# Laboratory and Numerical Modeling Results on Hydrate-Bearing Sediments


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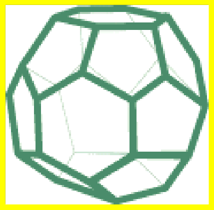
# OUTLINE

- THF (Tetrahydrofuran) Hydrate
- JIP Experimental Matrix
- Samples and Laboratory Equipment
- Properties
  - Mechanical Properties: large and small strain
  - Thermal Properties
  - Electrical Properties
- Lensing
- Process Monitoring (Phase Transformation)
- Core Recovery Numerical Modeling

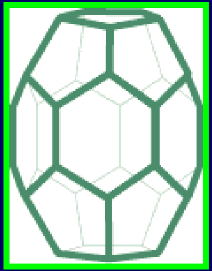
# Hydrate Structures

*All 3 occur in Gulf of Mexico, with I and II more common*

***Structure I:*** *46 water + 8 gas*
*methane, ethane (up to 5.2 Å)*
*sites: 2 x $5^{12}$ and 6 x $5^{12}6^{2}$*



***Structure II:*** *136 water + 24 gas*
*propane, tetrahydrofuran (5.9-6.9 Å)*
*sites: 16 x $5^{12}$ and 8 x $5^{12}6^{4}$*



***Structure H:*** *34 water + 6 gas*
*iso-pentane (> 6.9 Å)*
*small, medium, and large sites*

*(after Sassen)*

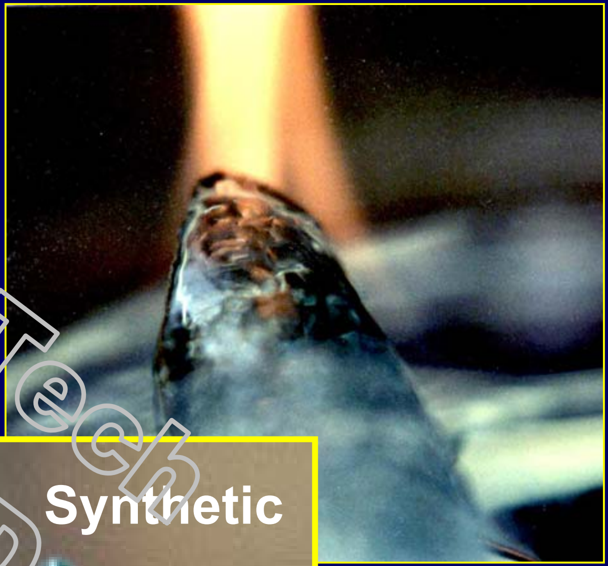
# Methane Hydrate

Structure I

# THF Hydrate

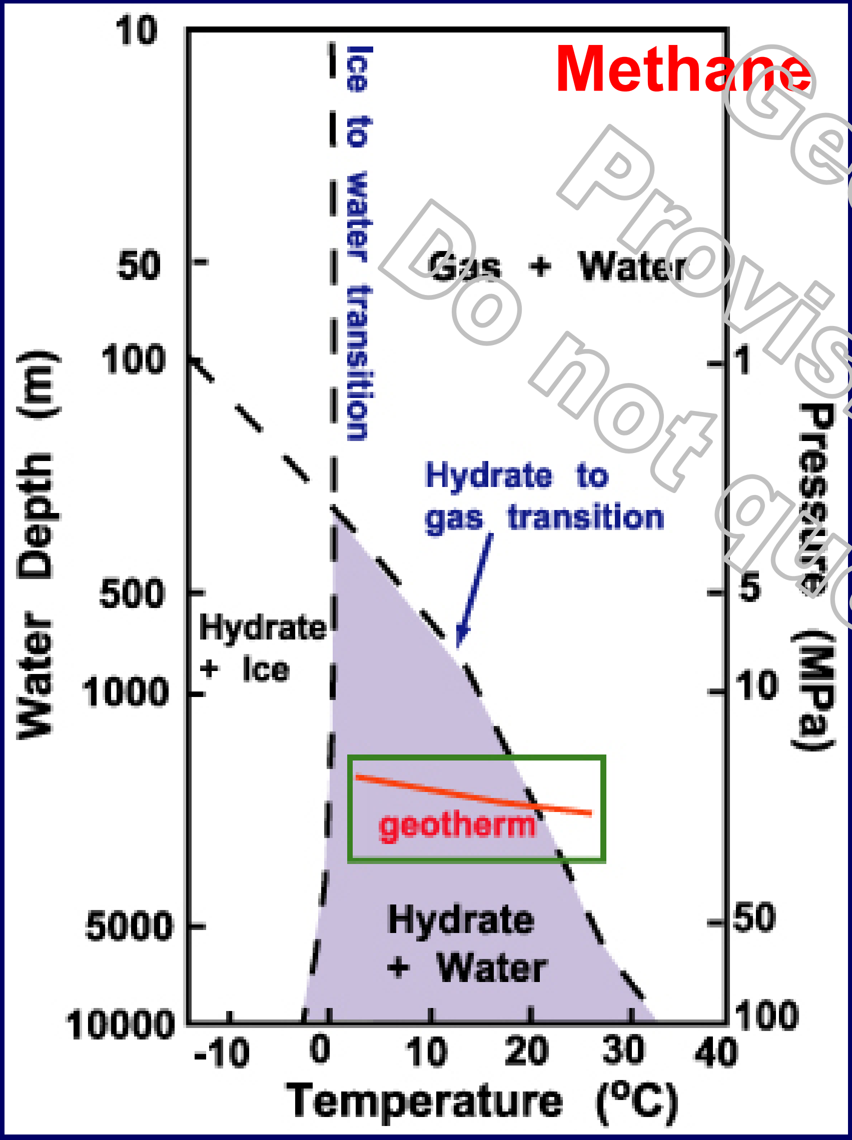
Structure II


Stern

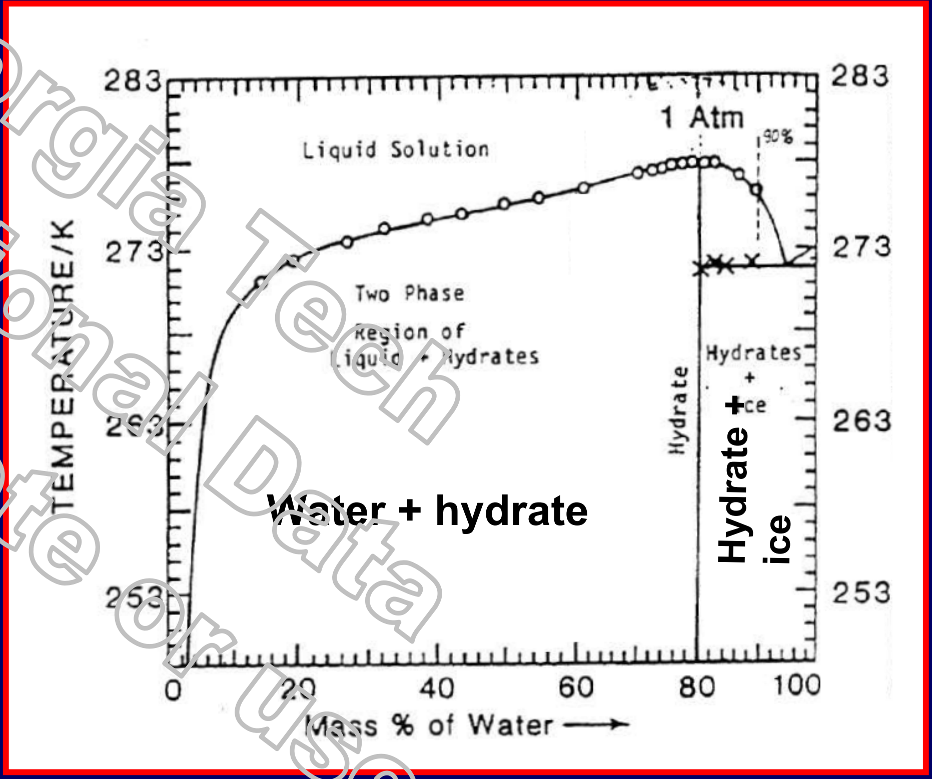



# Phase Diagrams

## METHANE




## THF



# Methane vs. THF Hydrate



**Pressure at phase transformation**

| | |
|---|---|
| Methane | 10 -100 MPa for T = 4-30ºC |
| THF | 1 atm at T=~4.4 º C (optimal stoichiometry) |

**Molecules per cage**

| | |
|---|---|
| Methane | 6 |
| THF | 17 |

**Solubility**

| | |
|---|---|
| Methane | $(CH_4 + 3.7 \times 10^5\ H_2O)$ |
| THF | fully soluble |

**Diffusion Time**

| | |
|---|---|
| Methane | 22 years for length of 1 meter |

***THF Advantages for Laboratory Study**: Structure II hydrate-former, completely miscible, hydrate formation at close to 1 atm and 0°C*

*" We completely understand our system"*

# Hydrate Properties: Methane vs. THF

| Property | Ice | $CH_4$ hydrate | THF hydrate |
|---|---|---|---|
| ***Thermal properties*** | | | |
| Heat capacity (J K-1 $g^{-1}$) | 2.097 @ 270 K | 2.07 @ 270 K | 2.07 @ 270 K |
| Heat of dissociation (kJ $kg^{-1}$) | -333.5 @ 273 K | +338.7 @ 273 K | +262.9 @ 273 K |
| Thermal conductivity (W $m^{-1}$ $K^{-1}$) | 2.23 @ 263 K | 0.5 @ 270 K | 0.53 @ 250 K |
| Thermal diffusivity ($m^2$ $s^{-1}$) | $15.4 \times 10^{-7}$ @ 250 K | $3 \times 10^{-7}$ @ 270 K | |
| Vol. strain liquid-to-solid | $168 \times 10^{-6}$ @ 200 K | $231 \times 10^{-6}$ @ 200 K | $156 \times 10^{-6}$ @ 200 K |
| Thermal linear expansivity ($K^{-1}$) | $56 \times 10^{-6}$ @ 200 K | $77 \times 10^{-6}$ @ 200 K | $52 \times 10^{-6}$ @ 200 K |
| ***Physical properties*** | | | |
| Bulk Compressibility (Pa) | $12 \times 10^{-11}$ @ 273 K | $\sim 14 \times 10^{-11}$ @ 273 K | $\sim 14 \times 10^{-11}$ @ 273 K |
| Density (kg $m^{-3}$) | 917 @ 273 K | 910 @ 273 K | ~ 910 @ 273 K |
| Diff. coef. in water ($cm^2$ s-1) | | $1.49 \times 10^{-5}$ | $0.56 \times 10^{-5}$ @ 0.059 M |
| Strength hydrate + sand (M Pa) | 10.5 for ε = $10^{-6}$ $s^{-1}$ | | 16.0 for ε = 10-6 s-1 |
| Vp (m $s^{-1}$) | ~3800 @ 273 K | 3369 @ 273 K | 3665 @ 273 K |
| ***Structural properties*** | | | |
| Cavity size (Å) | n/a | 3.95 | ~ 3.91 |
| Guest size (Å) | n/a | 4.36 | 6.3 |
| Saturation (mole/mole) | n/a | $3 \times 10^{-5}$ | 0.07 |
| Saturation (mL / L $H_2O$) | n/a | 3.5 | $1 \times 10^6$ |
| Stoichiometric ratio | n/a | $CH_4.6H_2O$ | $C_4H_8O.17H_2O$ |

| | Grain size | % Hydrate | Pressure | Mechanical Large/intermediate strain | | | | | | | | | Thermal | | Mechanical Low strain | | | | Electrical | | Distribution | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SAND | 100 | 0% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | | |
| | | 50% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| | | 100% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | S | in |
| SILT | 20 | 0% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | | |
| | | 50% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| | | 100% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| CLAY | 1 | 0% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | | |
| | | 50% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| | | 100% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | S | in |

# Georgia Tech JIP Characterization Matrix

## Defining Characteristics

**Mechanical** (high/intermediate strains)

- Grain Size (microns)
- Hydrate Concentration (%) - Target values
- EFFECTIVE Confining Pressure (MPa)
- Longitudinal and lateral stress-strain
- Elastic-Plastic Transition
- Tensile strength (indirect from Mohr-Coulomb intercept)
- Shear strength
- Compressive strength
- Failure/stability envelopes (Mohr-Coulomb)
- Bulk moduli (static)
- Triaxial compaction coefficient
- Young's modulus
- Volume-Pressure compaction curves

**Thermal**

- Thermal Conductivity
- Volume change during phase transformation X

**Mechanical** (low strains)

- P-wave velocities
- S-wave velocities
- Bulk moduli (dynamic)

**Electrical**

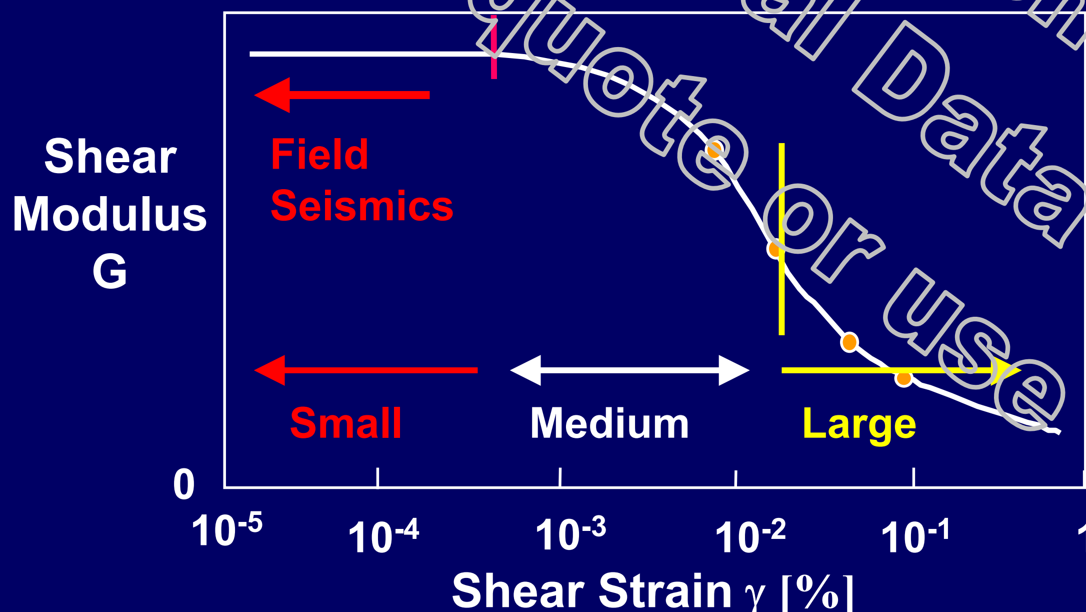
- Electrical Resistivity
- Real permittivity 200 MHz - 1.3 GHz (oedometer at low confinement)

**Distribution**

- Hydrate distribution (optical/visual--destructive of sample)
- Pore filling vs. grain boundaries

# Mechanical Properties

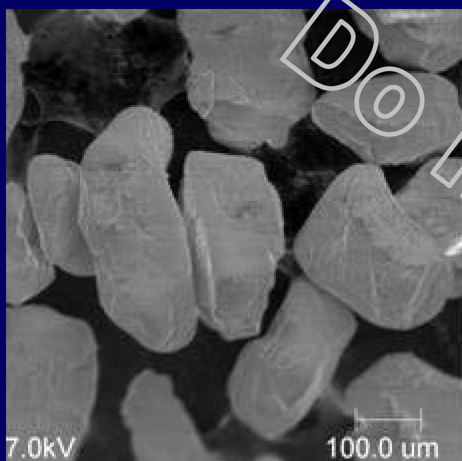
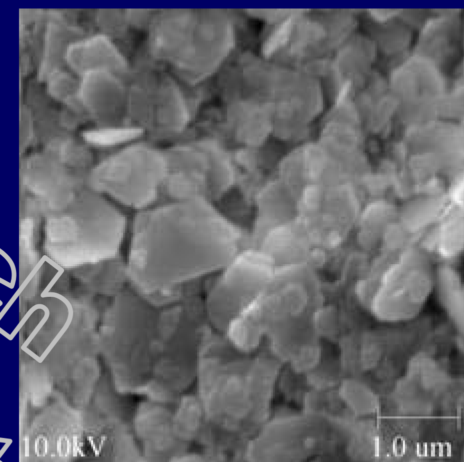
| | *Small Strain* | *Large Strain* |
|---|---|---|
| Deformation | at contacts | fabric changes |
| Stiffness | maximum | decreases |
| Losses | very low | large - frictional |
| Volume Change | minimal | potentially large |
| Diagenetic effects | potentially high | small in drained shear |
| Fabric | constant | changes to critical state |






JIP 9/03

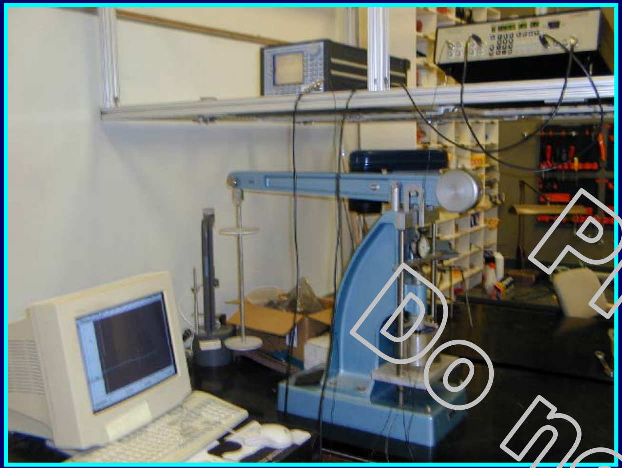
# Representative Soils

| SAND | SILT<br>(Silica Flour) | CLAY<br>(Kaolinite) |
|---|---|---|
|  |  |  |
| $D_{50}$ = 100 μm<br>Specific surface = < 0.1 $m^2/g$<br>Specific gravity = 2.65 | $D_{50}$ = 20 μm<br>Specific surface = 160 $m^2/g$<br>Specific gravity = 2.08 | $D_{50}$ = 1.1 μm<br>Specific surface =<br>10 to 20 $m^2/g$<br>Specific gravity = 2.6 |



Properties: Ordering by both grain size and specific surface

# Laboratory Devices

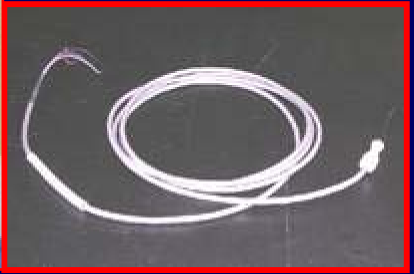


Oedometer ($\varepsilon_h = 0$)

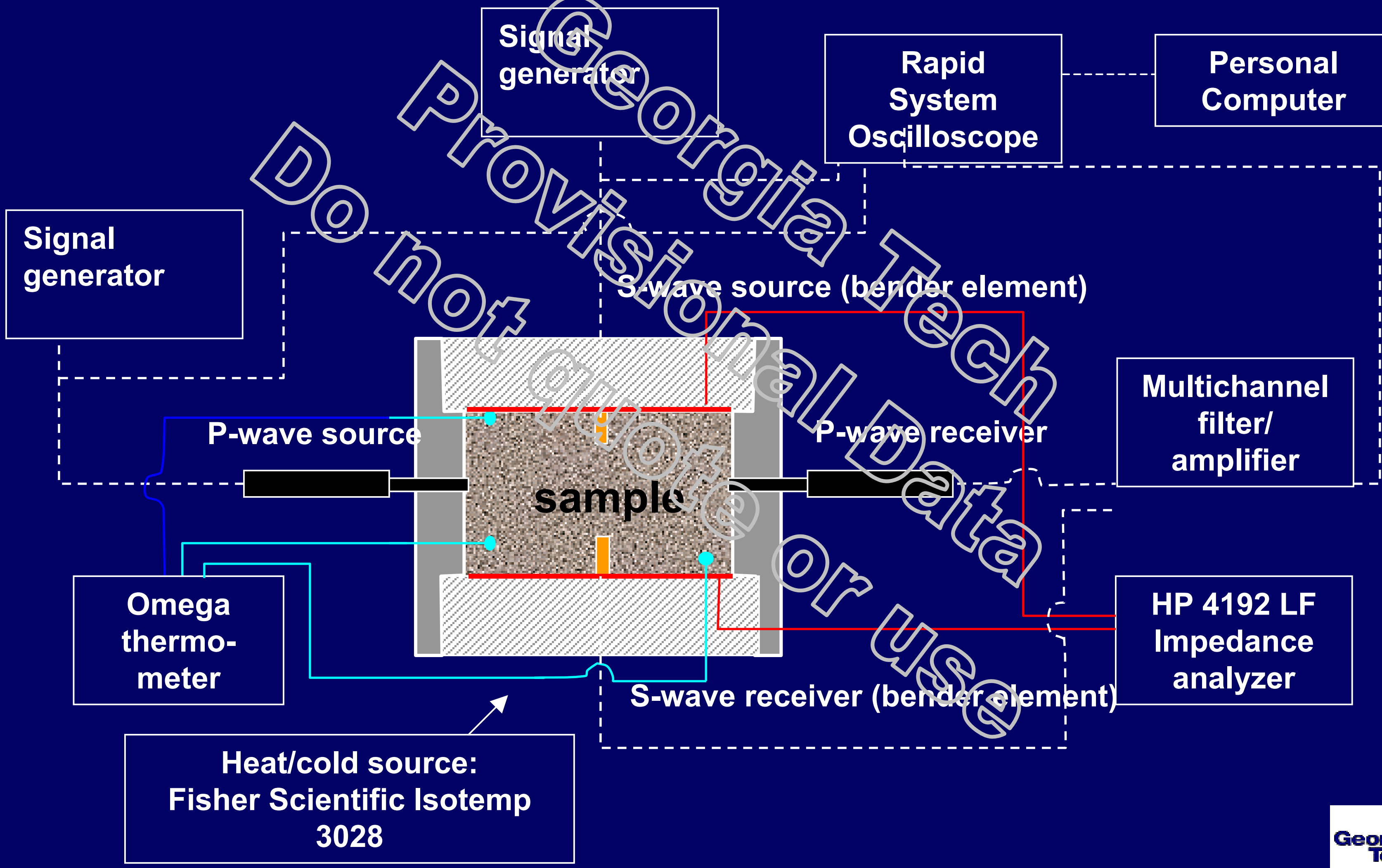
Triaxial test

High-pressure cell

Thermal properties



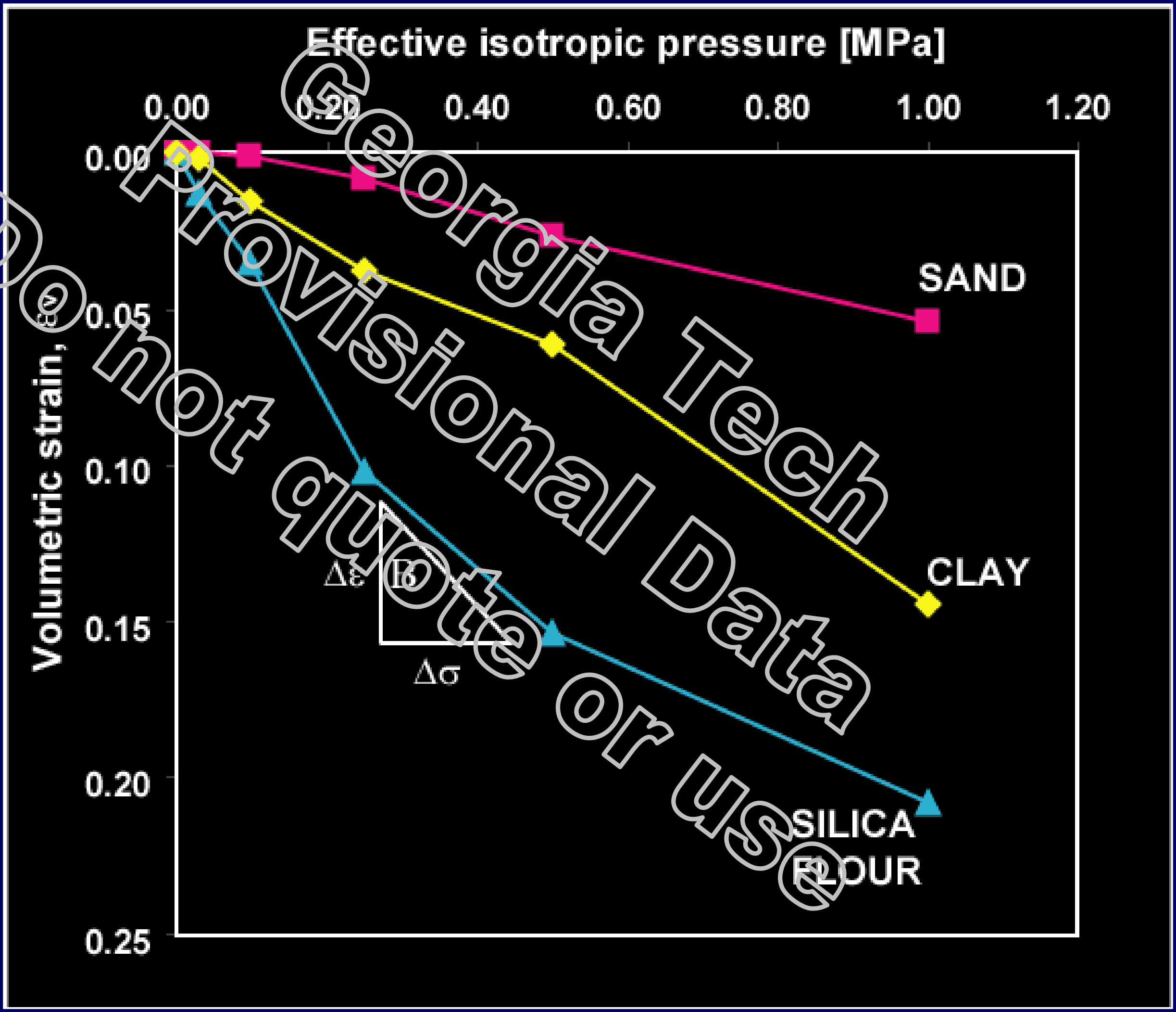
# Oedometer cell and peripheral equipment



*Mechanical Properties*

# Isotropic Loading

**(bulk modulus B)**

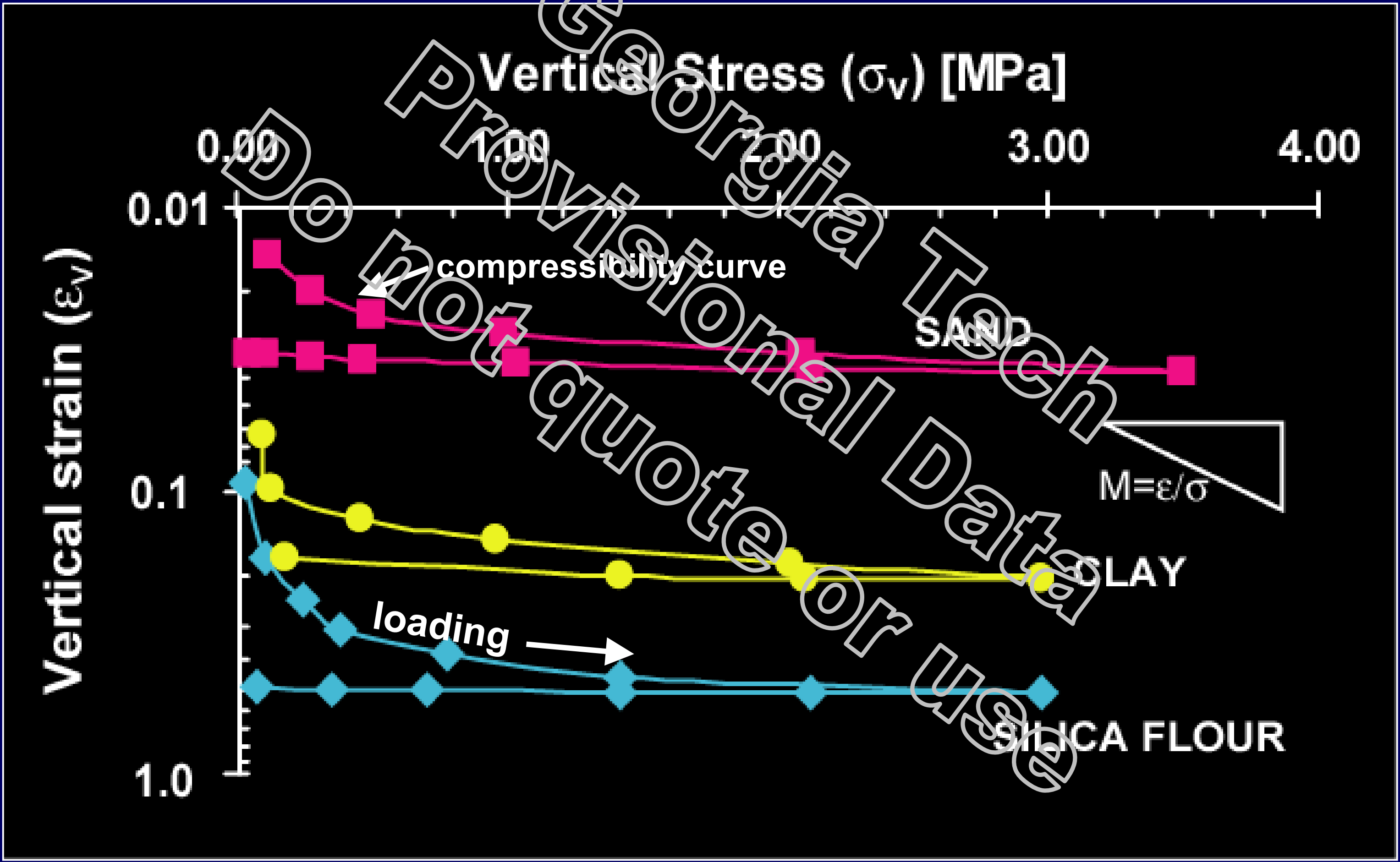



**Constrains bulk moduli of soils after hydrate has formed & dissociated (100%)**

*Mechanical Properties*

# Zero-Lateral Strain Loading

**(constrained modulus M)**





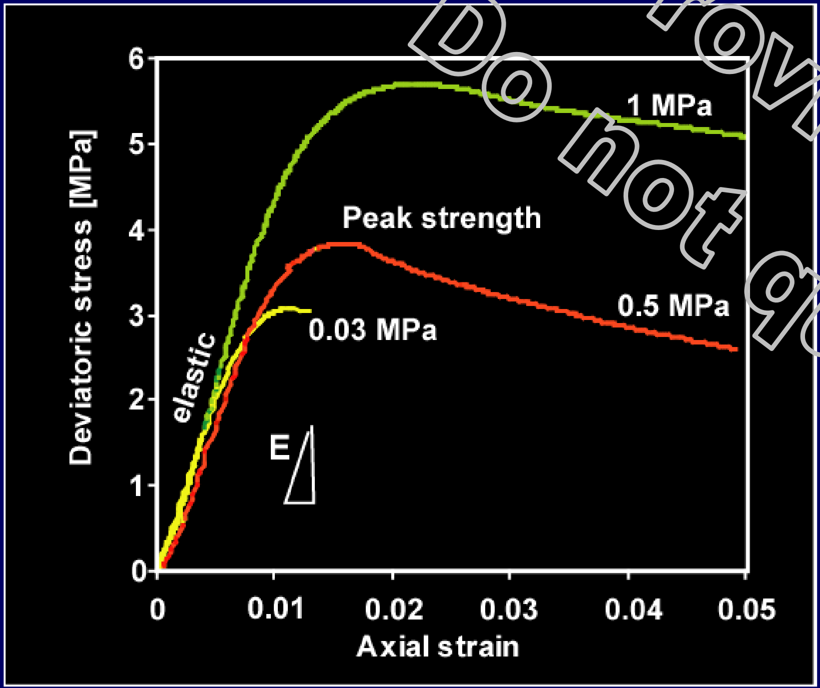
Differences in non-recoverable strain after formation/dissociation of hydrate

T

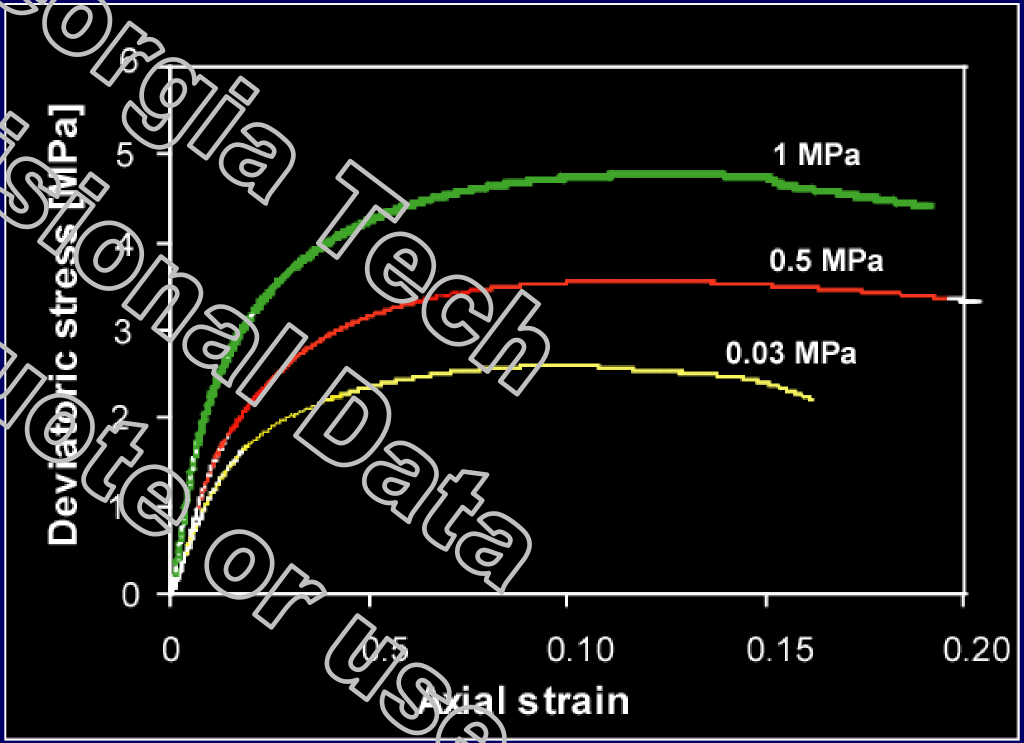
*Mechanical Properties*

# Stress-Strain Path

## (Young's modulus E)




Sand + 50% hydrate



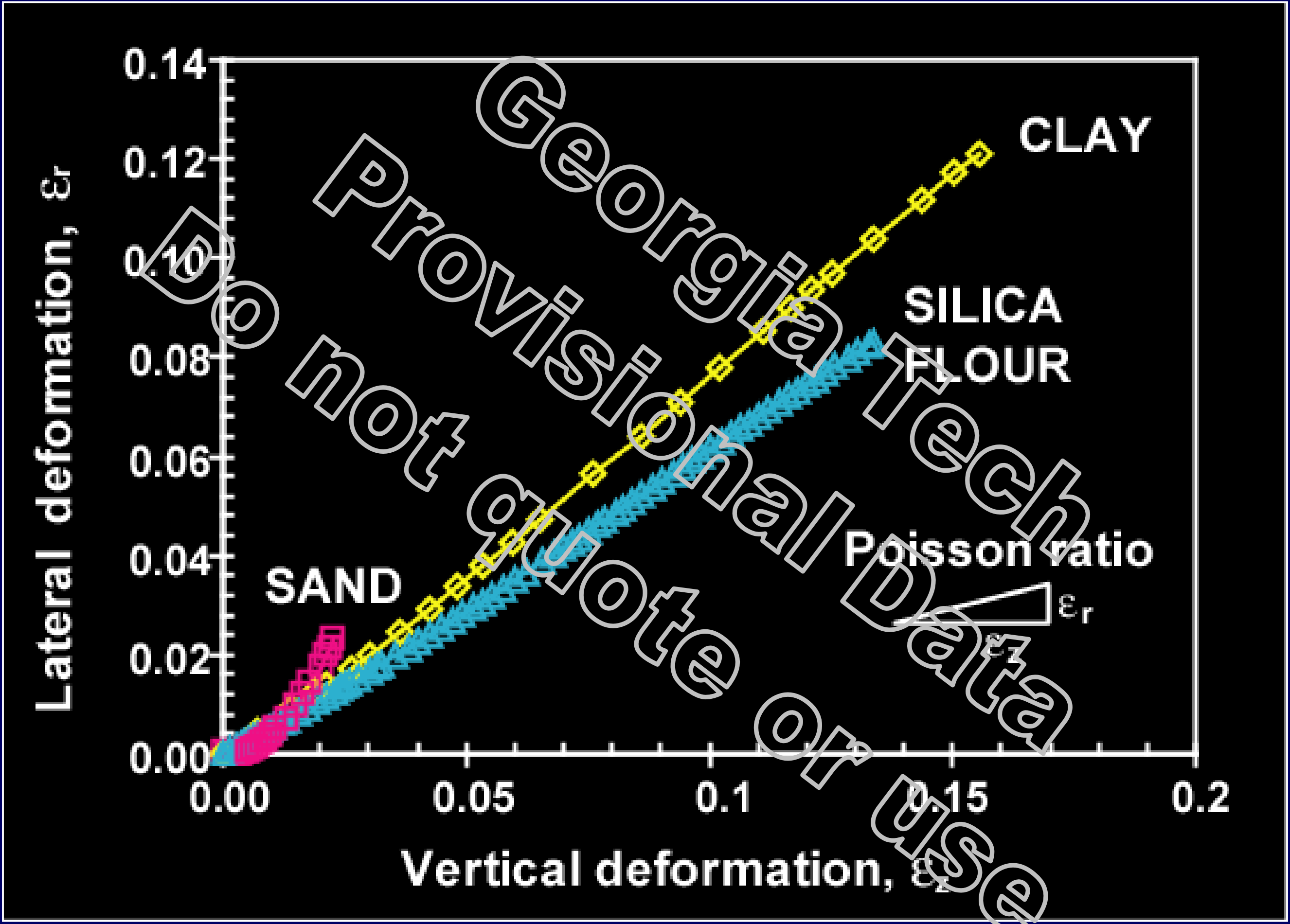

Silica flour + 50% hydrate



**Undrained, elastoplastic deformation**

*Mechanical Properties*

# Poisson Ratio





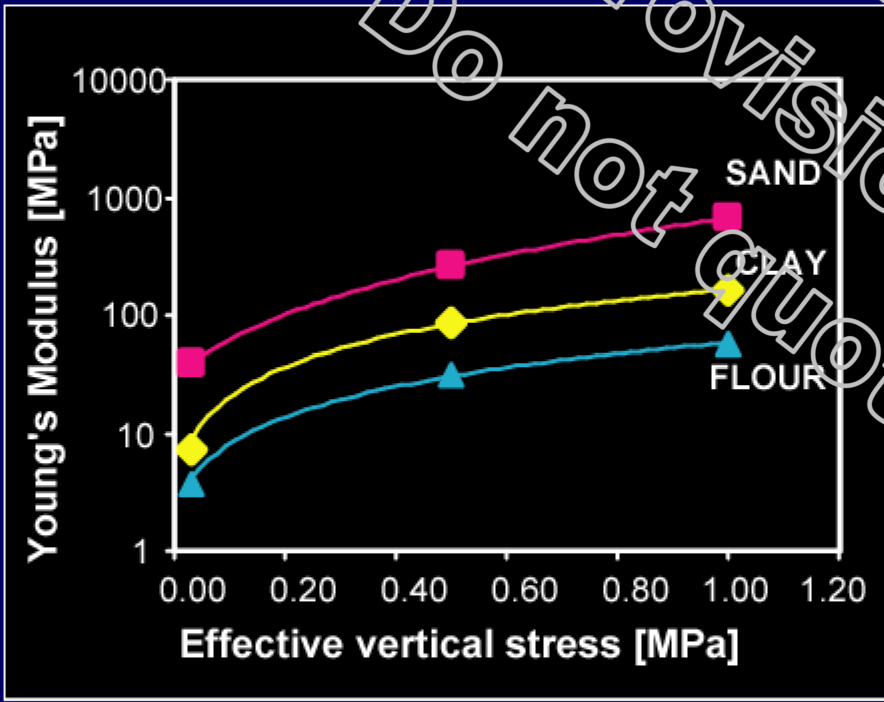

Poisson ratio greater than 0.5, as is common in dilatant soil

*Mechanical Properties*

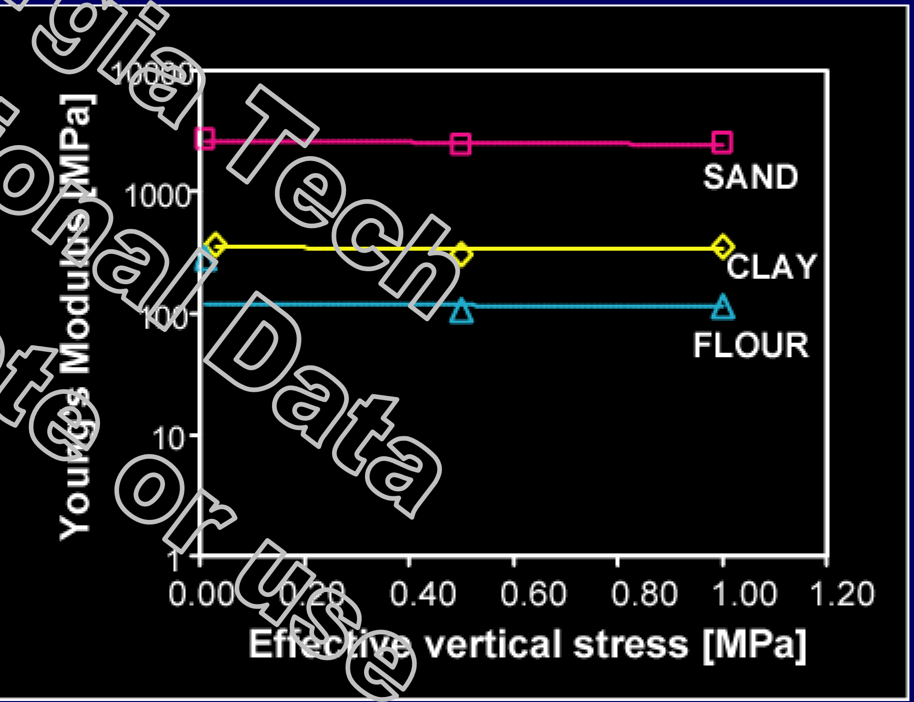
# Young's Modulus (E)



**Sediment and Water**



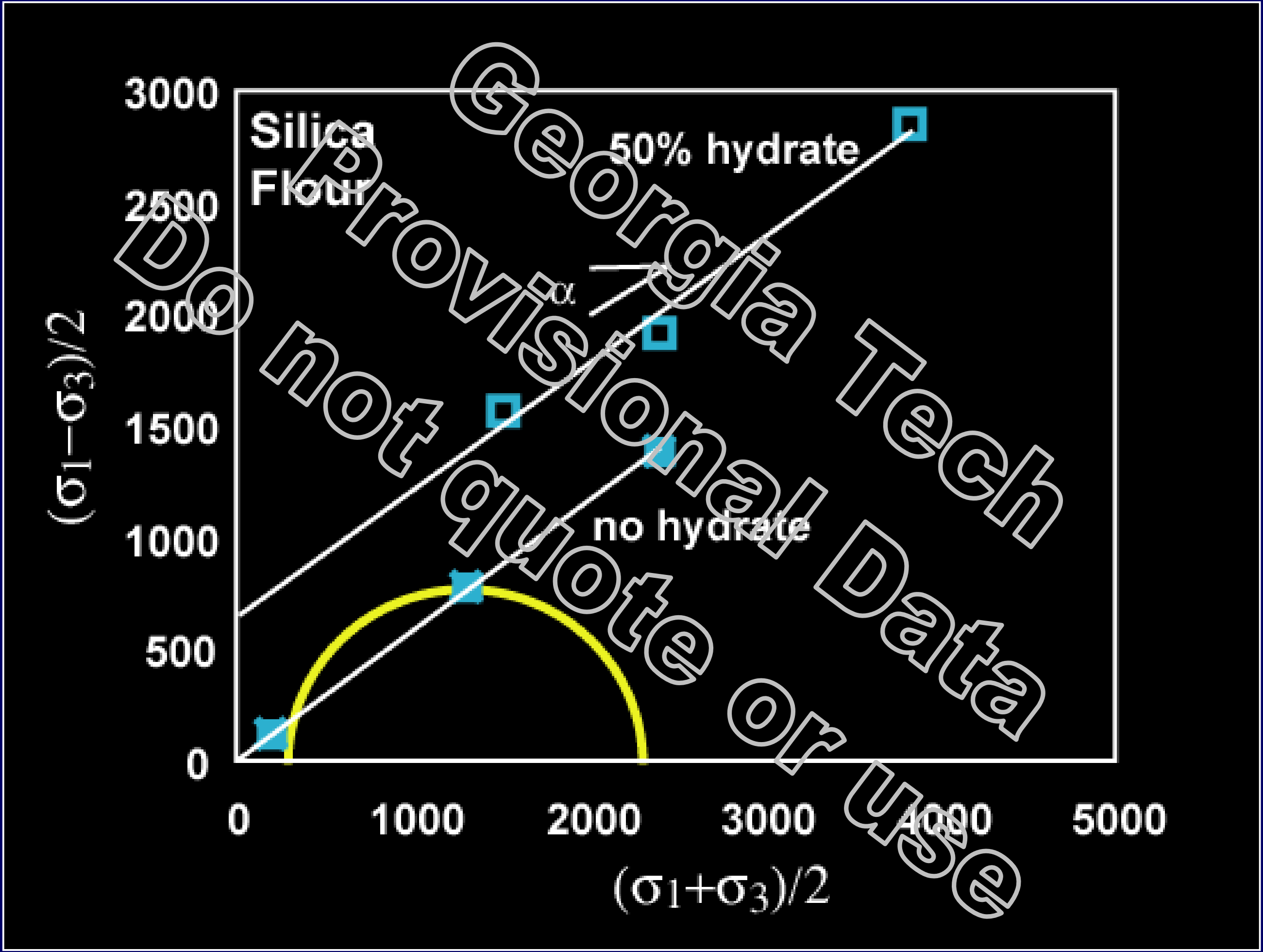

**Sediment and 50% Hydrate**




Once hydrate has formed, high-strain elastic properties remain constant

*Mechanical Properties*

# Mohr-Coulomb failure criterion



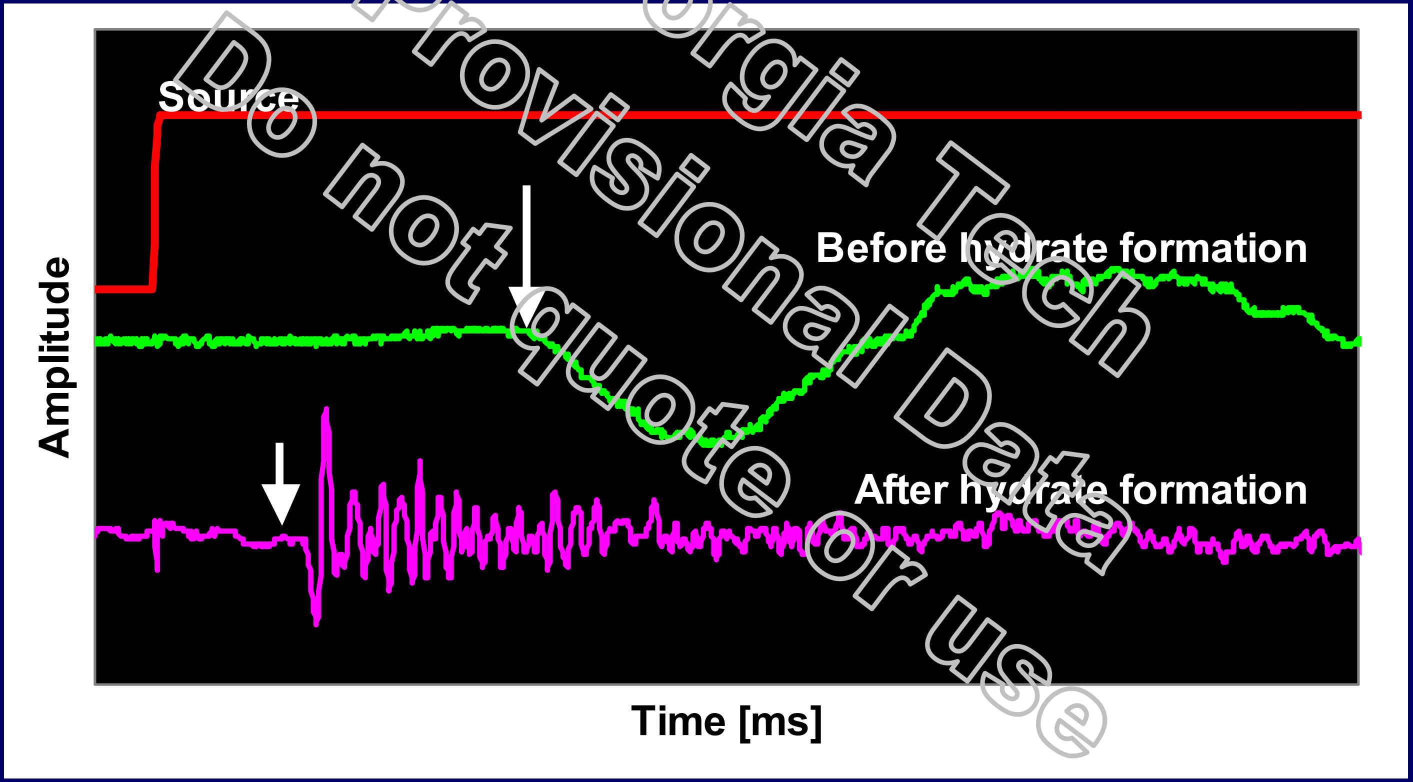



**Hydrate affects cohesion and frictional properties**

# Mechanical Properties

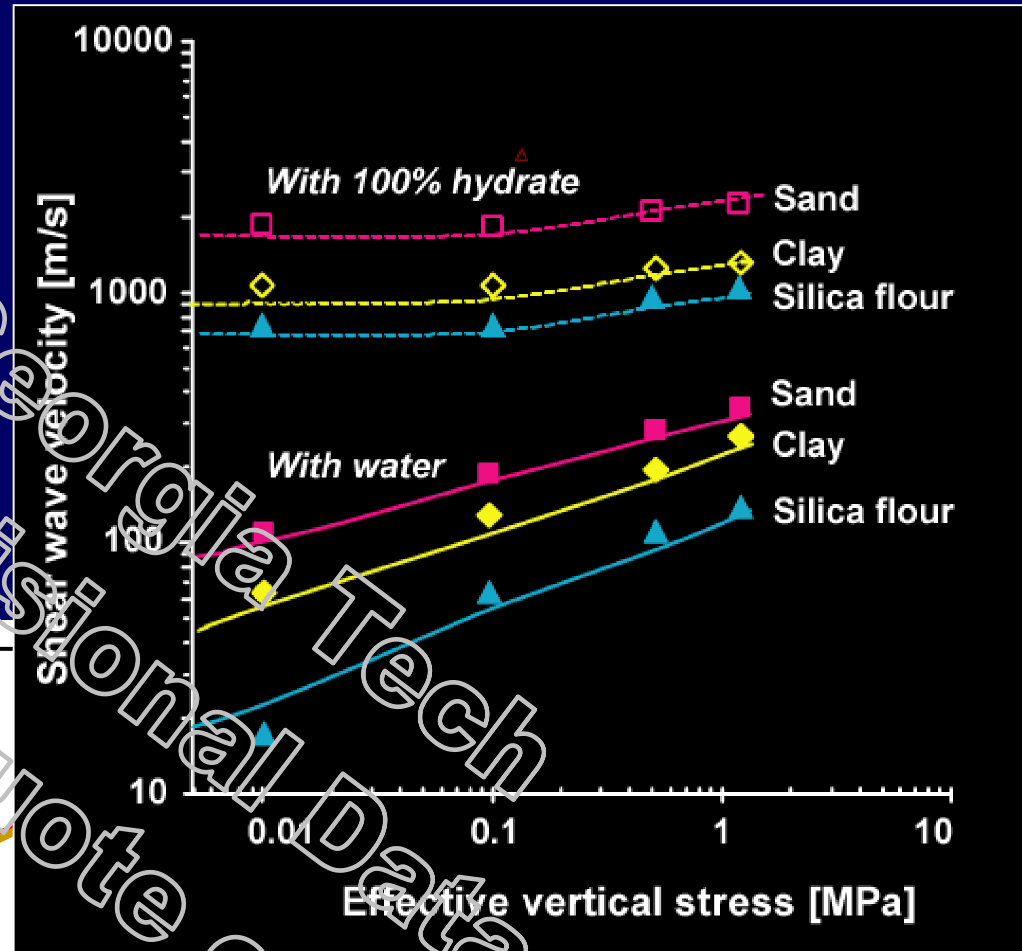
**Small strain: deformation can be related to seismic properties and monitored by seismic waves**

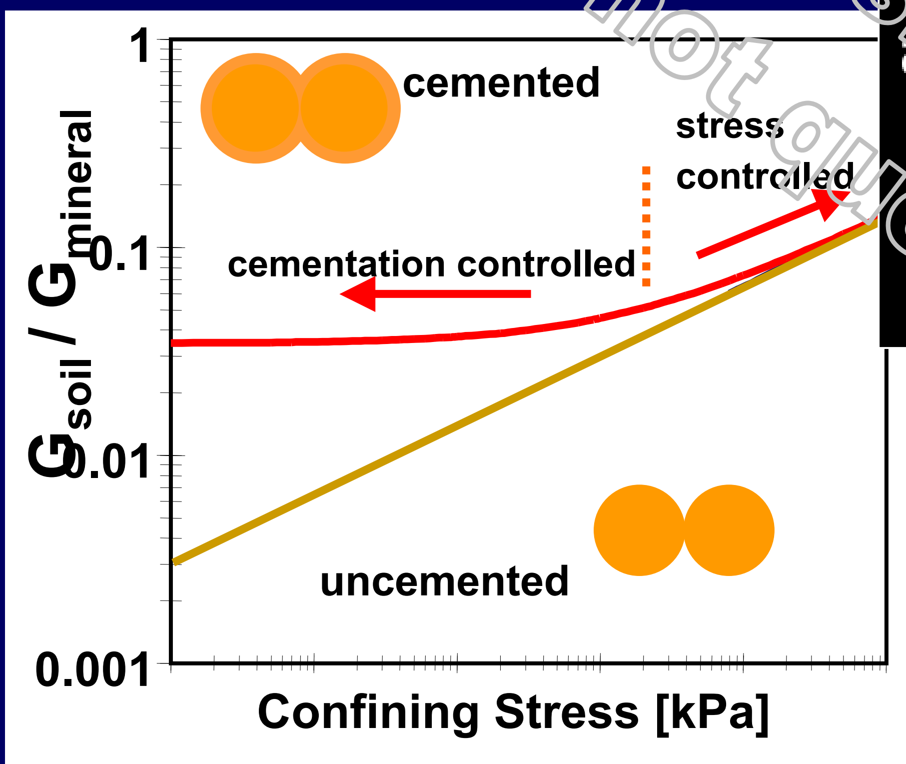
**Typical Shear Waveform**



*Mechanical Properties*

# Shear Stiffness



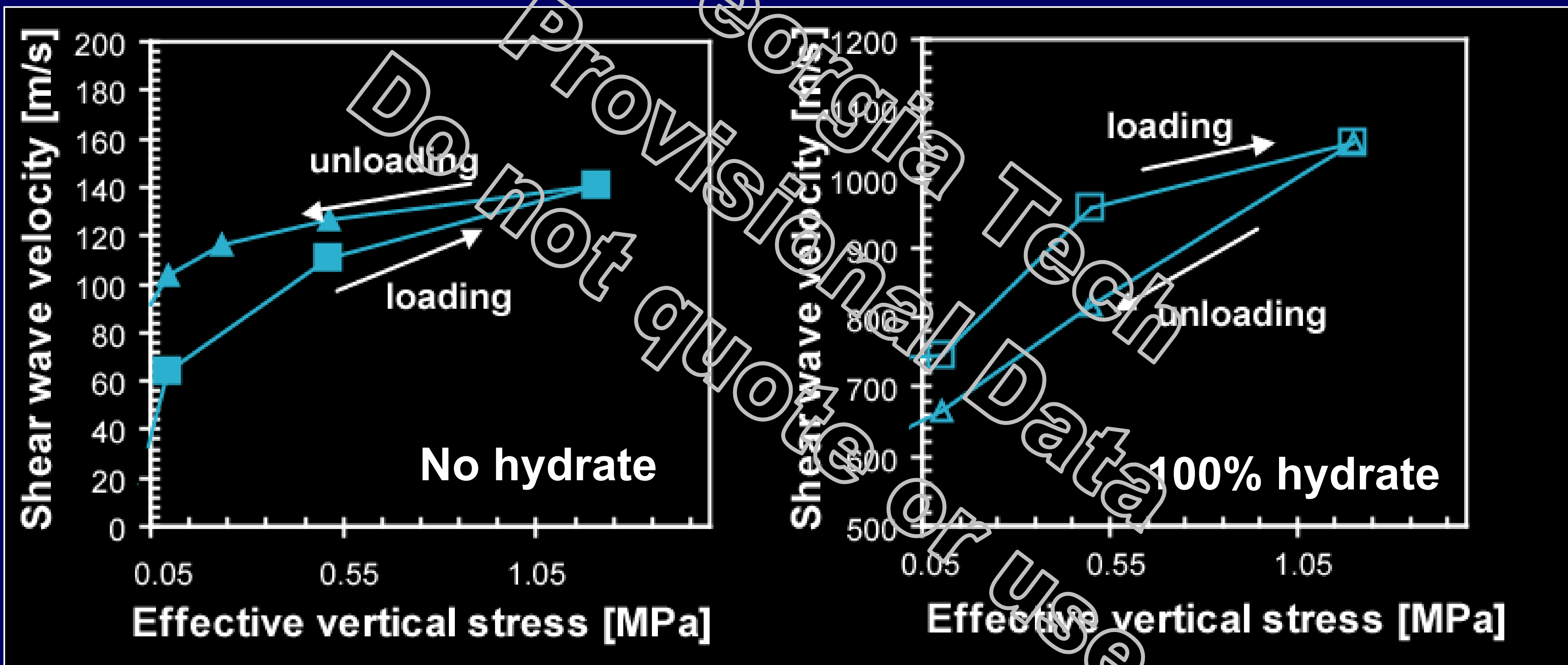



*Mechanical Properties*

# Loading and Unloading Cycles

**Relevant for seafloor sampling**

**Silica flour**



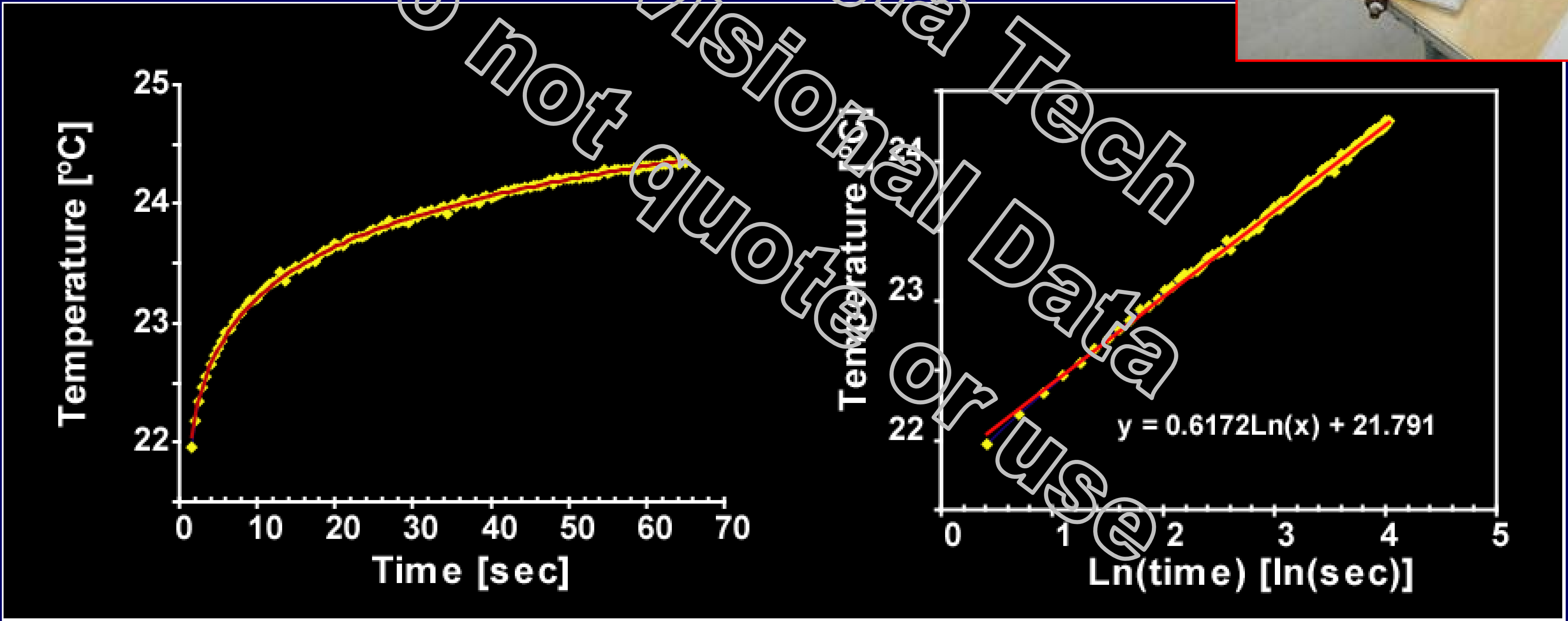



**Hydrate-bearing sediment behaves like a cemented soil**

*Thermal Properties*

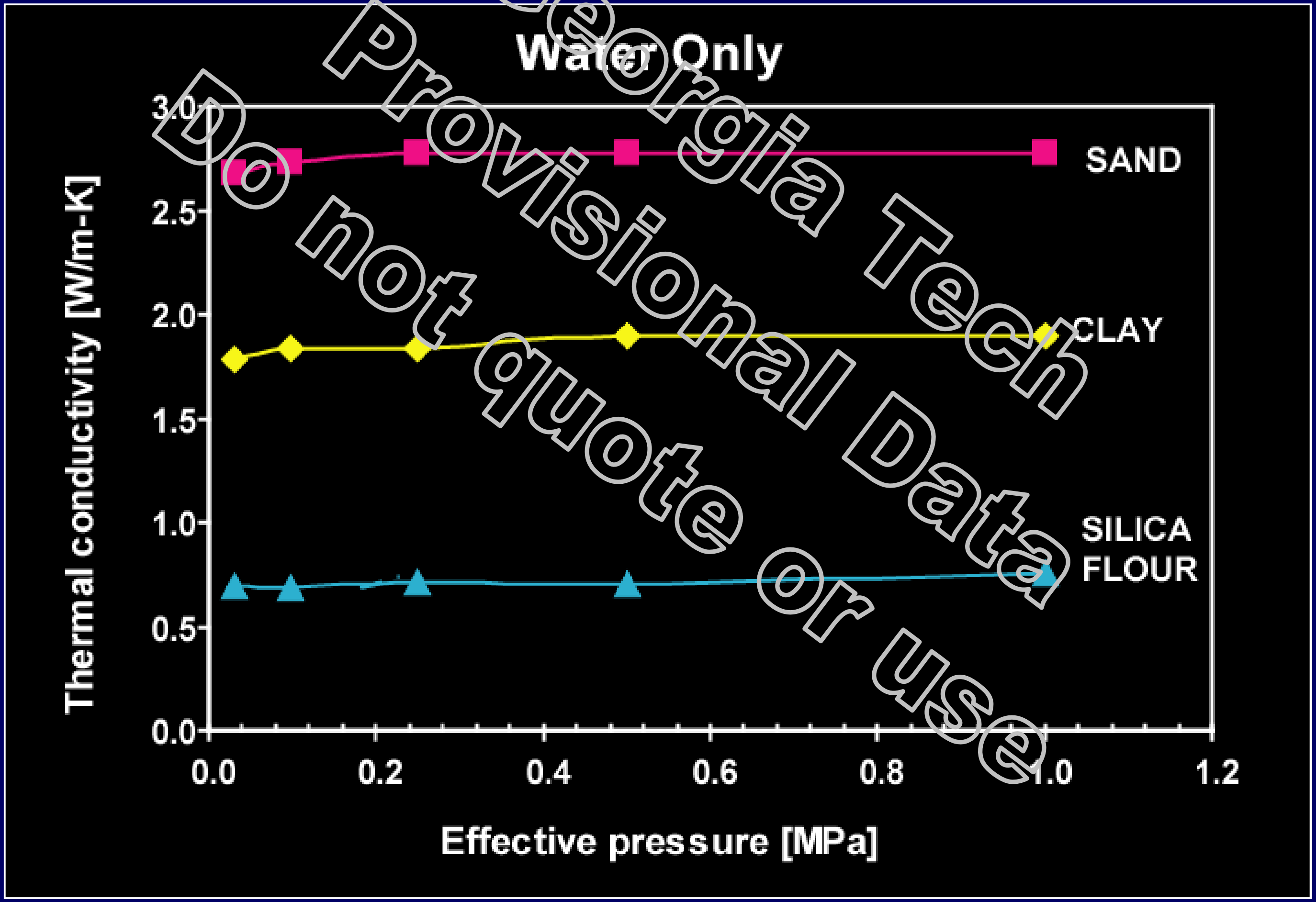
# Thermal conductivity

**Raw data**



*Thermal Properties*

# Thermal conductivity (baseline)

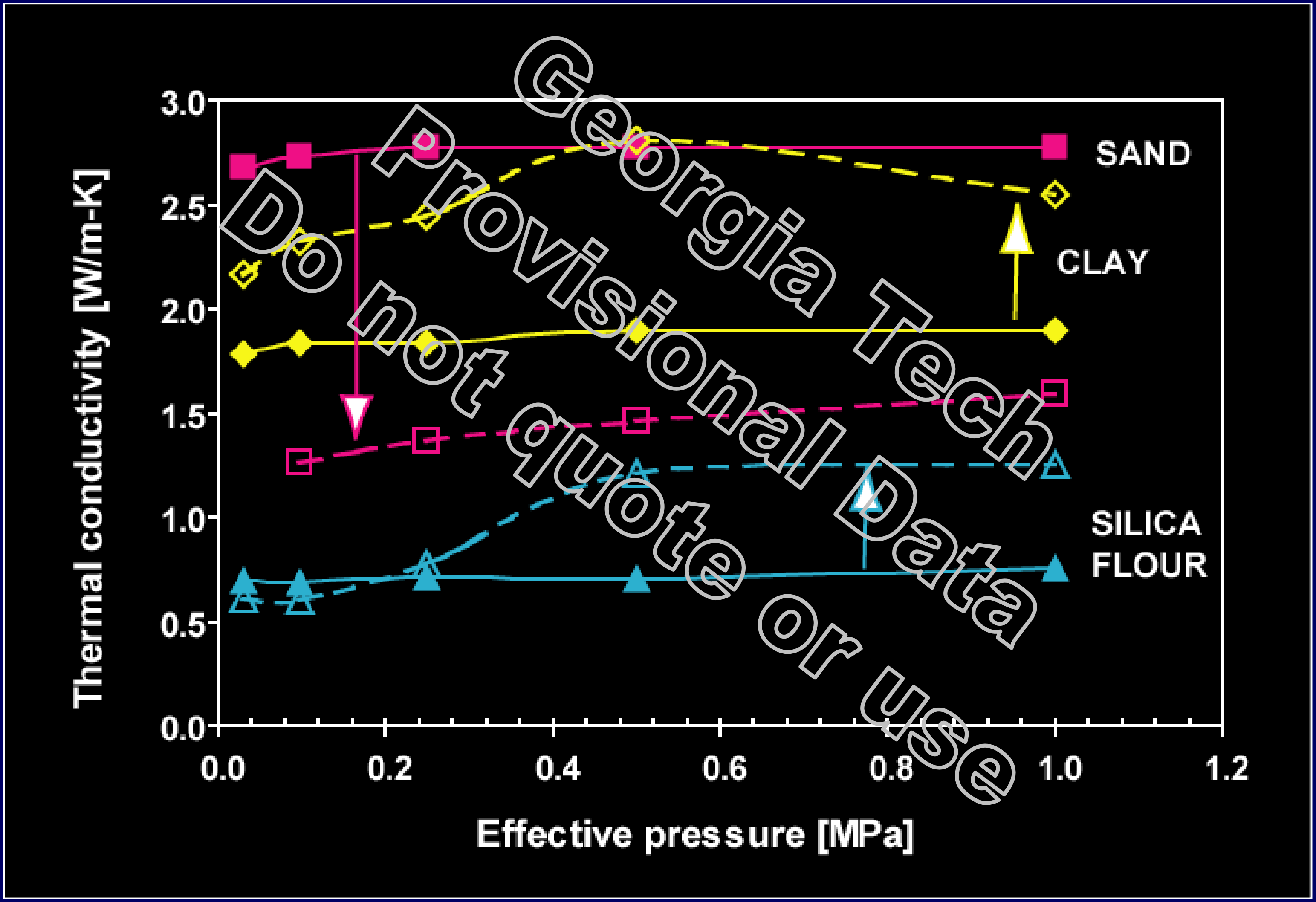





**Thermal conductivity not dependent on pressure**

*Thermal Properties*

# Thermal conductivity (with hydrate)

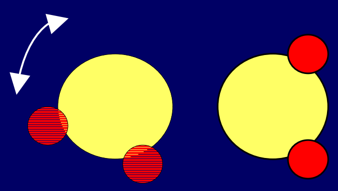



**Complex impact of hydrate formation on bulk thermal conductivity**

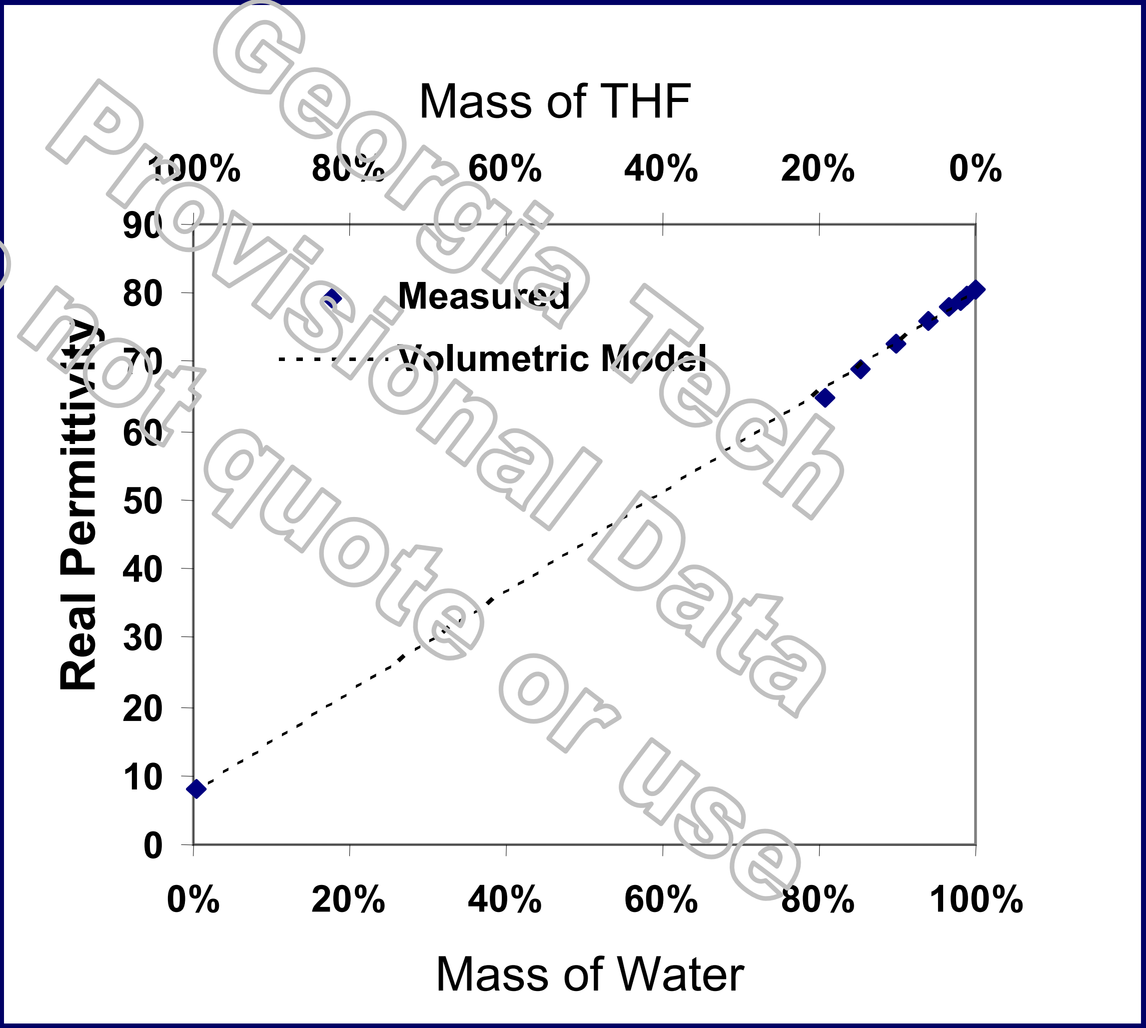
*Electrical Properties*

# Real Permittivity Water-THF mixtures at 200MHz

ORIENTATIONAL



$t = 9\times10^{12}$ s
(Microwave – water)



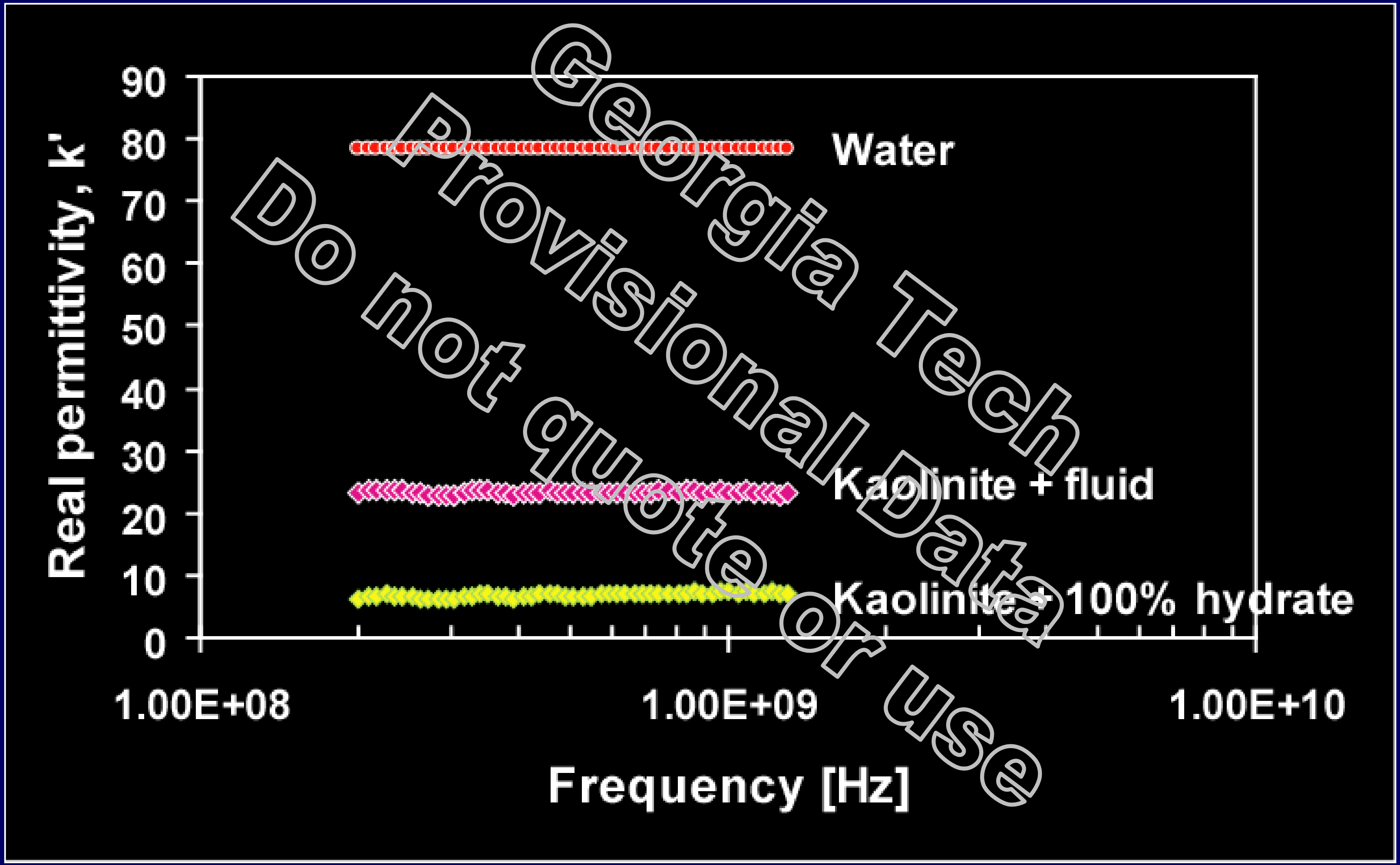



**Permittivity is a measure of the degree of polarizability of pore-filling fluid**

O

*Electrical Properties*

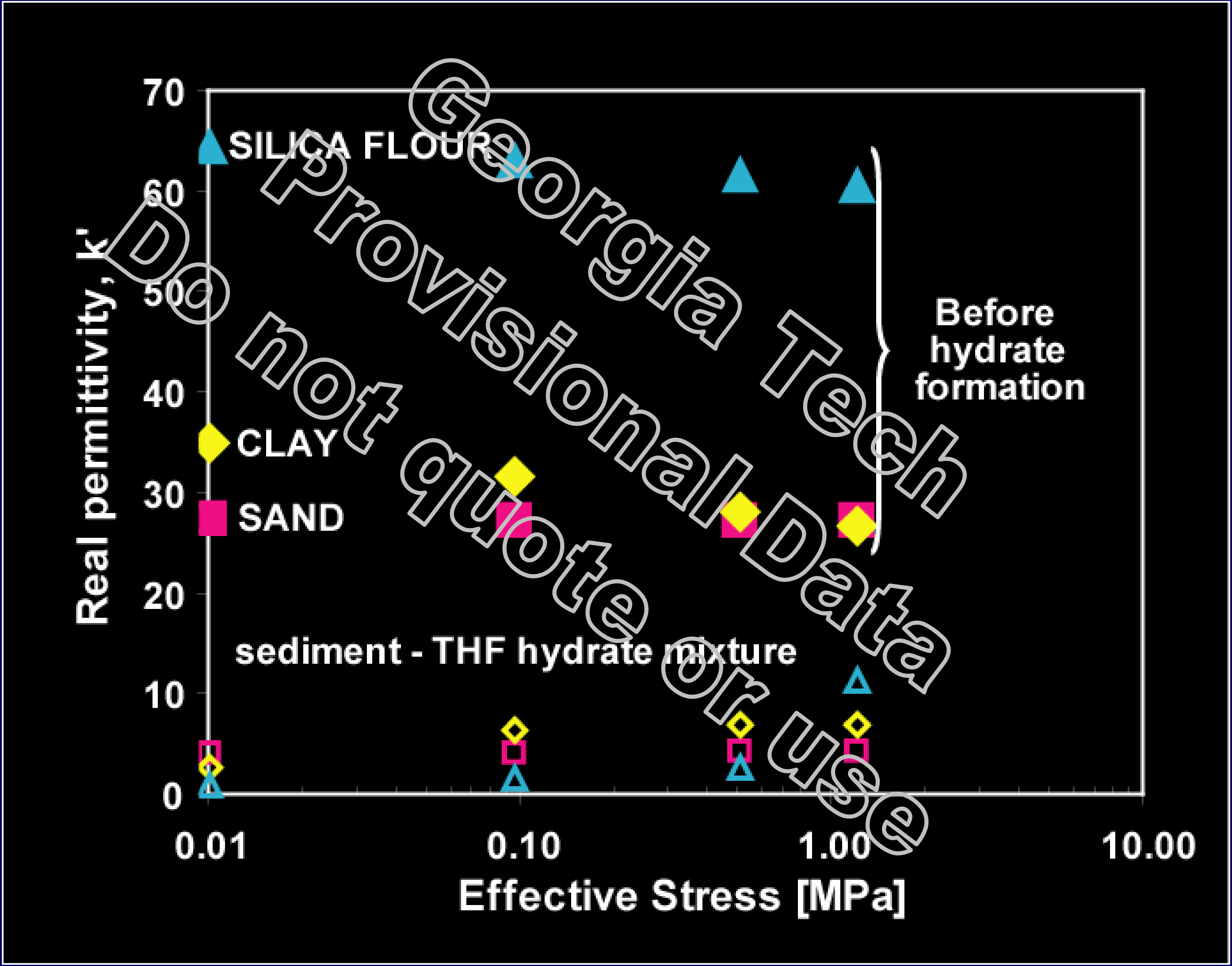
# Real Permittivity




**Permittivity is independent of frequency. Note impact of hydrate formation.**

*Electrical Properties*

# Real Permittivity

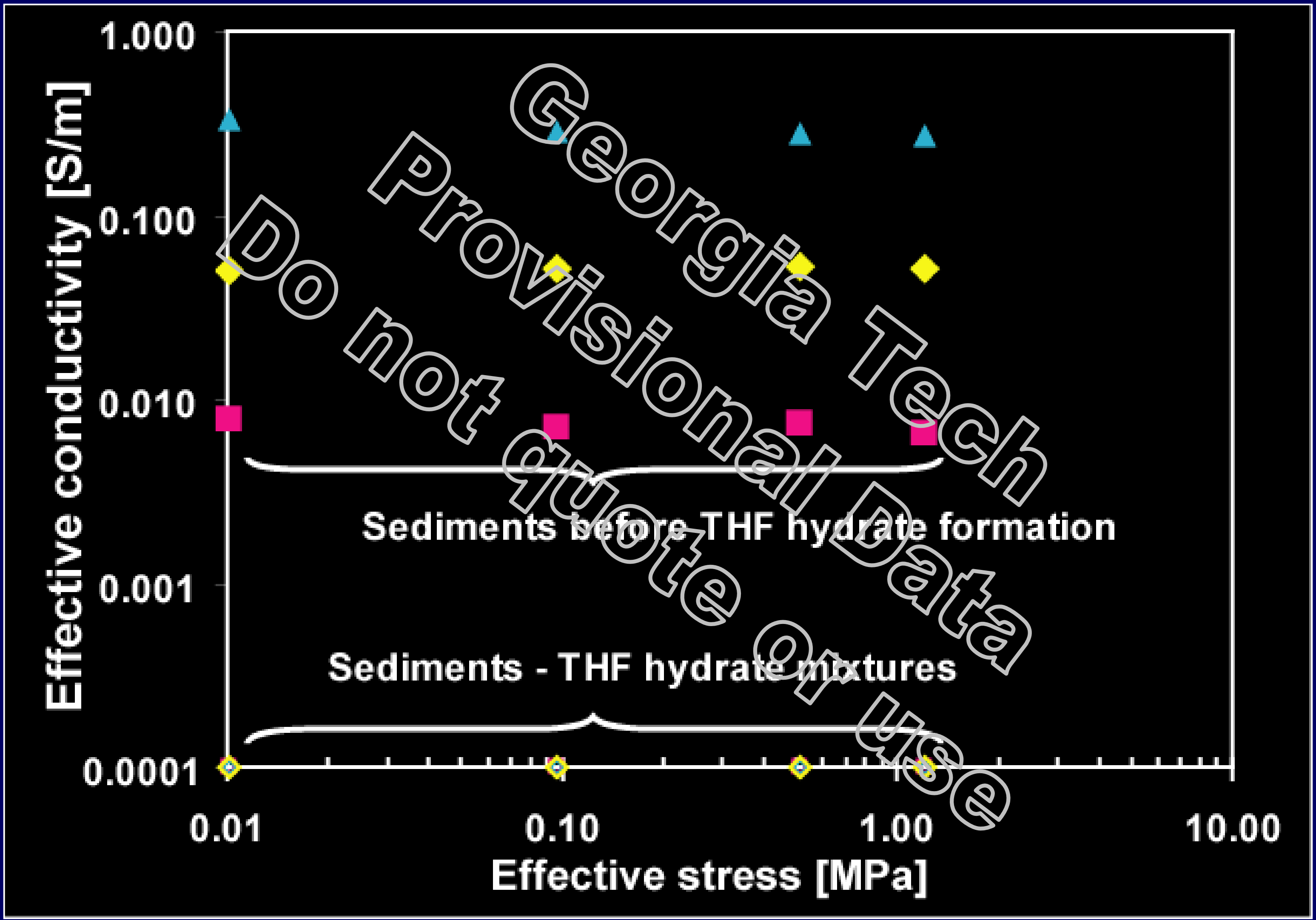




**Hydrate formation sharply decreases dielectric permittivity**

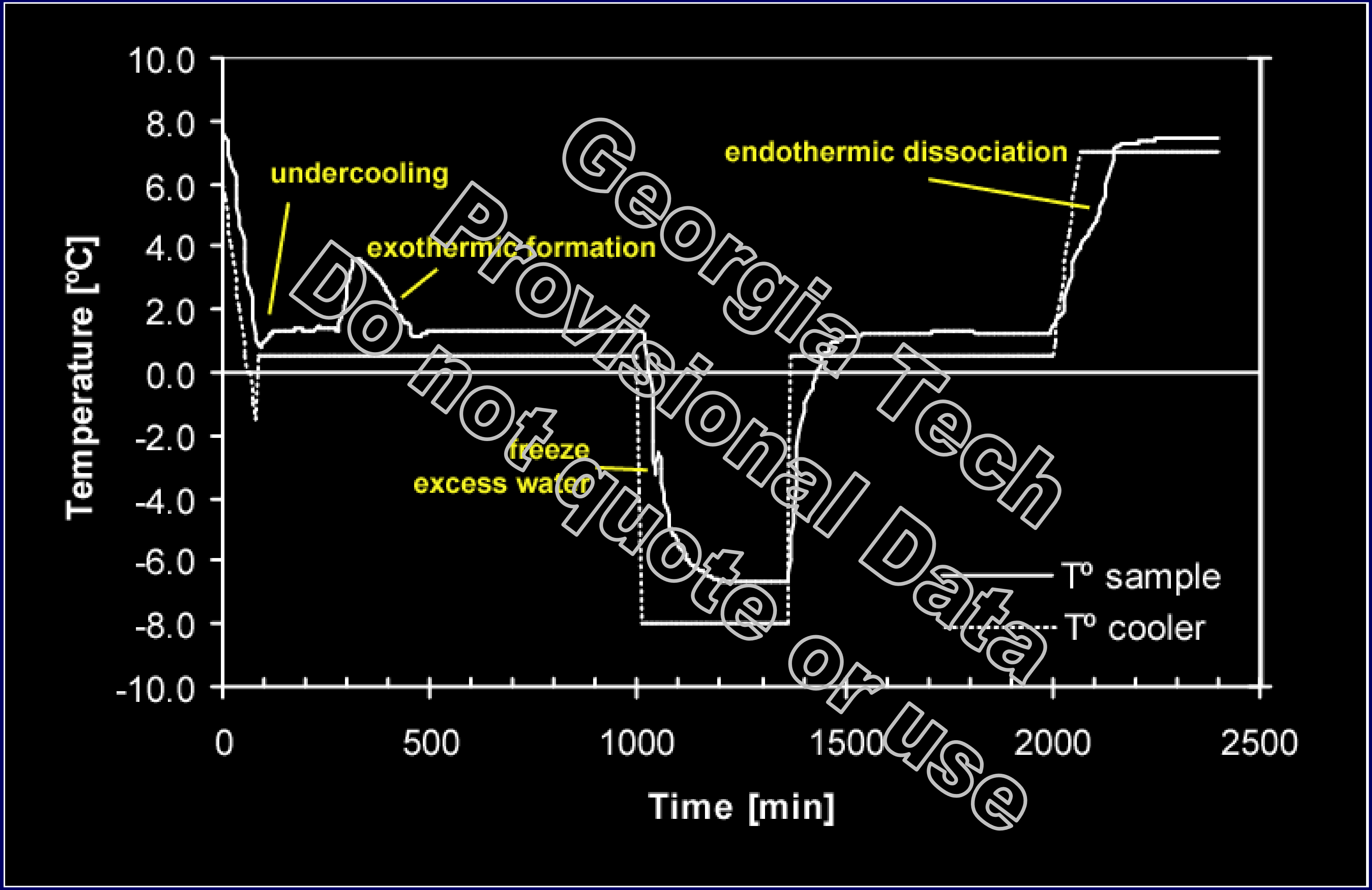
*Electrical Properties*

# Conductivity



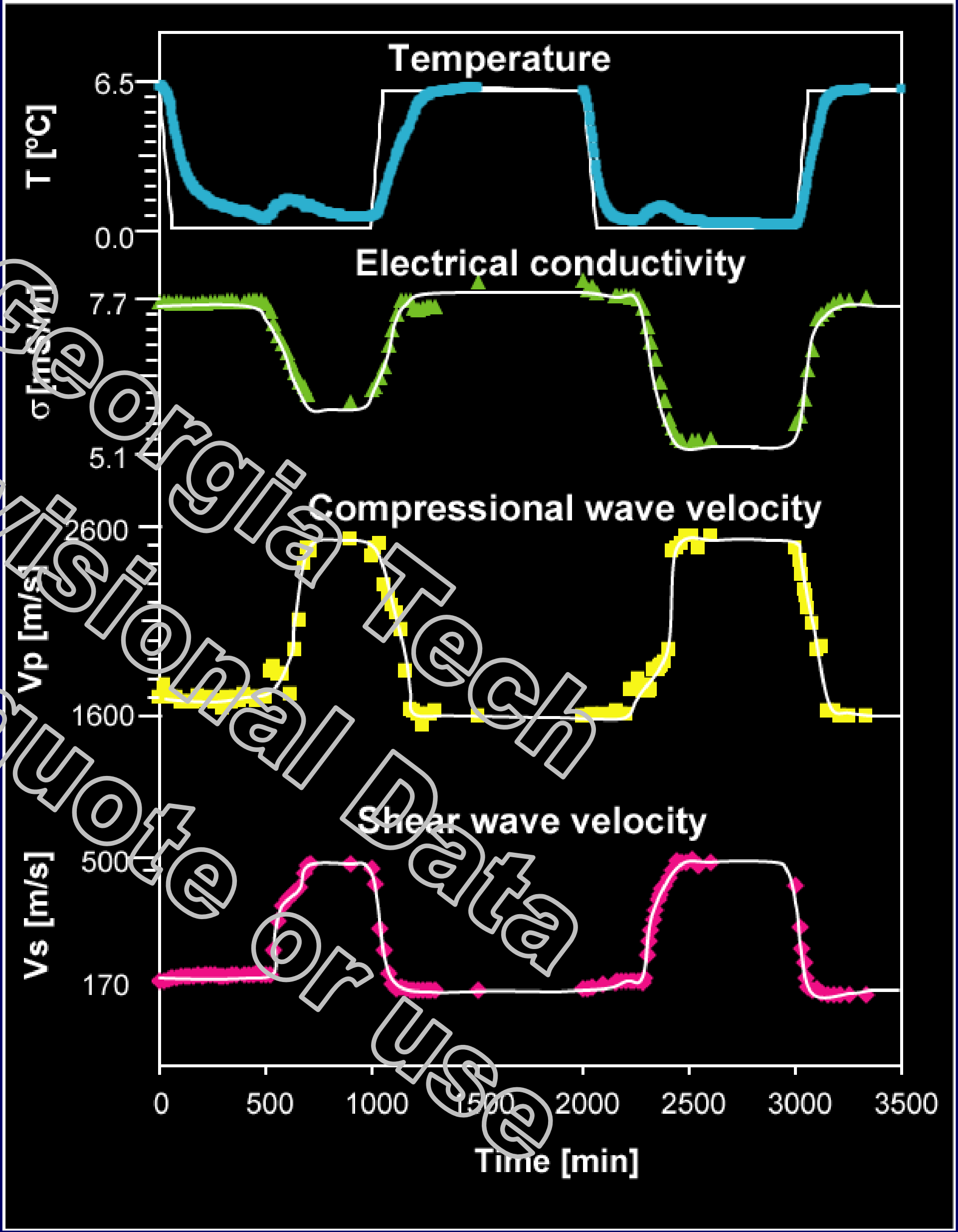

Hydrate formation lowers electrical conductivity to below detection limit

# Phase Transformation Studies



# DELETED SLIDES (LENSING)

# Process Monitoring




**Multi-parameter monitoring during phase transformations and multiple cycles**



Francisca, Santamarina, and Ruppel (submitted, 2003)

# DELETED SLIDES

| Grain size | | % Hydrate | Pressure | Mechanical Large/intermediate strain | | | | | | | | | Thermal | | Mechanical Low strain | | | | Electrical | | Distribution | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SAND | 100 | 0% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | | |
| | | 50% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| | | 100% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | S | in |
| SILT | 20 | 0% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | | |
| | | 50% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| | | 100% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| CLAY | 1 | 0% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | | O | O | O | O | C | | |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | | |
| | | 50% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | O | O | O | O | O | C | S | in |
| | | 100% | 0.01 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 0.50 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 1.00 | T | T | T | T | T | T | T | T | T | O | O | O | O | O | O | O | C | S | in |
| | | | 2.00 | | | | | | | | | | O | O | | O | O | O | O | C | S | in |

# SUMMARY

- Shown < 20% of results acquired to date
- Significant analysis required to place results in context
- Processes
  - Hydrate formation initiates at particle surfaces
  - Loading-unloading cycles reveal cementation behavior
  - P- and S-waves monitor phase transformation in lab and possibly during core recovery
  - Lensing under specific laboratory conditions
- Properties
  - Mechanical: Hydrate-bearing sediments behave like cemented soils (strength parameters, moduli, P- and S-wave) and hydrate impact is similar at both large and small strains
  - Electrical: Hydrate radically lowers both real permittivity and conductivity
  - Thermal: Hydrate increases pressure-dependence of conductivity