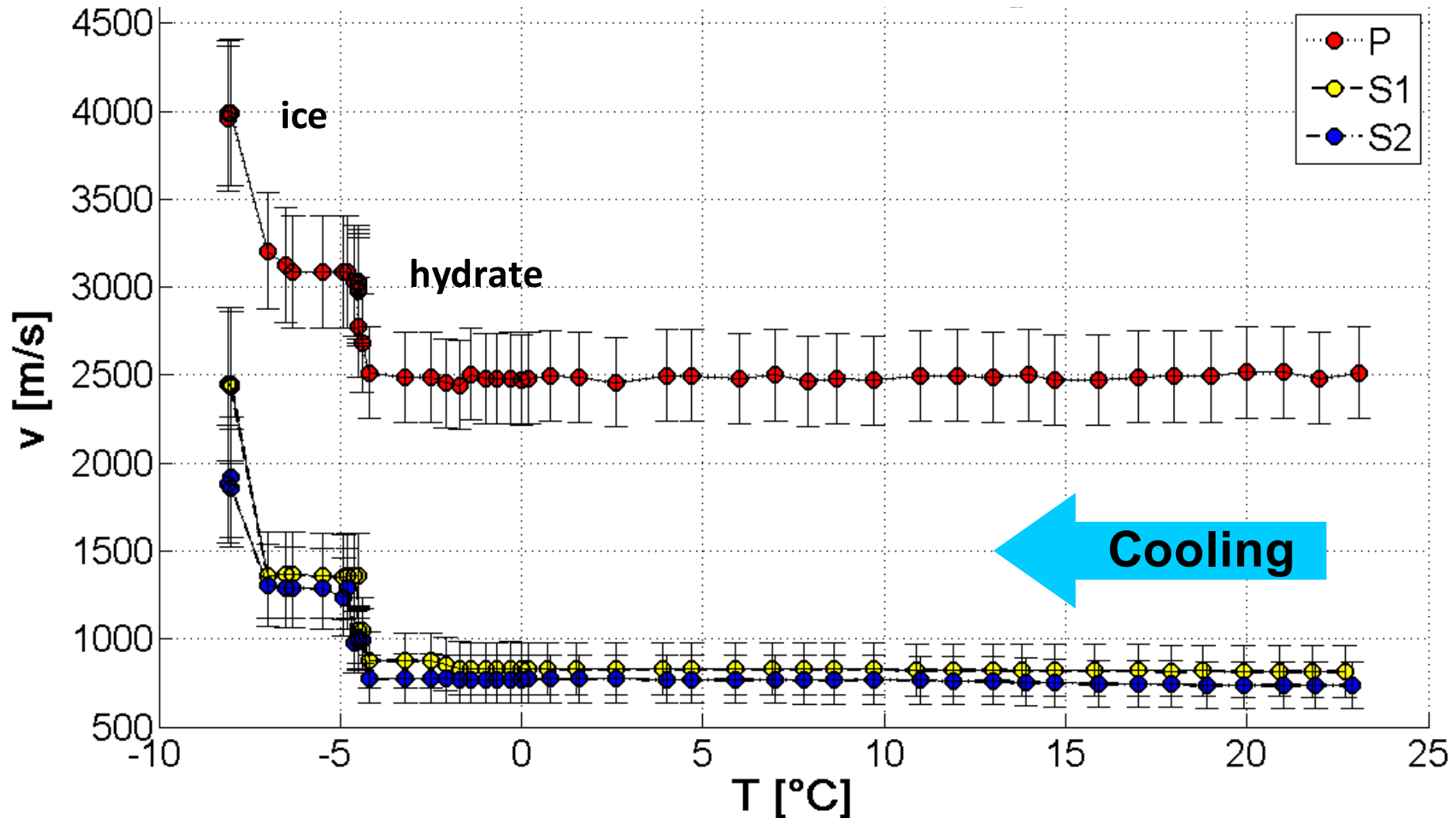


Tomograms for a glass bead sample with  $S_{GH} = 80\%$



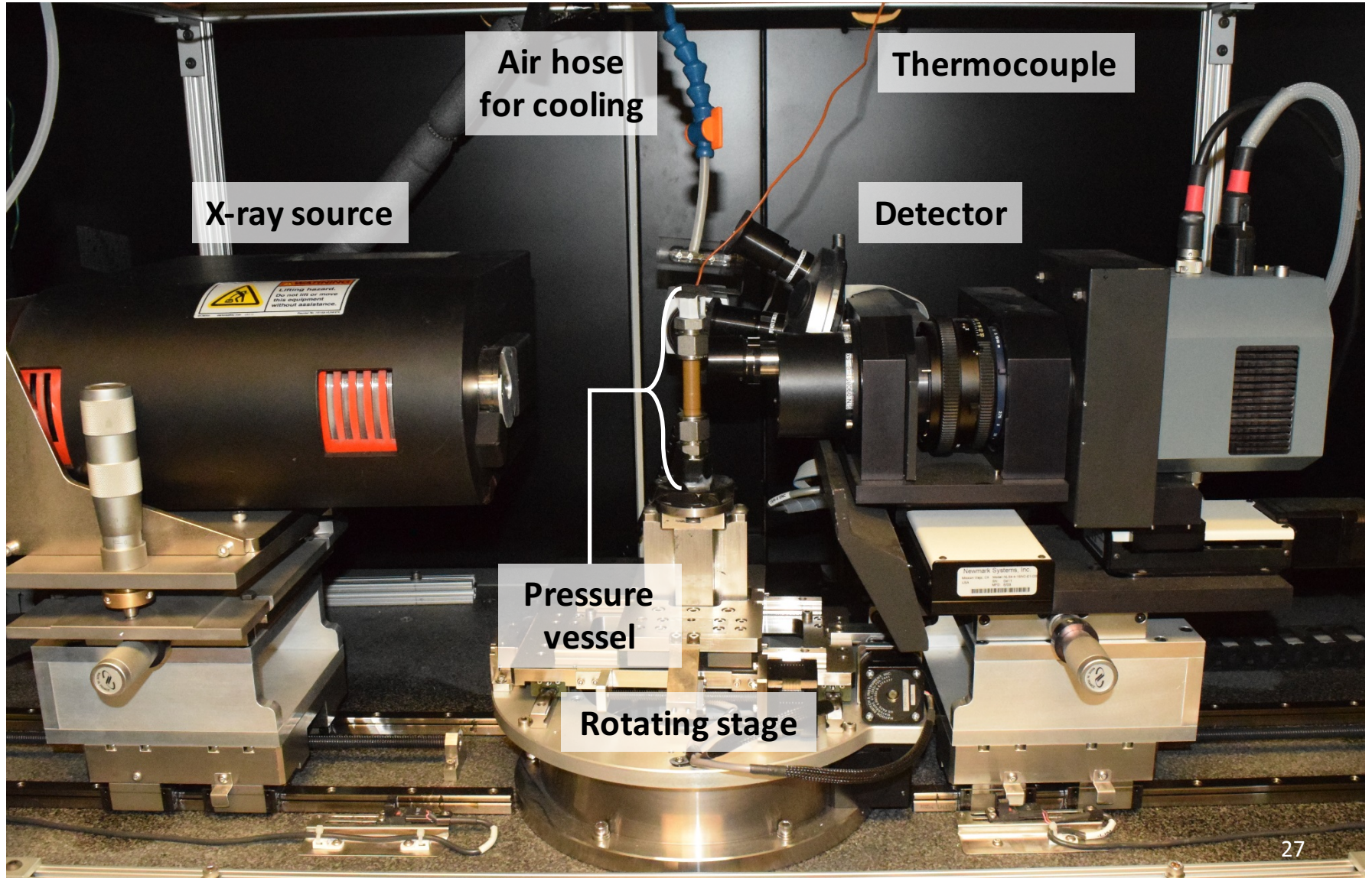
# Ultrasonic Velocities

$P_d=3 \text{ MPa}$ ,  $S_h=40\%$

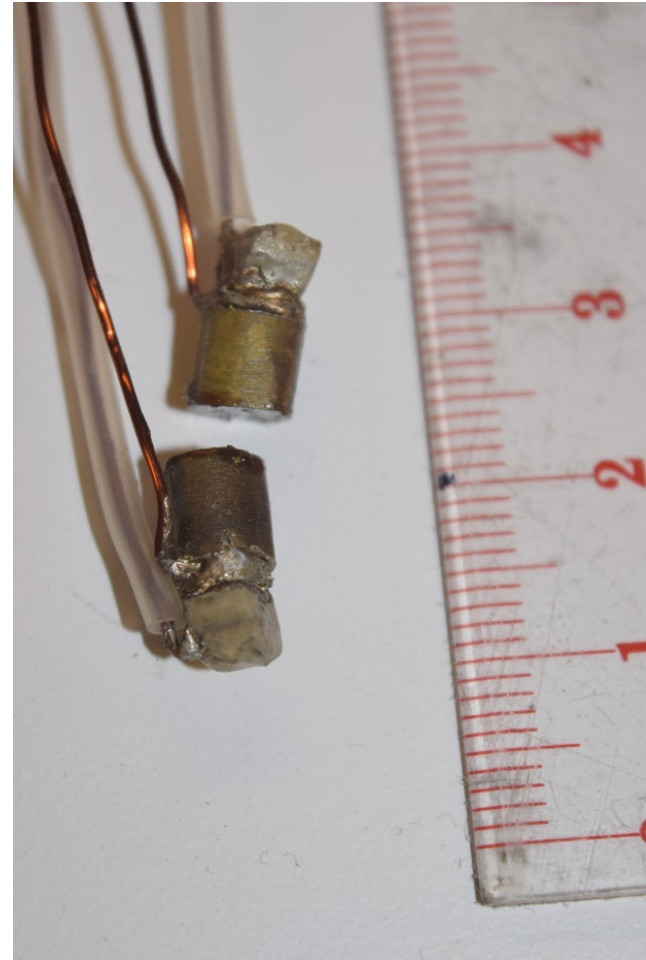
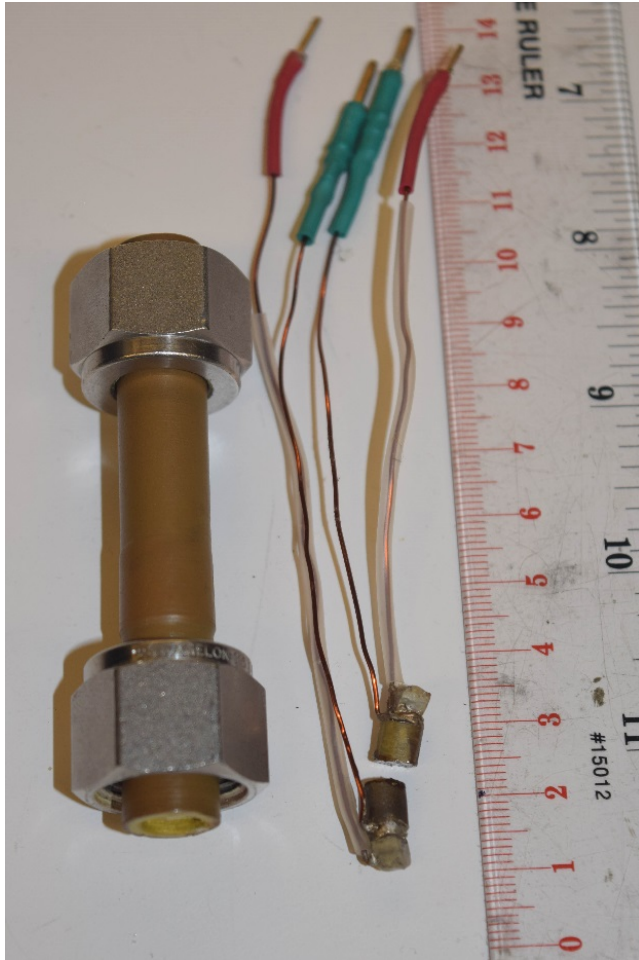




# Micro CT Experimental Setup



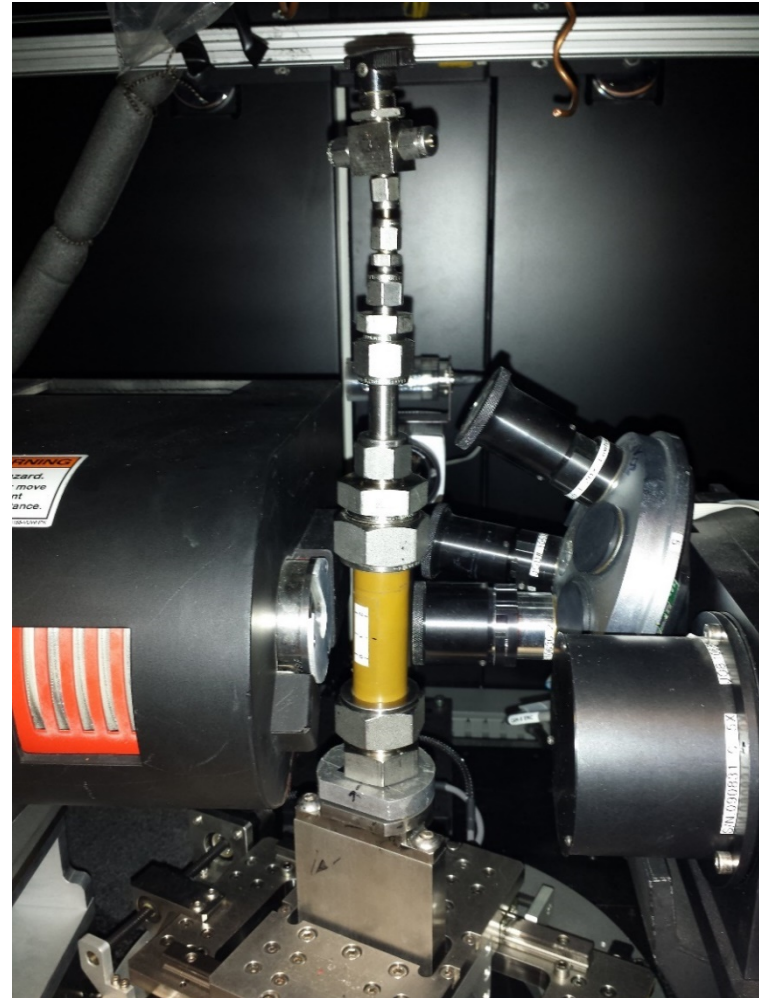
# Ultrasonic Transducers



**Ultrasonic transducers: P-wave only, 3 mm diameter  
For use in Torlon pressure vessels**



# MXCT Imaging Under Pressure



**Pressure up to 5000 psi – 34.5 MPa**

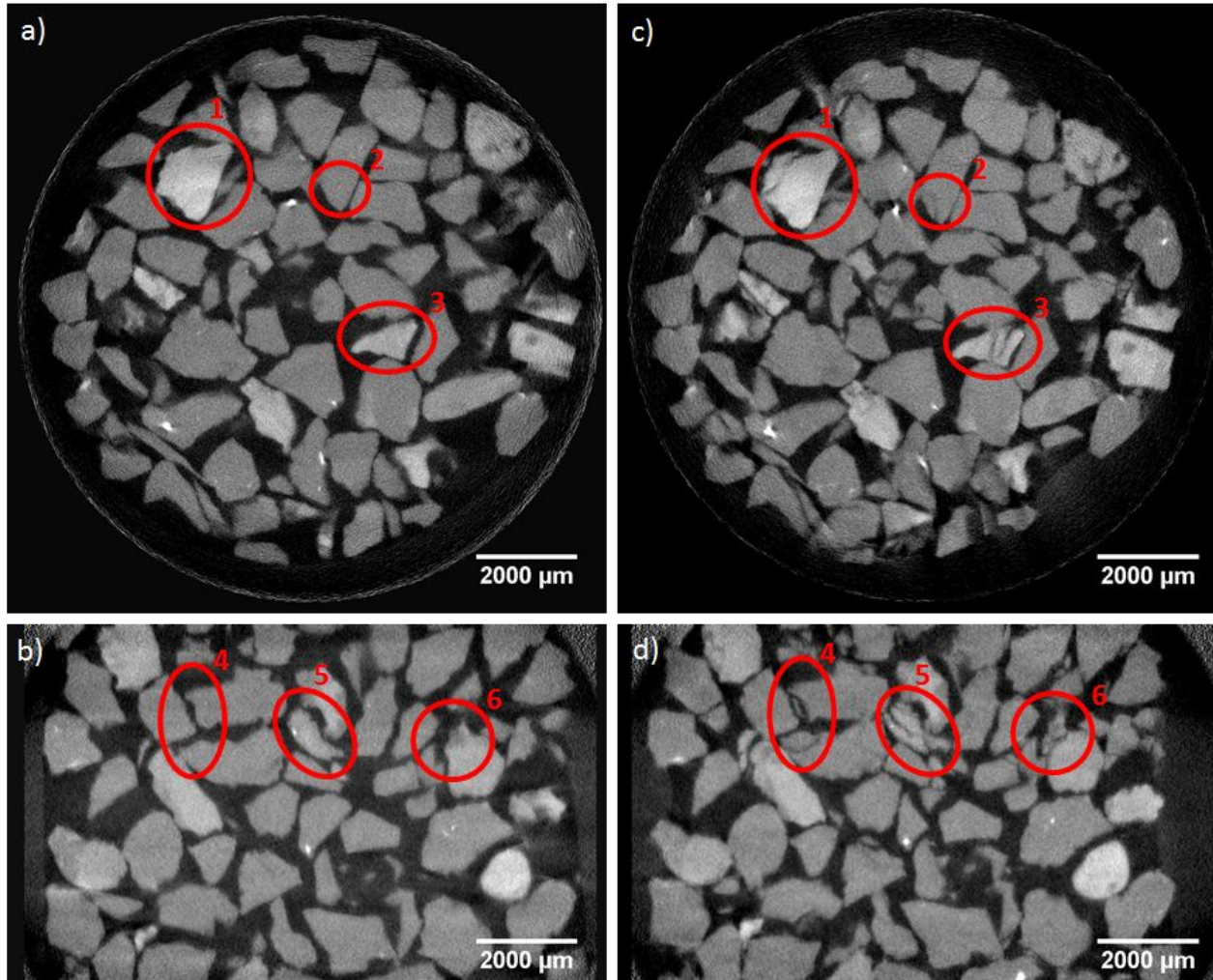
**Inner diameter: 14 mm, outer diameter: 25.4 mm (1 inch)**

**Plans to include pore pressure and confining pressure**

# MXCT Imaging Under Pressure

atmospheric pressure

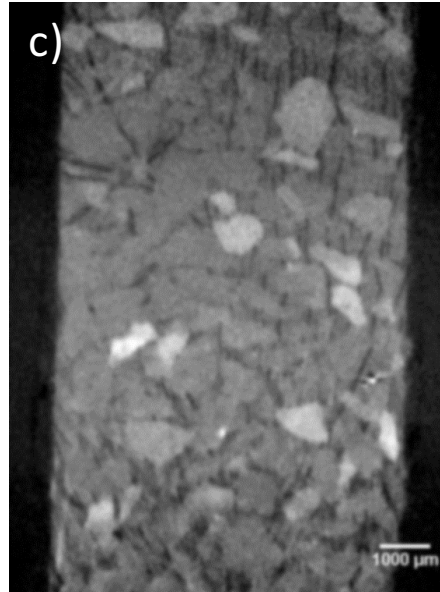
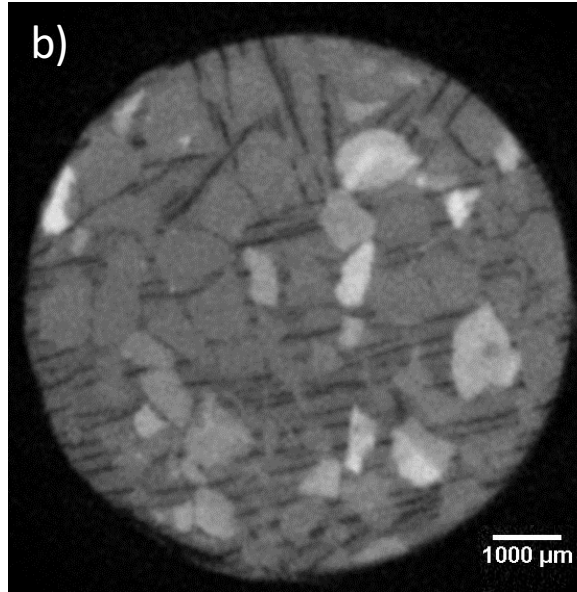
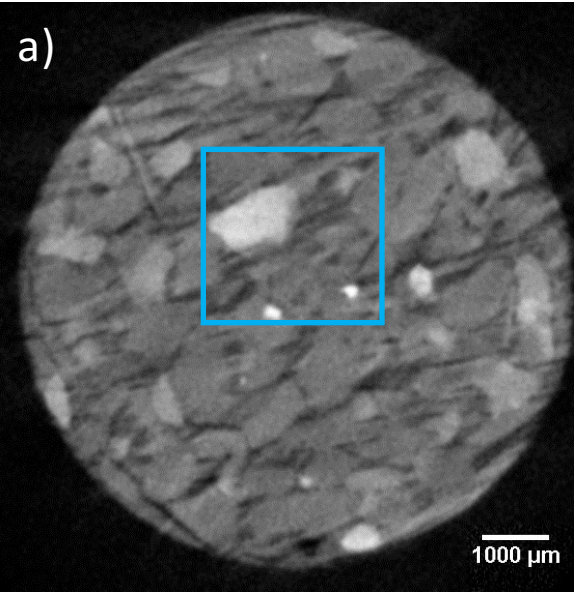
1500 psi



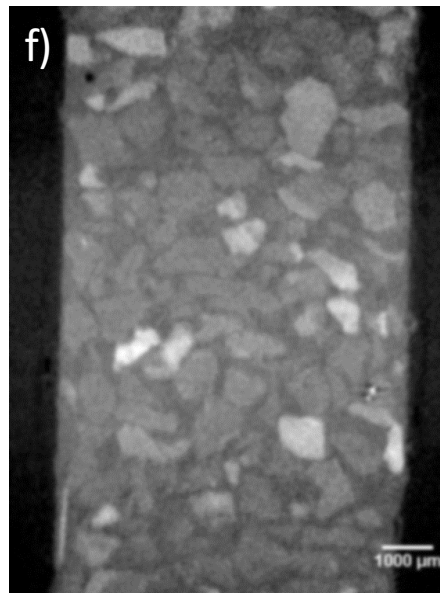
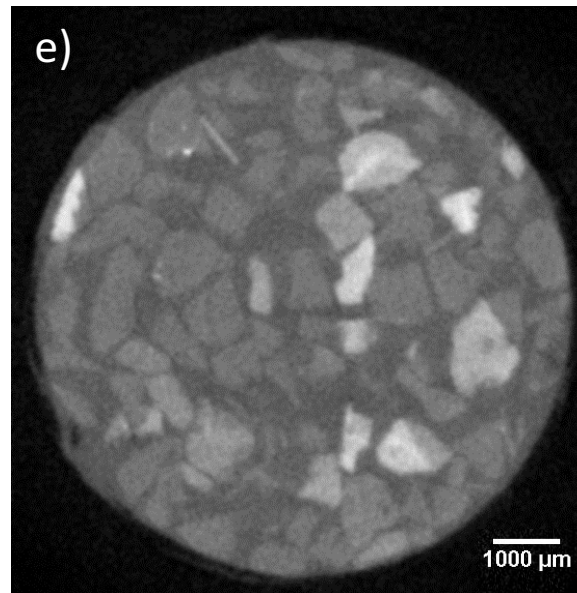
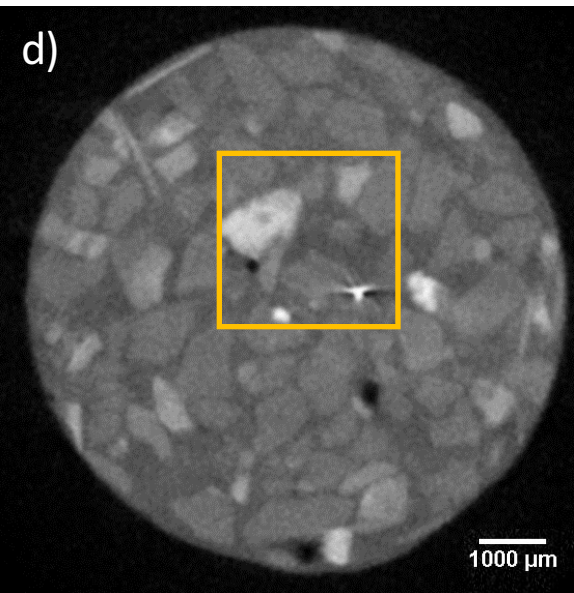
Observed grain damage and porosity reduction



# Quartz With $S_h=40\%$



w/ hyd.



w/o hyd.

# Introduction

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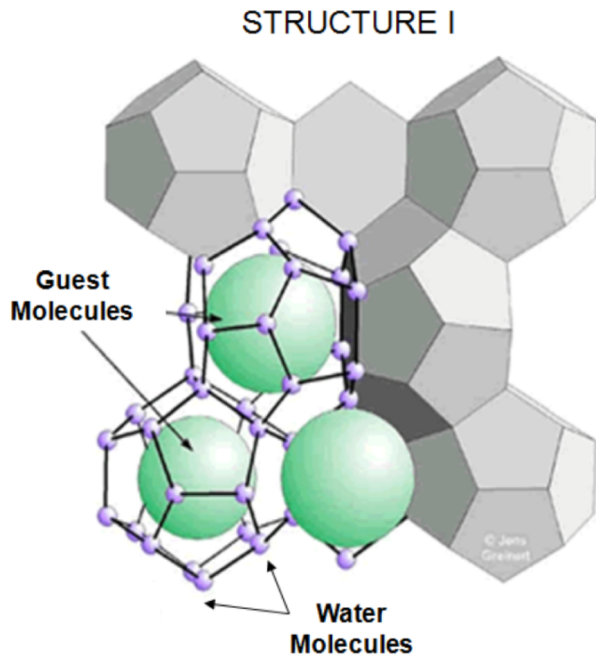
- **Low Temperature, High Pressure**

- Arctic permafrost
- Marine sediments (> 500m deep)

- **Availability of methane and water**

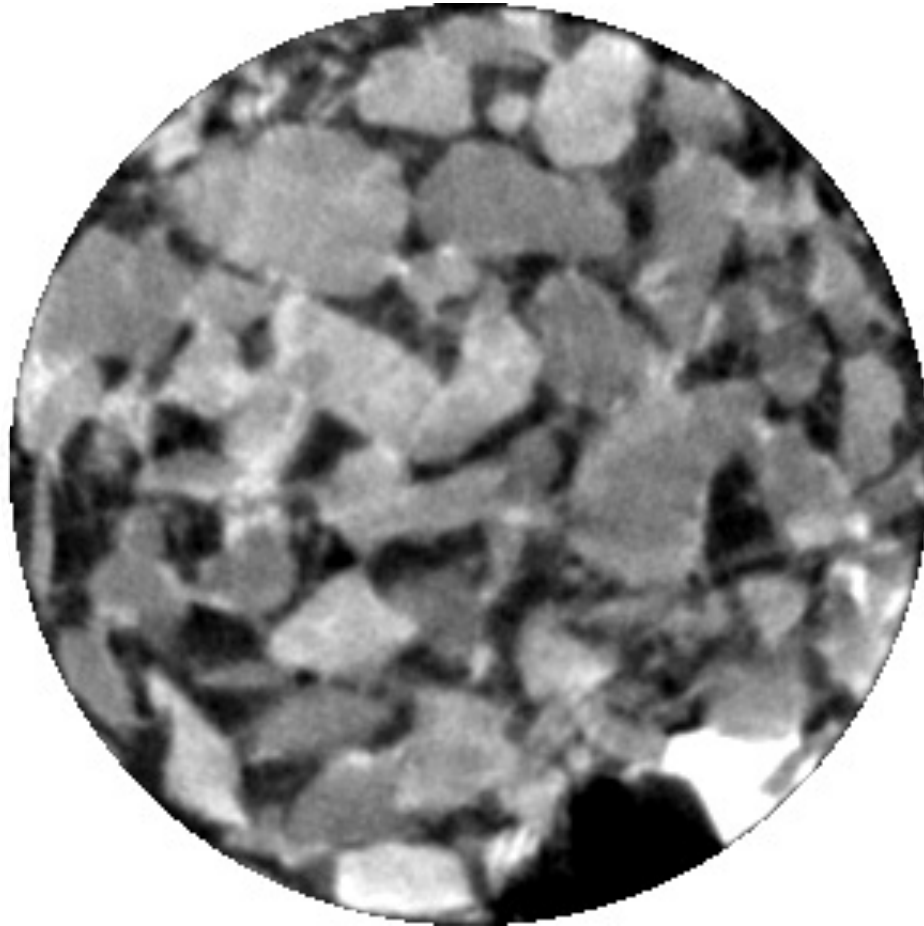
- **Formation: gas dissolved in water or free gas phase**

- **For laboratory experiments: tetrahydrofuran hydrate**



# Status 1<sup>st</sup> Comps vs. 2<sup>nd</sup> Comps

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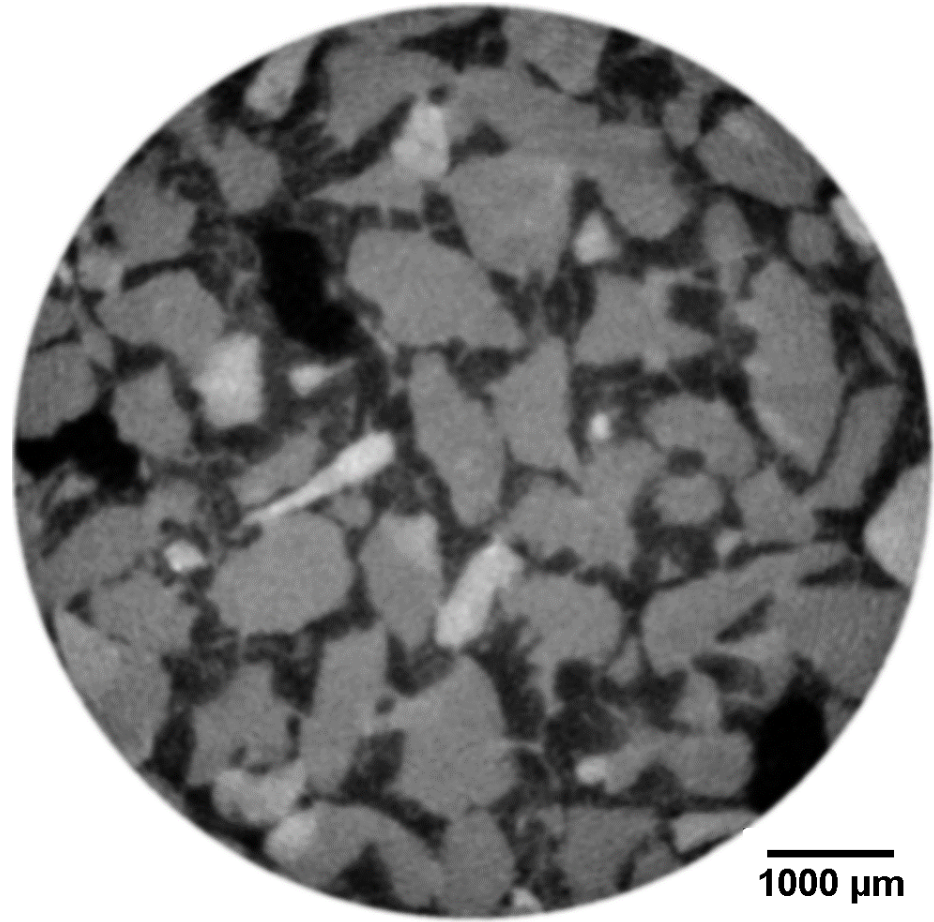
**Resolution: ~70  $\mu\text{m}$**

**Cooling with dry ice for ~1 hour**

**Formation of samples outside of  $\mu\text{CT}$  machine**

**→ ice & hydrate present, not distinguishable**

**Glass beads as host sediment**



**1000  $\mu\text{m}$**

**Resolution: ~10  $\mu\text{m}$**

**Cooling for ~8 hours**

**Hydrate formation in  $\mu\text{CT}$  machine**

**Just hydrate & residual brine, no ice**

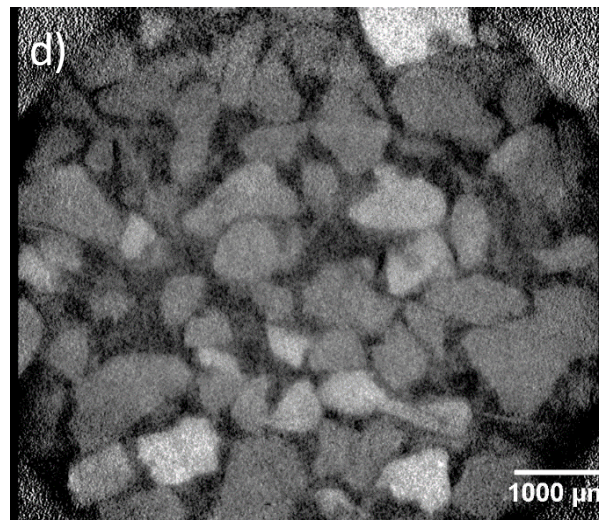
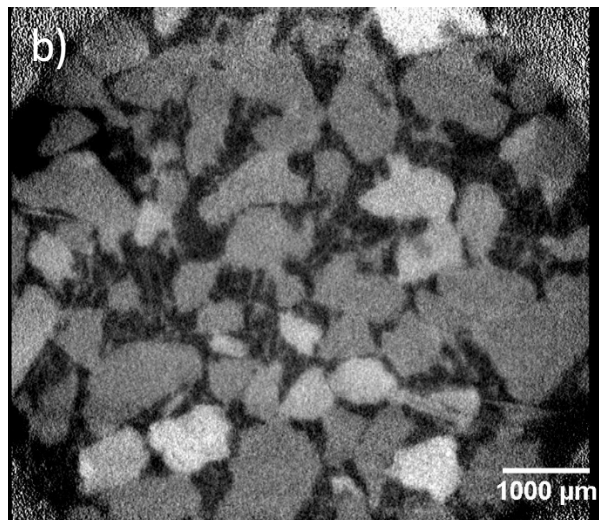
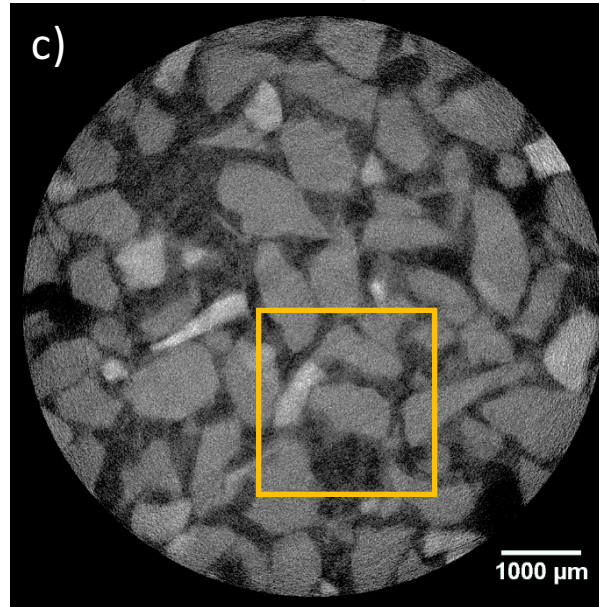
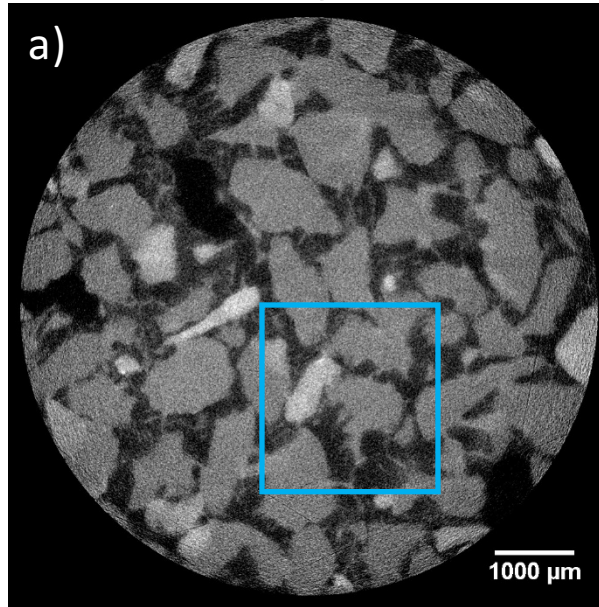
**Quartz sand (and clay) as host sediment**



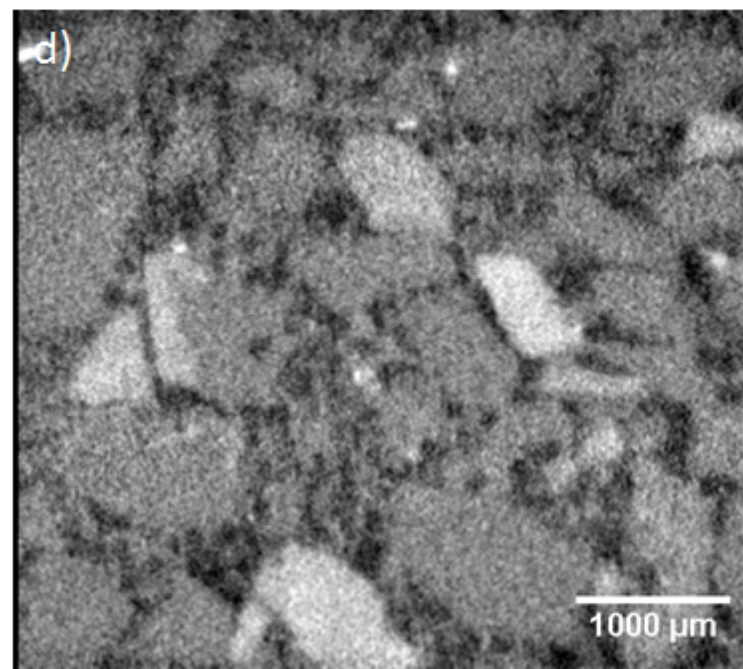
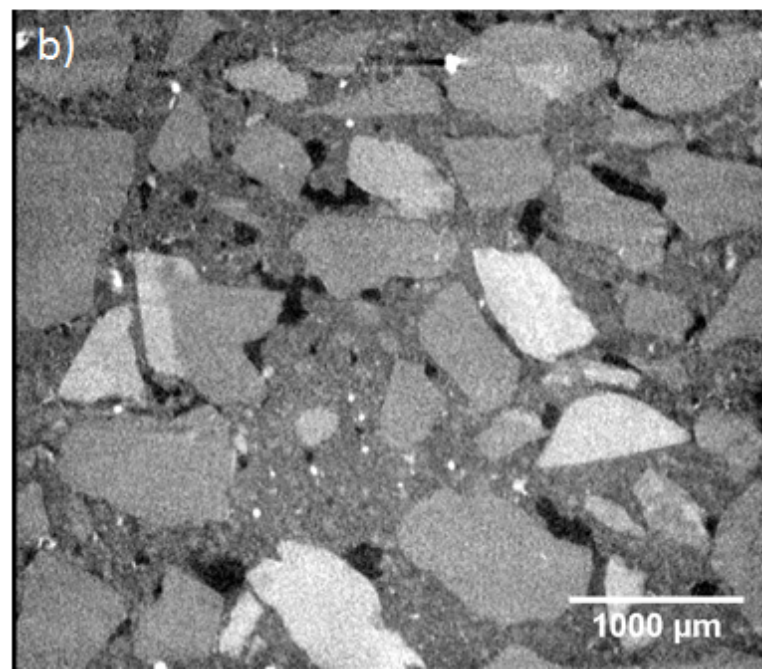
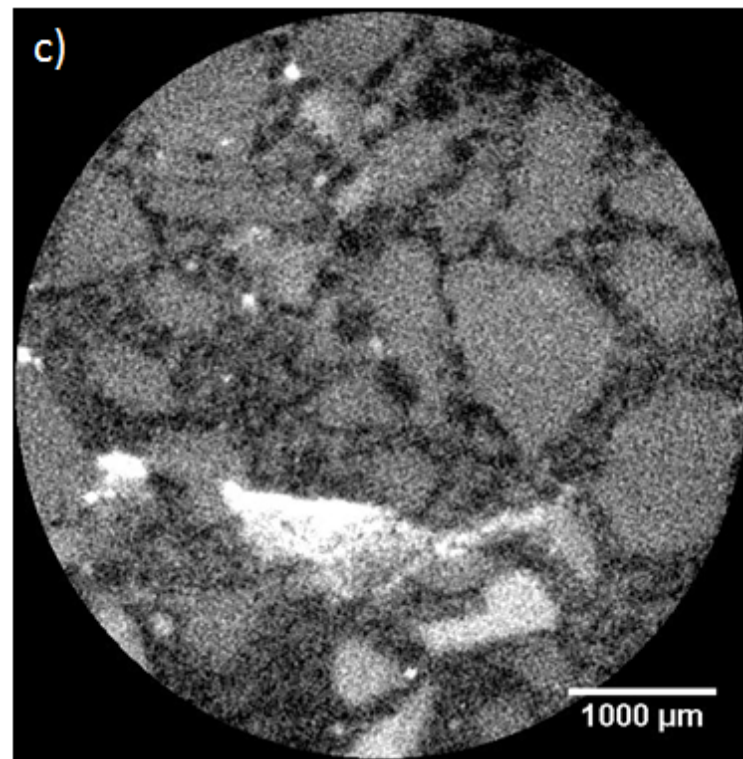
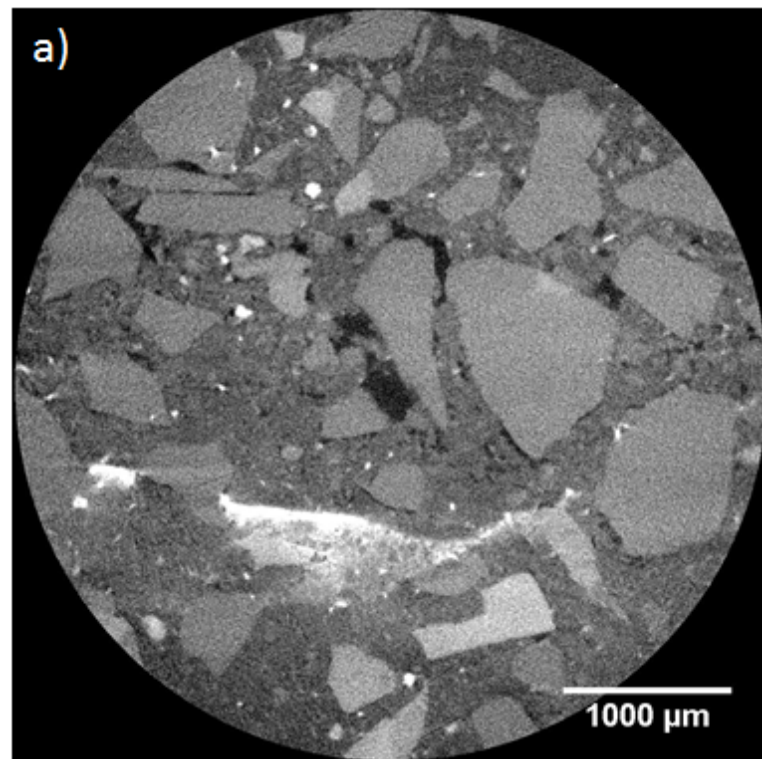
# Quartz With $S_h=80\%$

With Hydrate

Without Hydrate

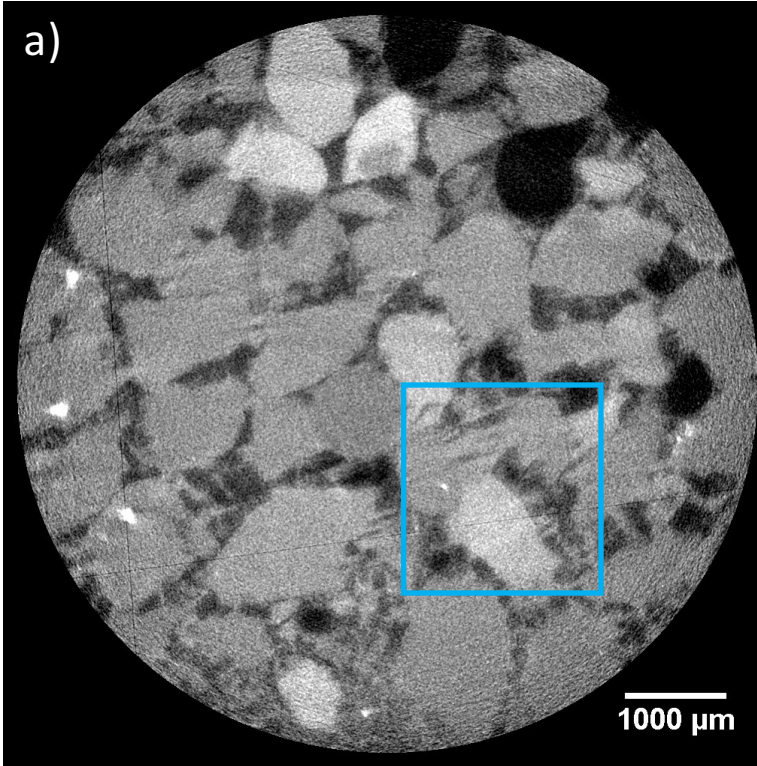




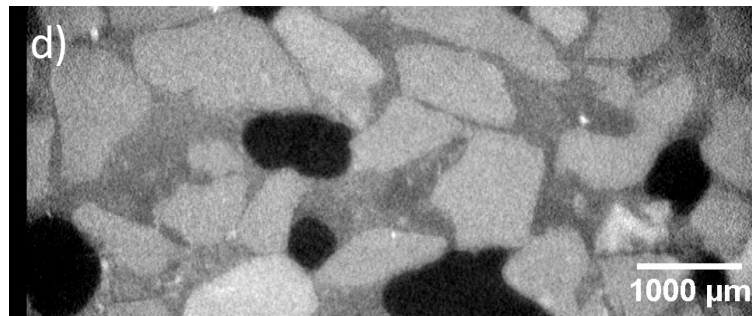
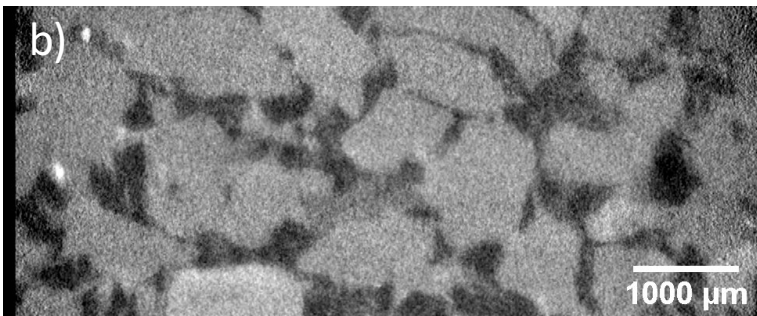
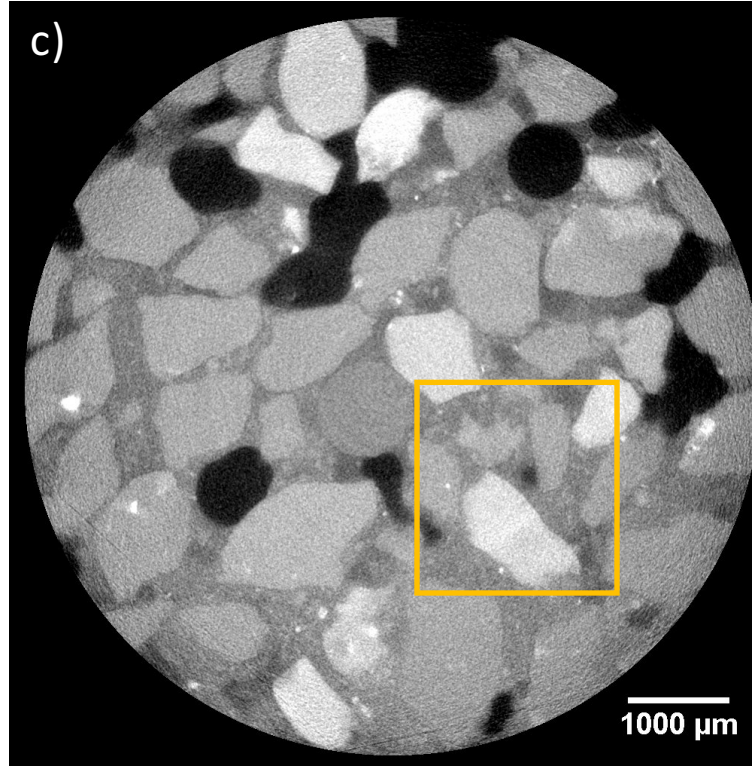


# Quartz and Clay With $S_h=80\%$

With Hydrate



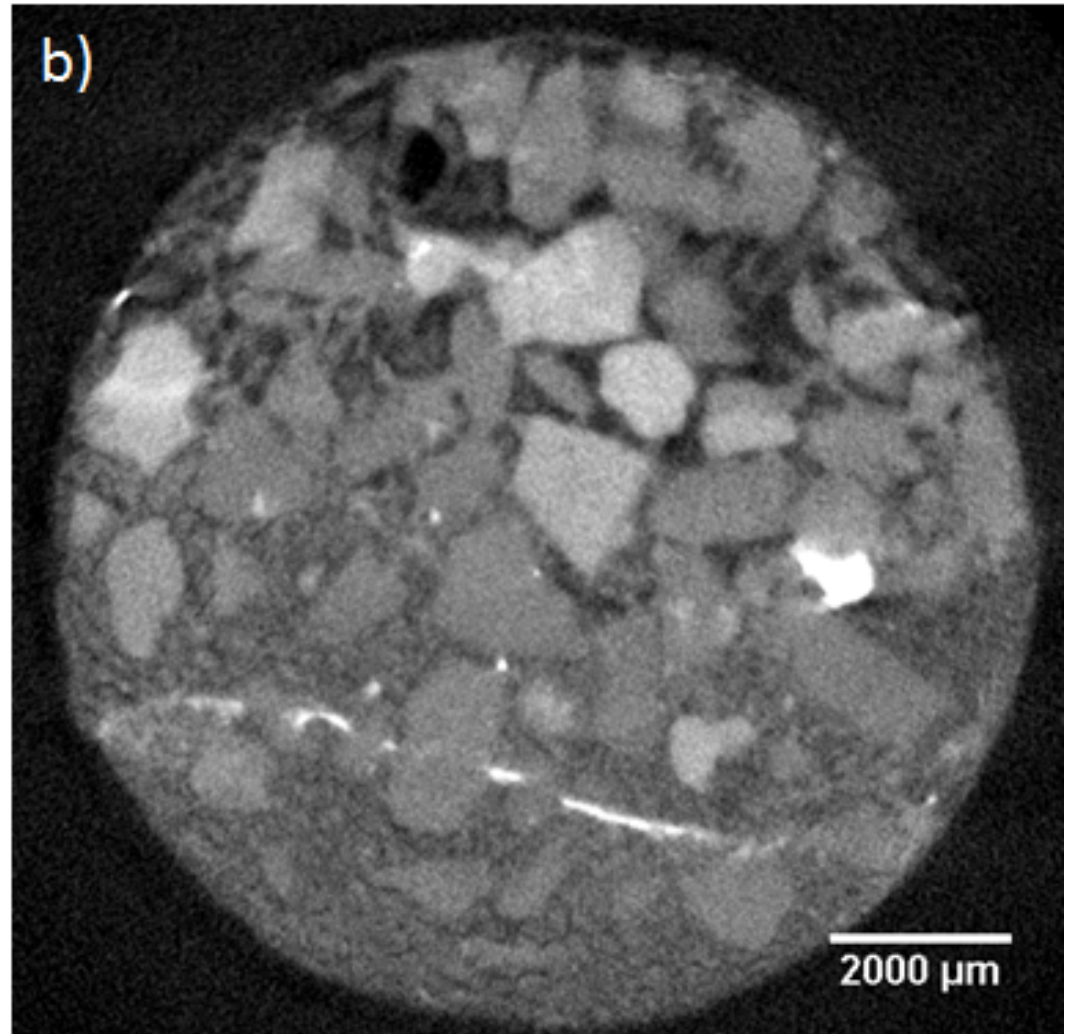
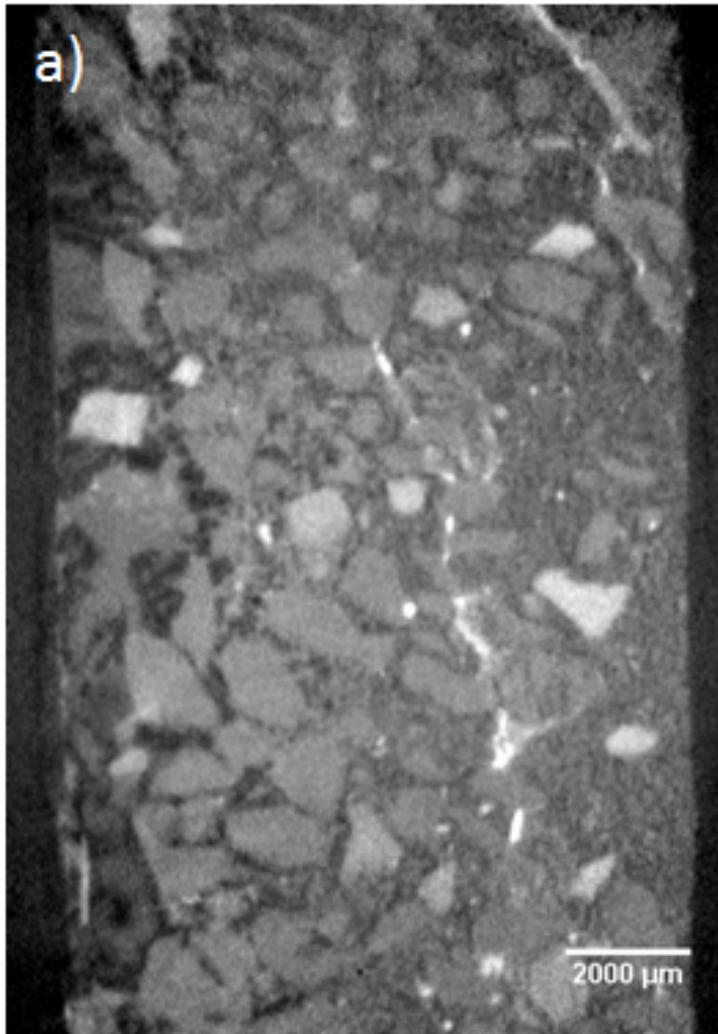
Without Hydrate





# Quartz and Clay With $S_h=80\%$

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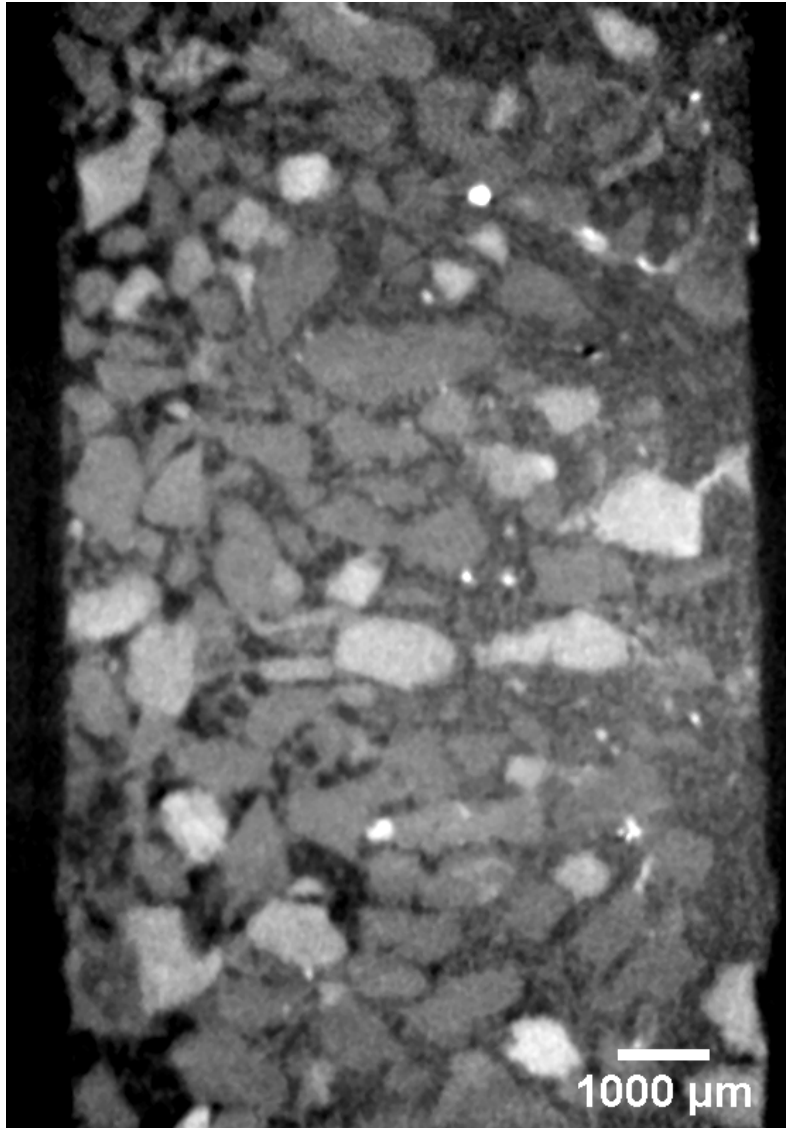


**Heterogeneity in hydrate and clay distribution**  
**Clay moved by hydrate**

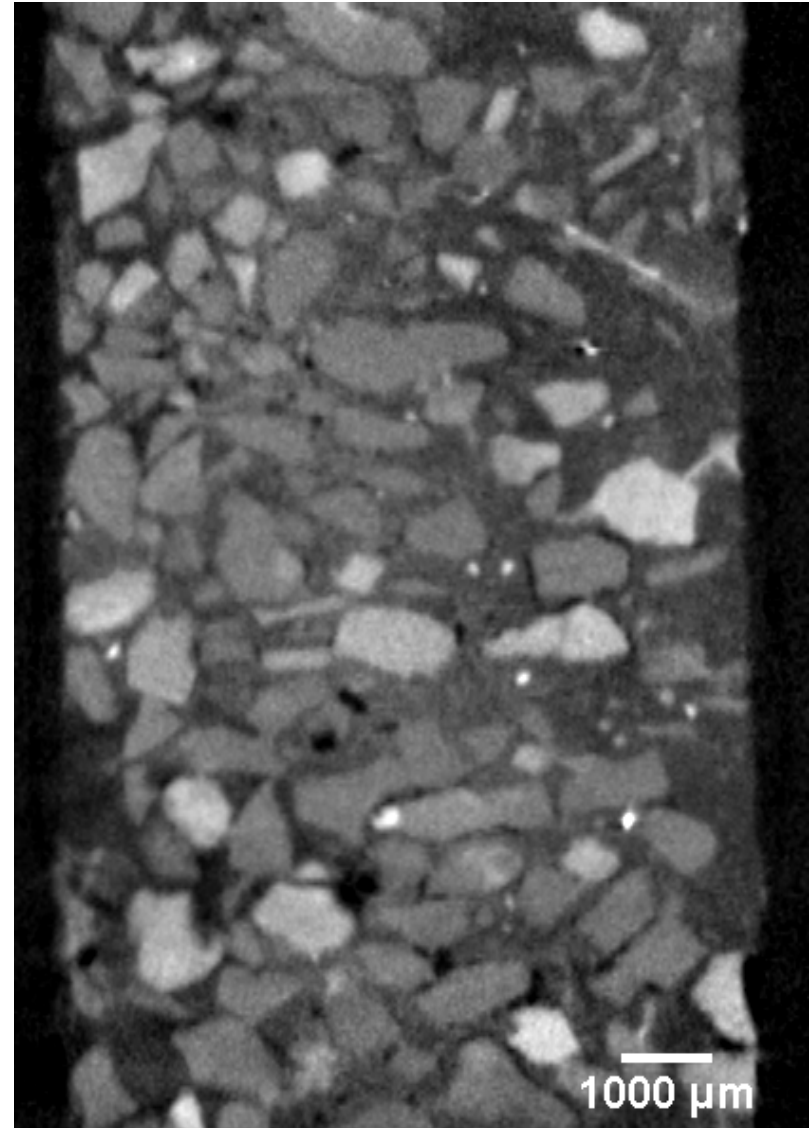
# Quartz and Clay With $S_h=80\%$

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With Hydrate



Without Hydrate



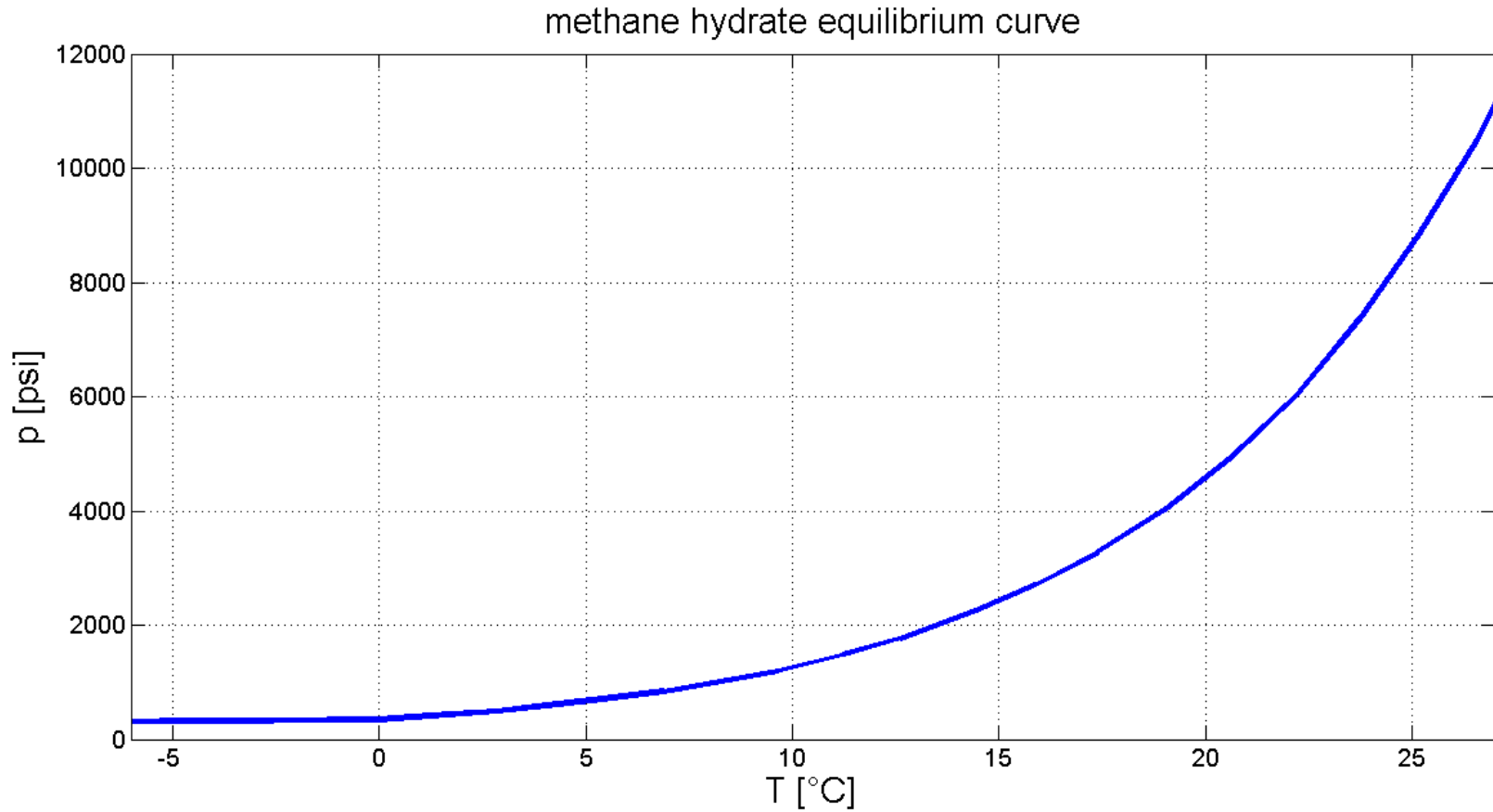
# Research Scope

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- Properties of pure gas hydrate well understood
- Interaction of gas hydrate and sediment less so
- Elastic properties of gas hydrate bearing sediments  
e.g. Waite, Priest, Spangenberg
- Imaging of gas-hydrate bearing sediments  
e.g. Kerkar, Sell
- Combination of imaging and elastic properties:  
e.g. Kneafsey & Nakagawa
- Pore-scale imaging & elastic properties → MY  
NICHE

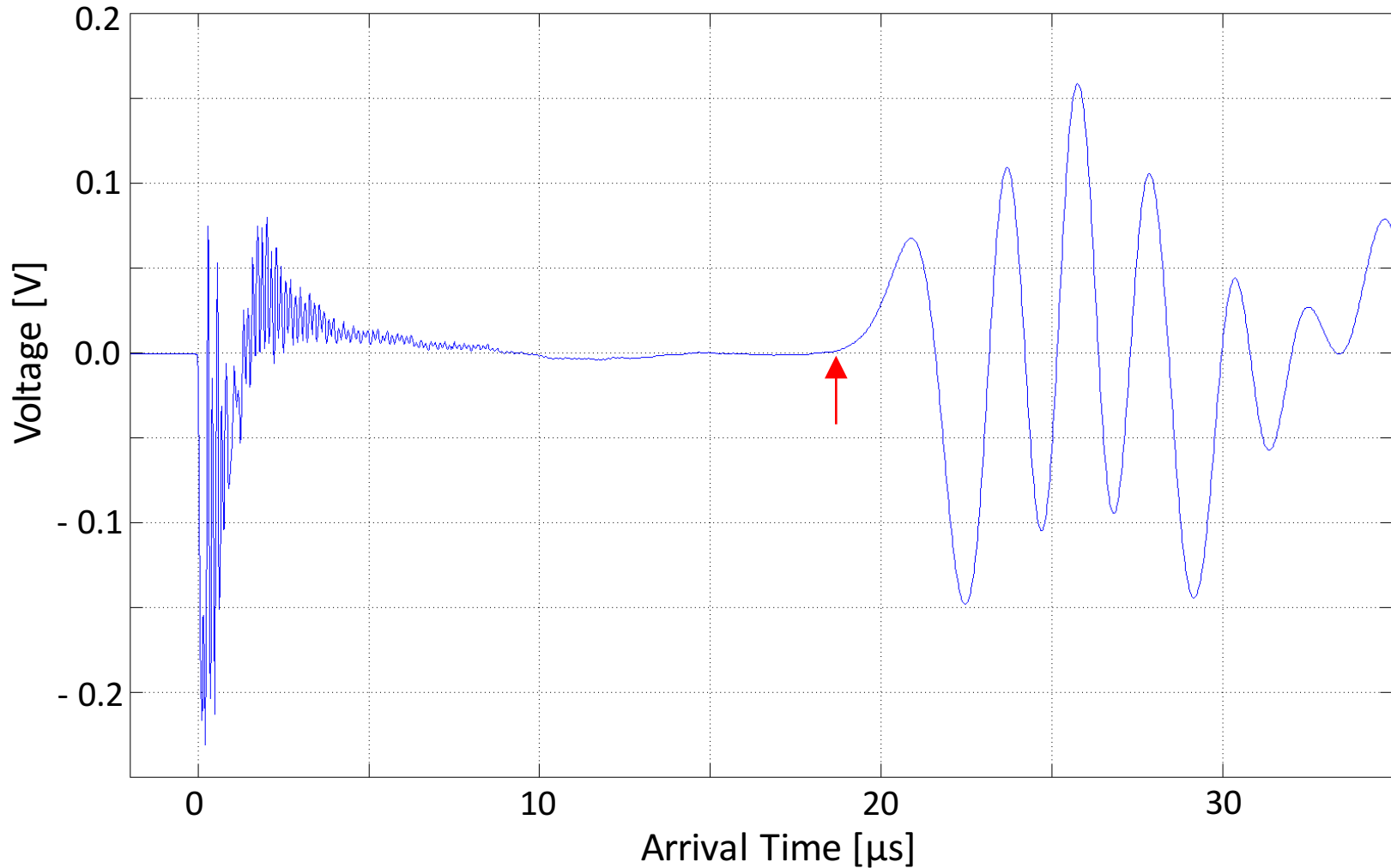
# Methane hydrate equilibrium curve

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# Test Waveform on Bentheim Sandstone



**Calculated P-wave velocity: 1687 m/s**

# Sample Components

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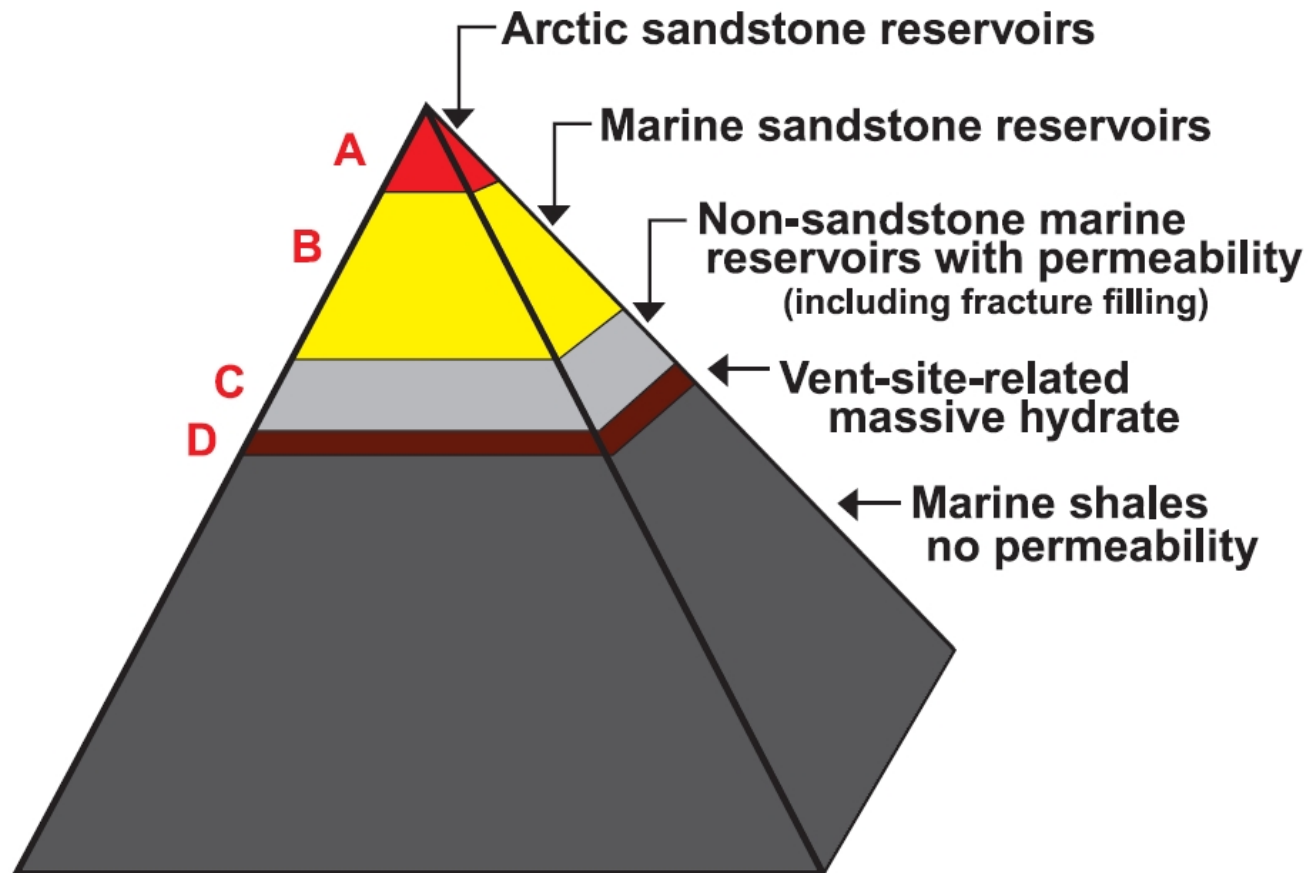
Component	Density [g/cm <sup>3</sup> ]
water	1.00
BaCl <sub>2</sub>	3.84 <sup>(a)</sup>
BaCl <sub>2</sub> brine (12.3 wt%)	1.1
THF hydrate	0.97 <sup>(b)</sup>
THF-water-BaCl <sub>2</sub> mixture	1.00

# Types of Gas Hydrate Deposits

Estimated amount of methane stored in hydrates :

$10^{15}$  to  $10^{18}$  m<sup>3</sup> (STP)

(methane in conventional reservoirs:  $4 \cdot 10^{13}$  m<sup>3</sup>)



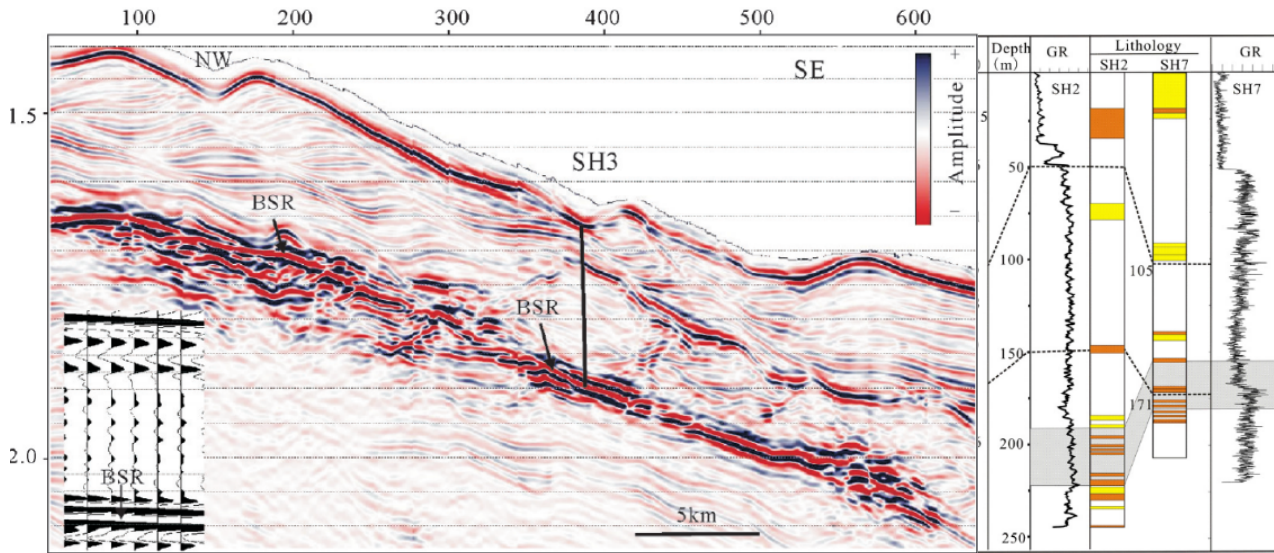
Collett and Boswell, 2006

# Measured Samples

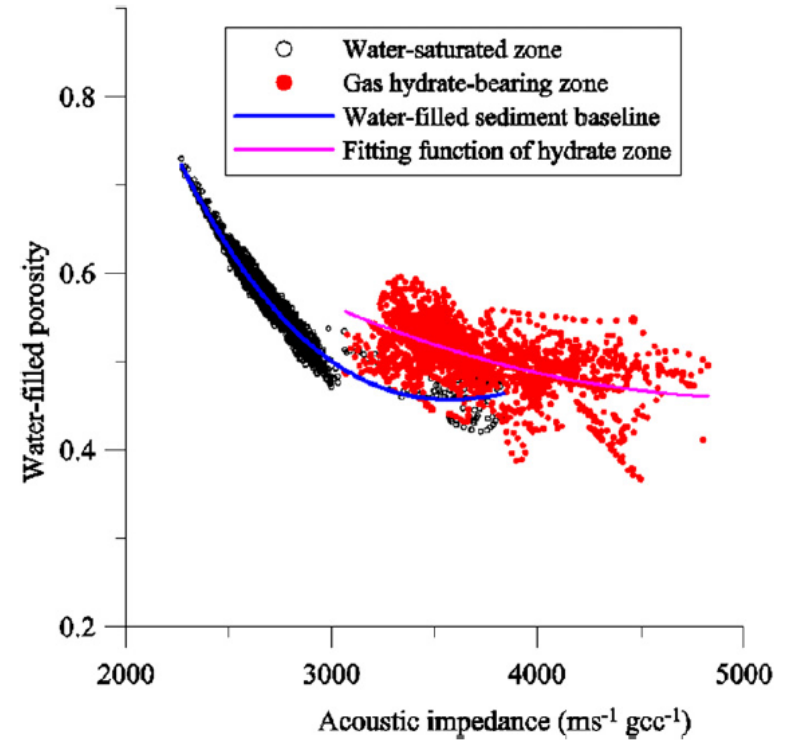
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$S_h$	Host Sediment	$\mu$ CT	Ultrasonic
40%	glass beads	2	1
40%	quartz sand	2	0
60%	glass beads	0	2
80%	glass beads	2	1
80%	quartz sand	2	0
80%	quartz sand with bentonite	1	0
100%	glass beads	0	1

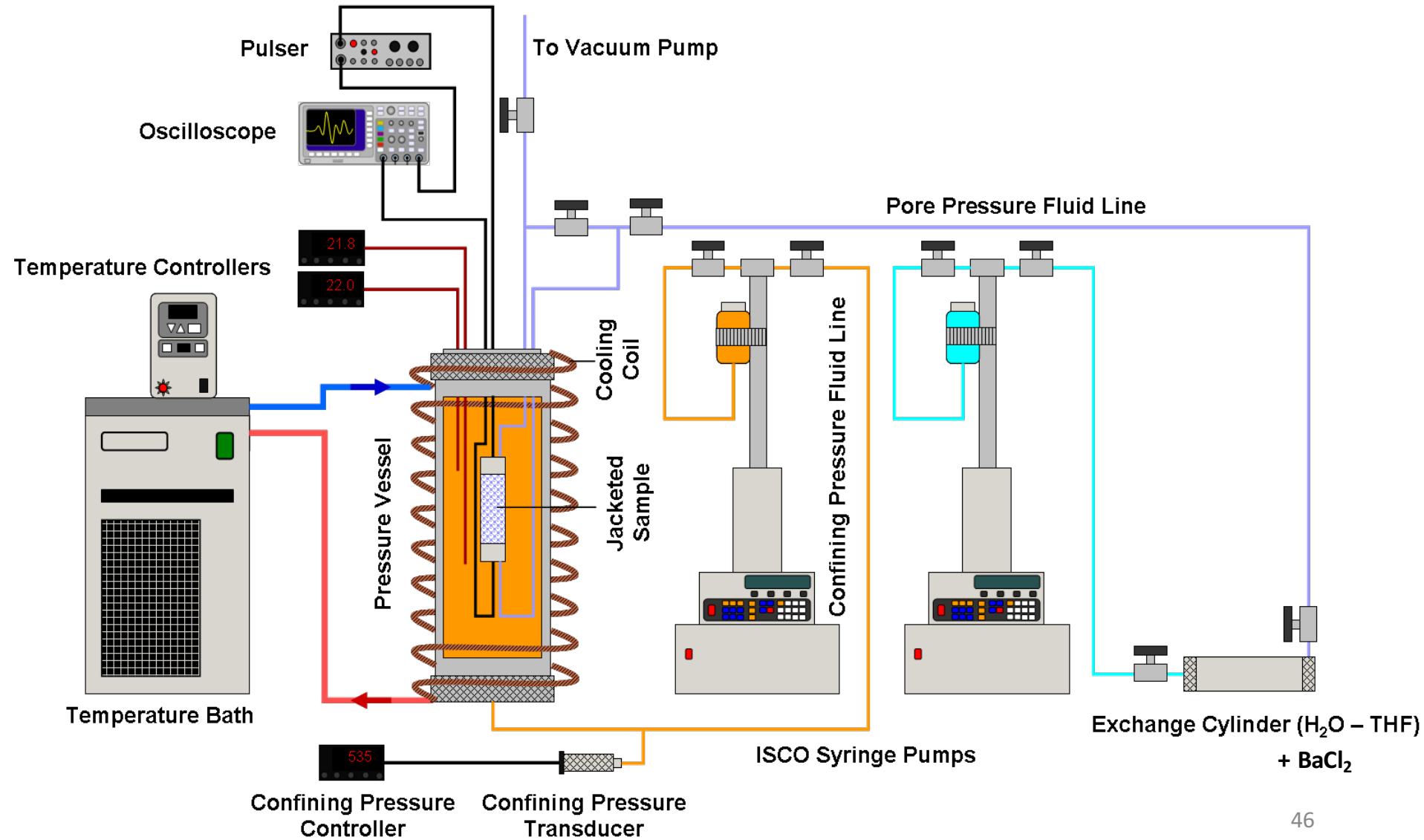




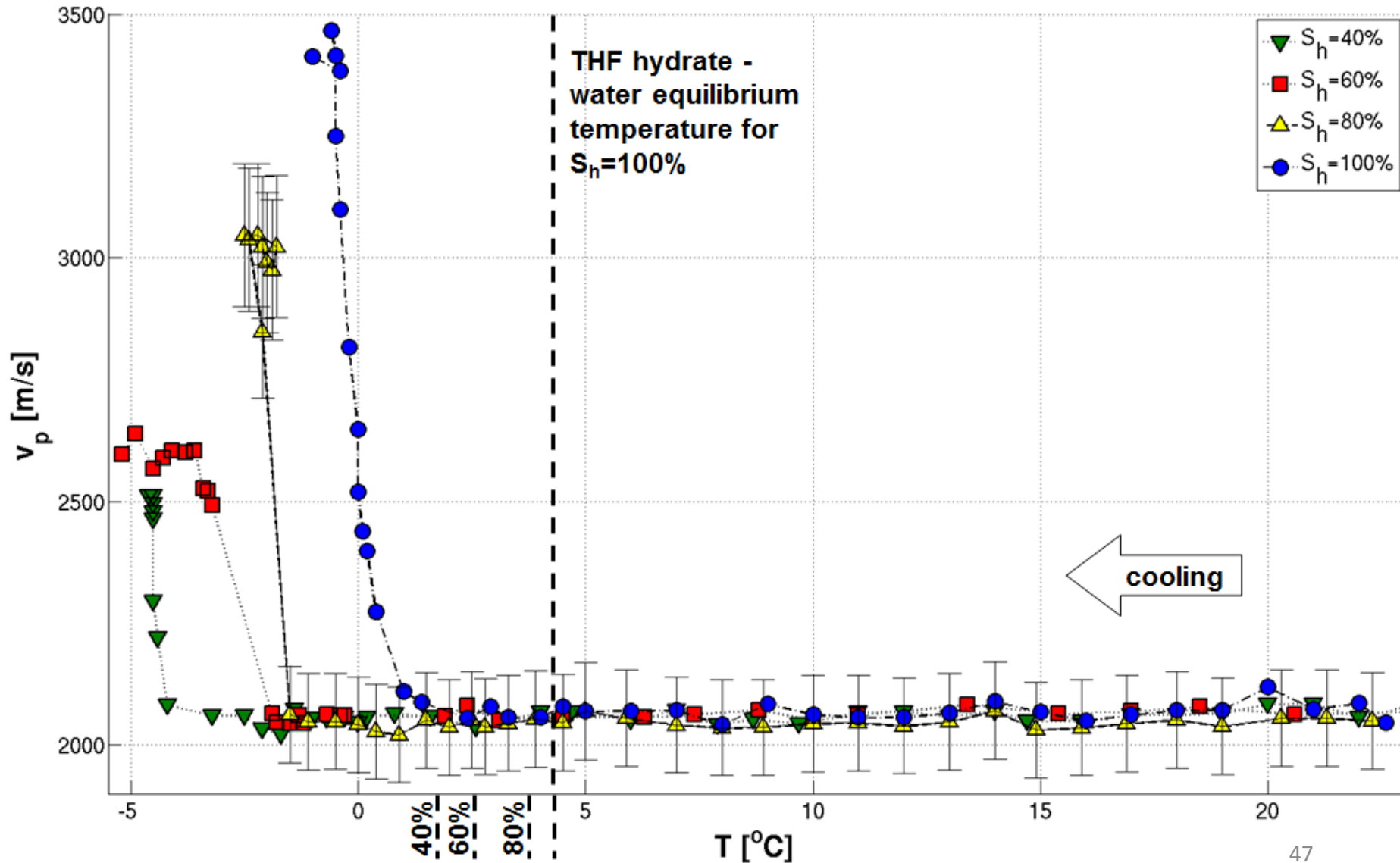
- Use of seismic and well logs
- Hydrate saturation from Archie's equation
- Connected to acoustic impedance by empirical relationship
- Physical model preferred over empirical
- Use sonic logs to quantify hydrate saturation
- connect to seismic (acoustic impedance)



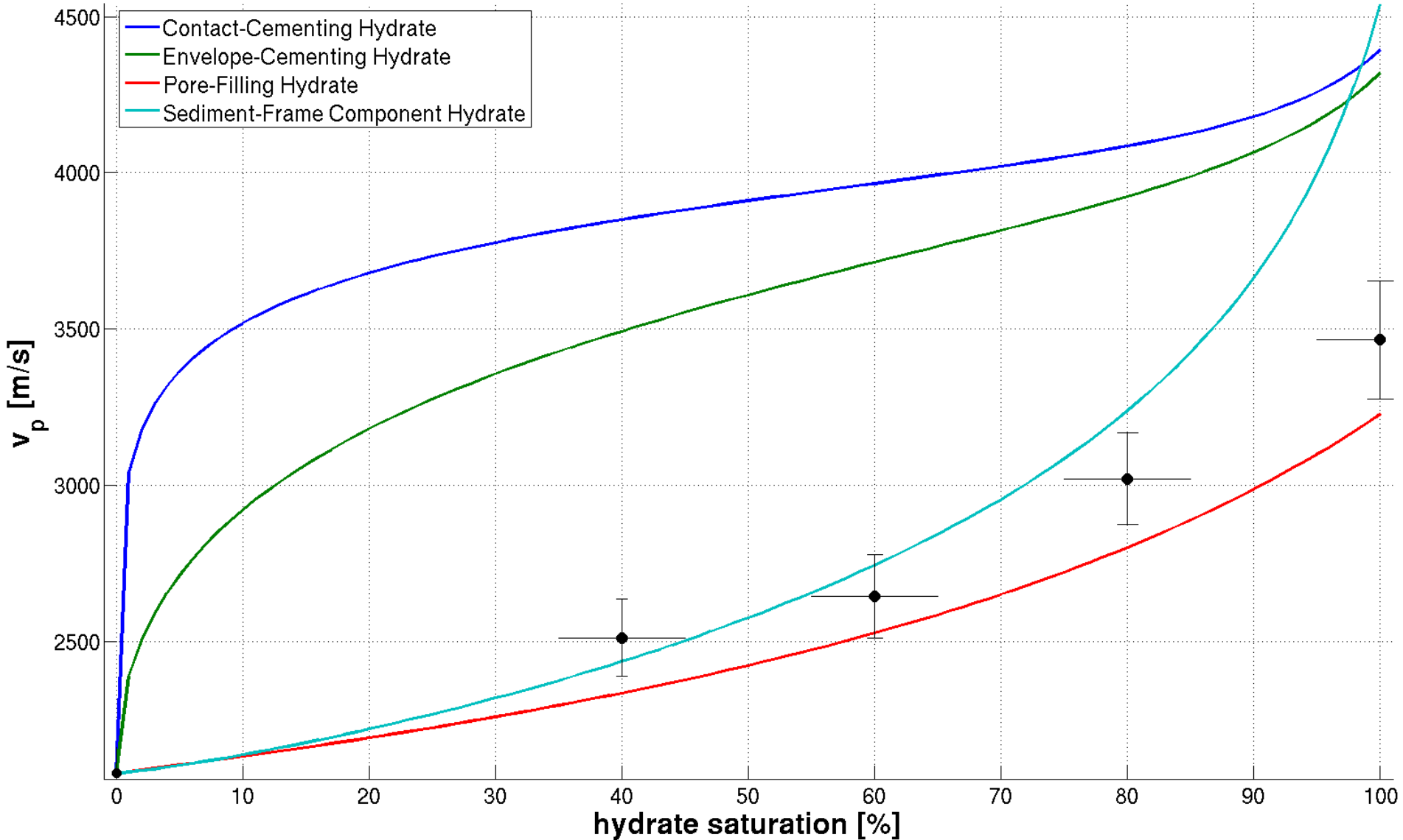
# Ultrasonic Velocity Measurements



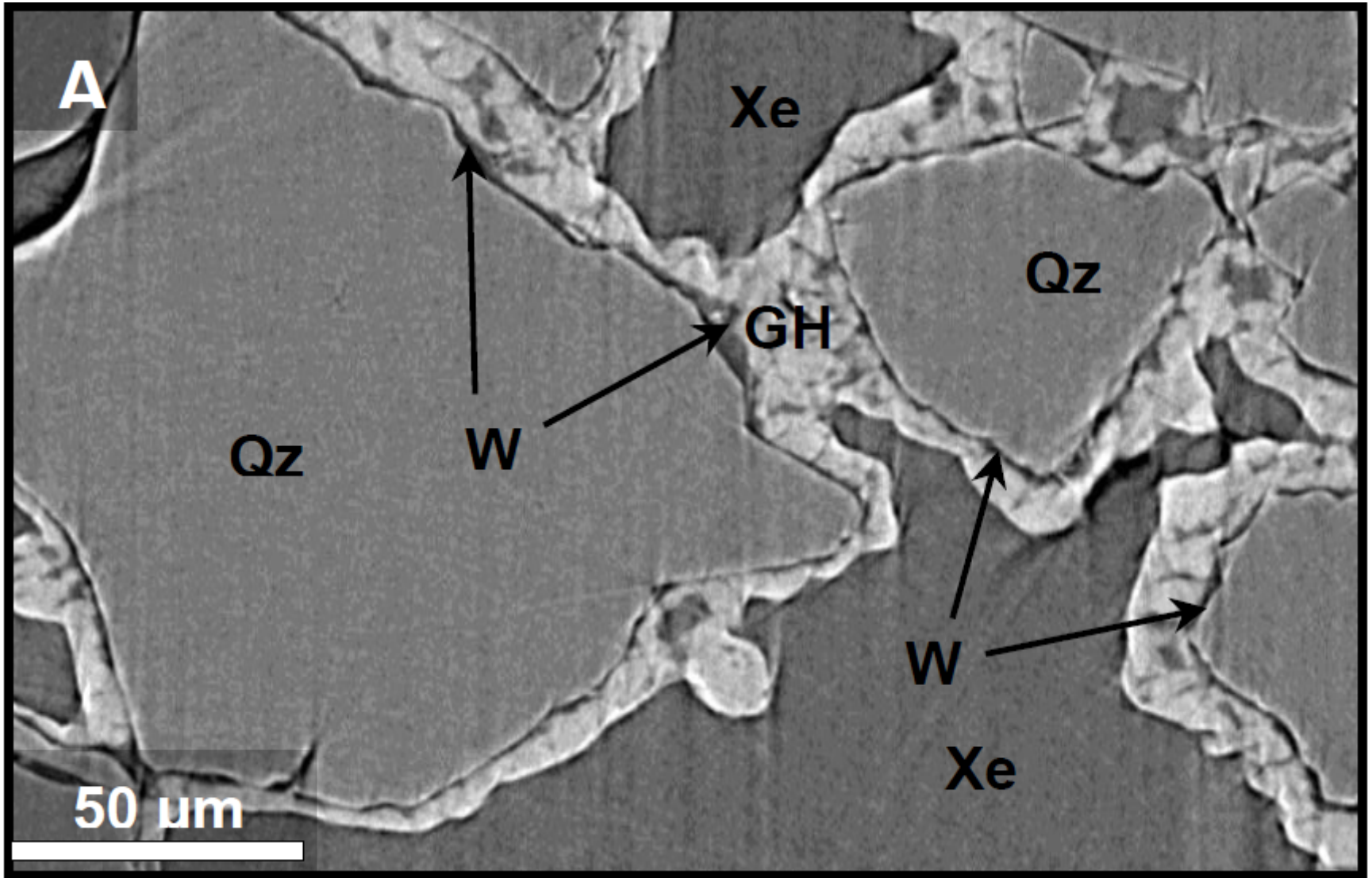
# Different Hydrate Saturations



# Effective Medium Models: P-Wave



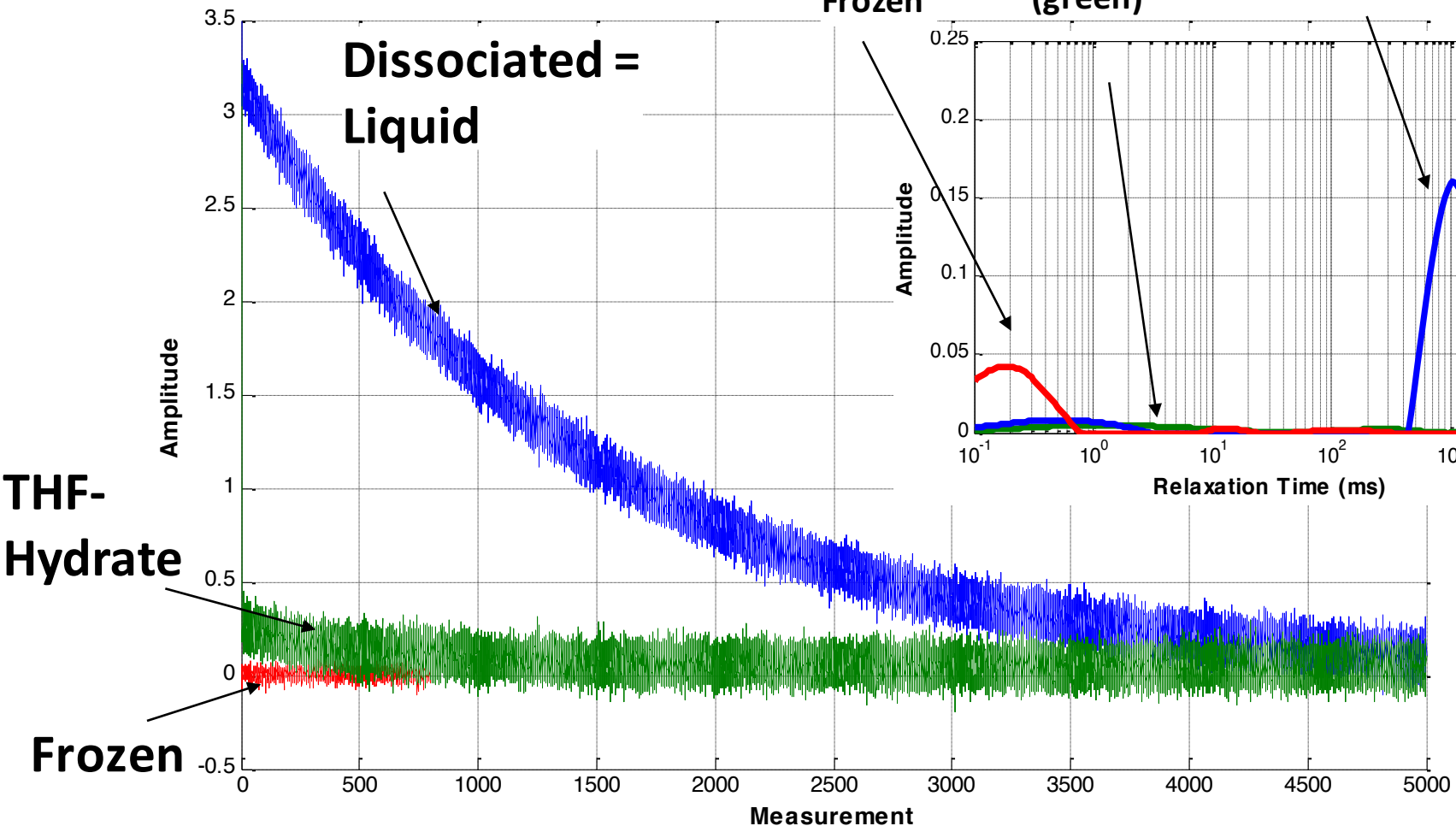




# NMR Signals

from Pohl, Prasad, Batzle, *submitted to Geophysical Prospecting*

## Raw Data



## Relaxation Spectra

