

# Surface Controls on Storage, Stiffness, and Transport Properties of Rocks

Manika Prasad, Colorado School of Mines

(presenting work of Kumar, Livo, Ou, Panfiloff, Drs. Niu, Saidian, Zargari, Kuila, Rahman)



# OUTLINE

- Fluids effects on elastic properties
- Selective sorption of fluids in different components of rocks
- Fluids and CEC effects on dielectric constant
- Specific surface area controls on conductivity
- Clay and Organic Matter Effects on Surface area and CEC
- Specific surface area controls on NMR Surface Relaxivity

# POROSITY IN SOURCE ROCKS

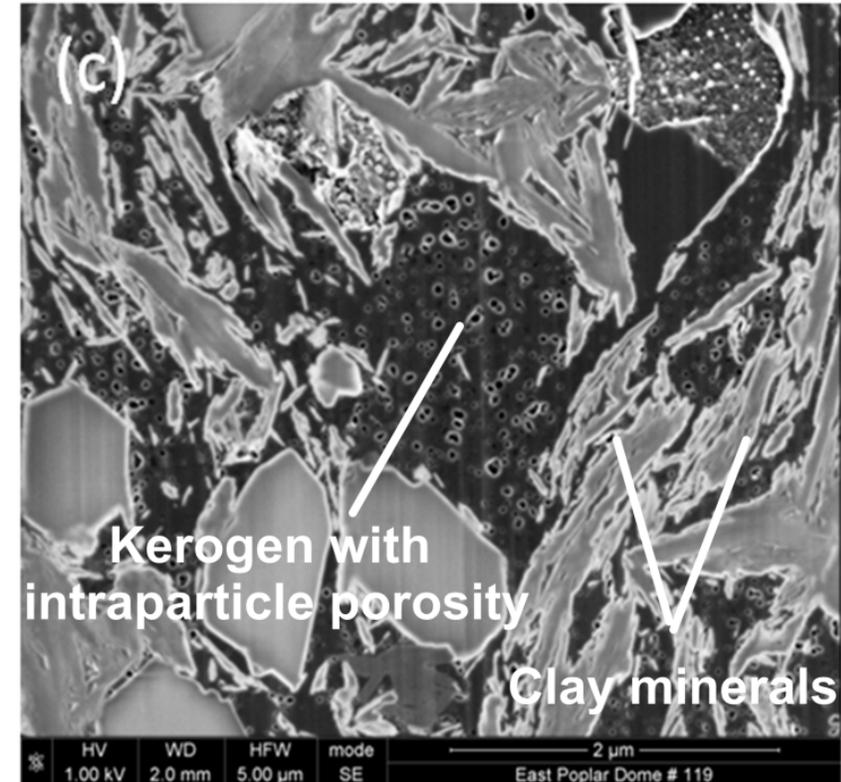
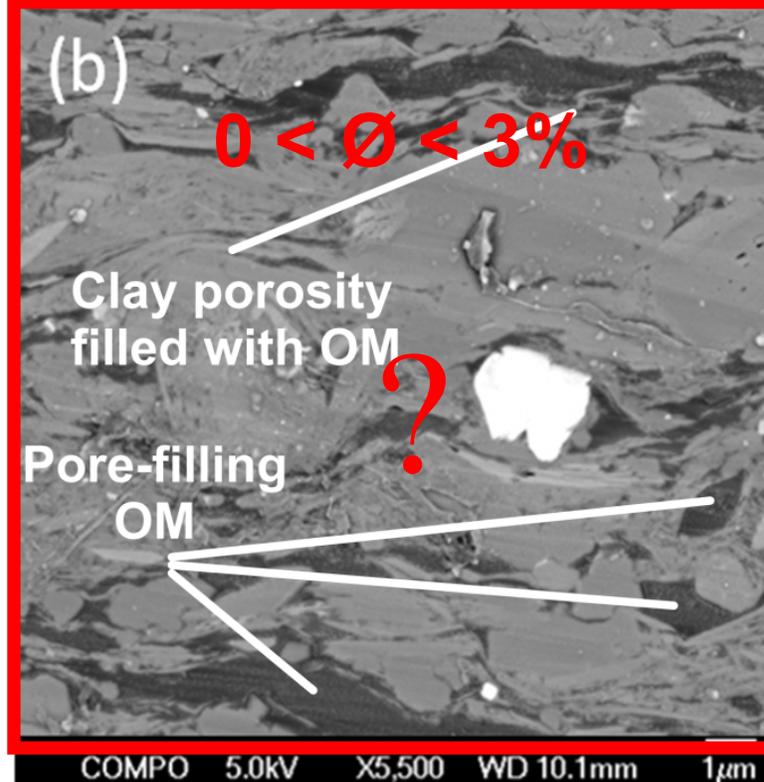
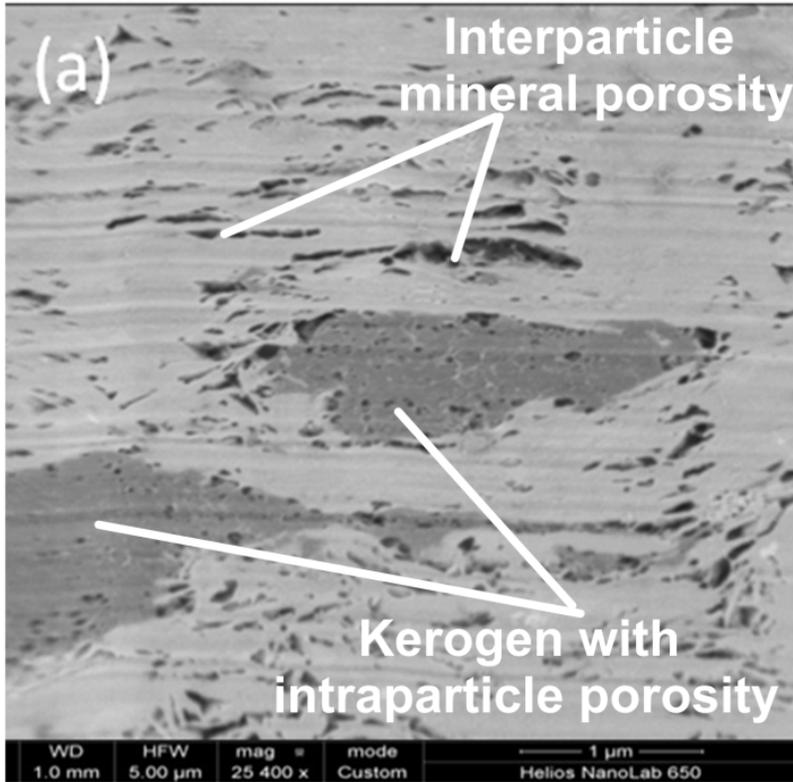
Zargari et al., 2015

Bakken Shales

Immature

Oil window

Gas window



$$R_{o_e} = 0.3$$

$$R_{o_e} = 0.8$$

$$R_{o_e} = 3.0$$

OM= Kerogen + HC + Bitumen

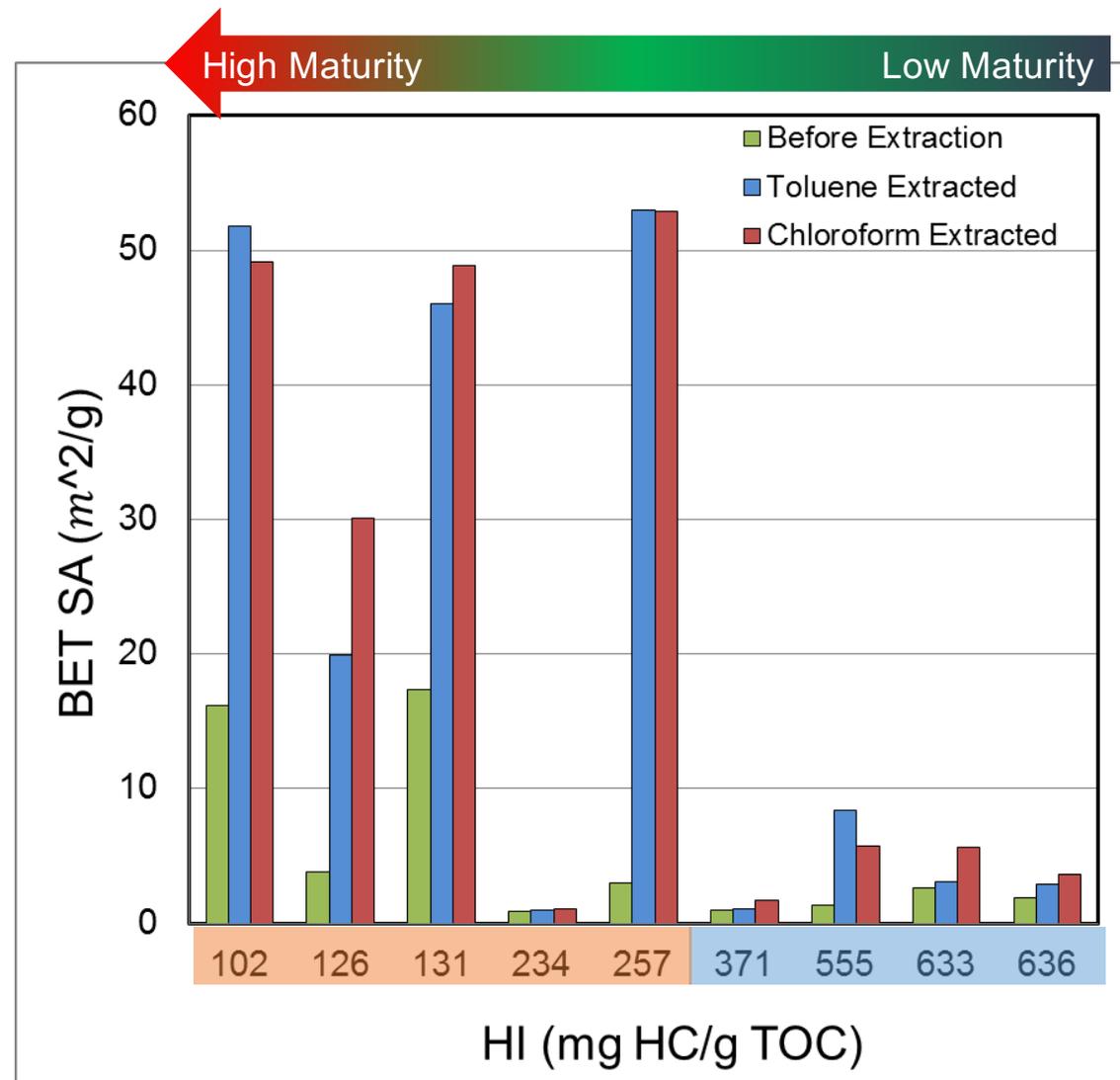
# SURFACE AREA / PORE CHARACTERIZATION

Zargari et al., 2015

## Gain surface area with solvent extraction

Bakken Shale samples were solvent-extracted using toluene and chloroform

Surface Area and Pore Size Distributions measured using N<sub>2</sub> adsorption



BET: Brunauer–Emmett–Teller theory

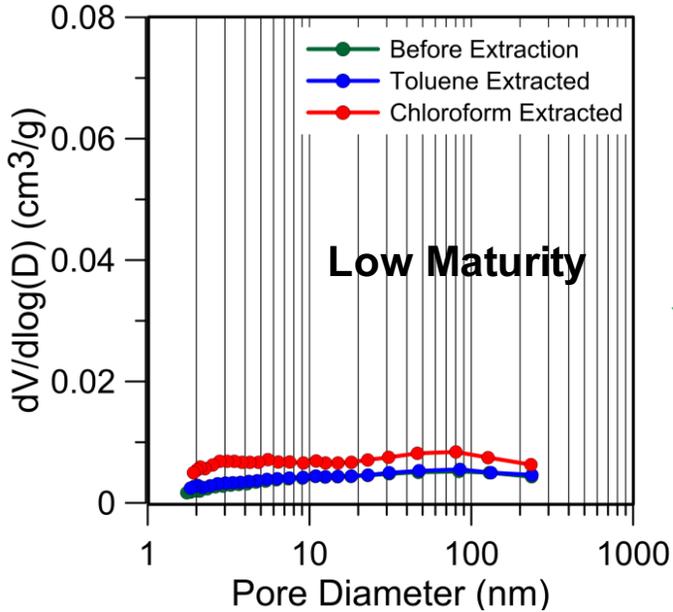
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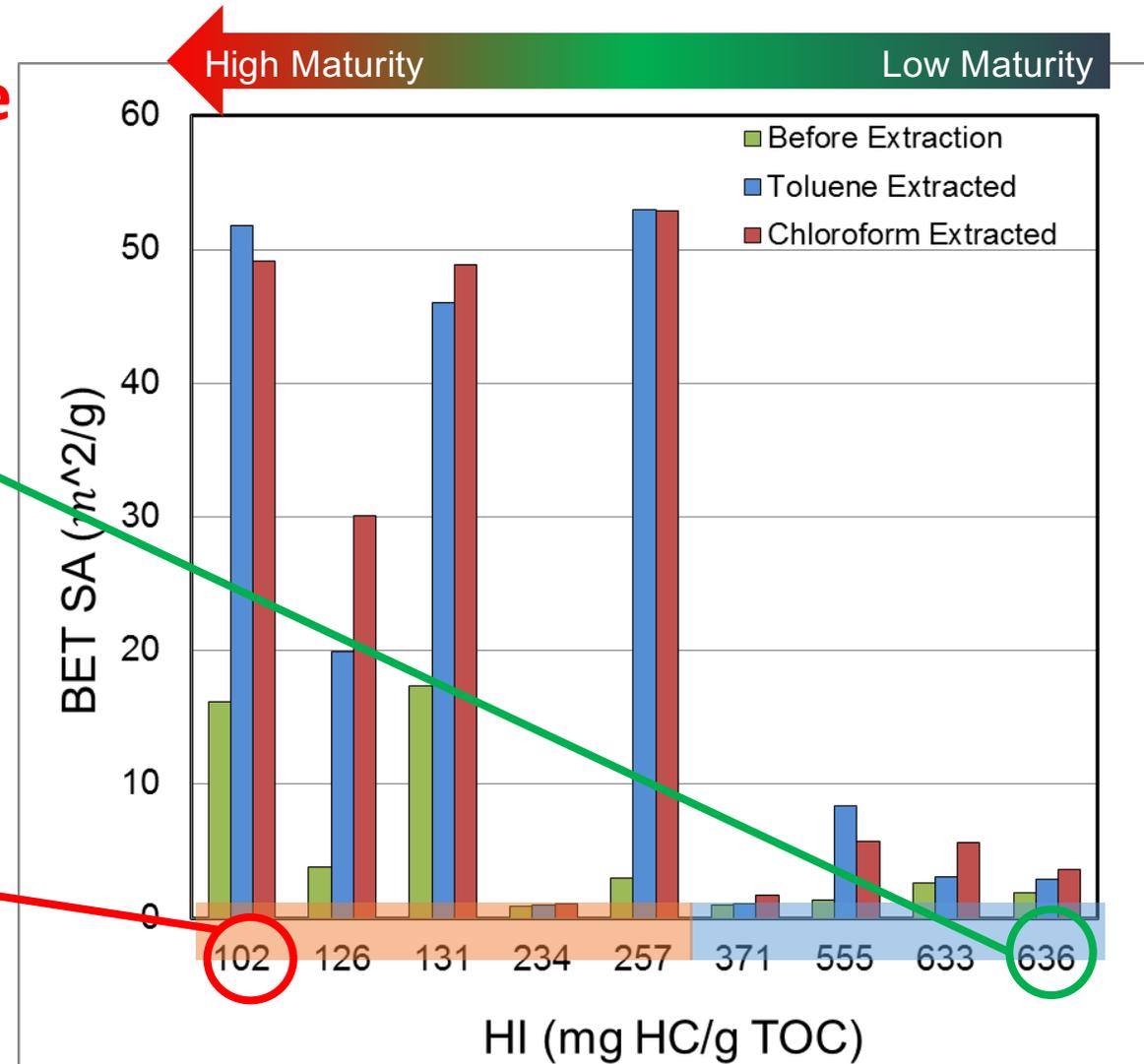
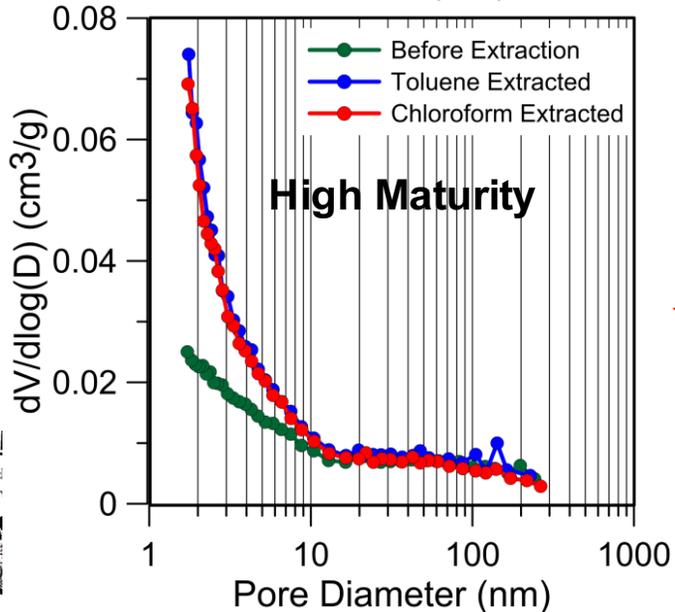
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# PORE SIZE DISTRIBUTION



**Higher maturity shale shows large change**



# NANOMECHANICAL MODULUS: IMMATURE

Zargari et al., 2016

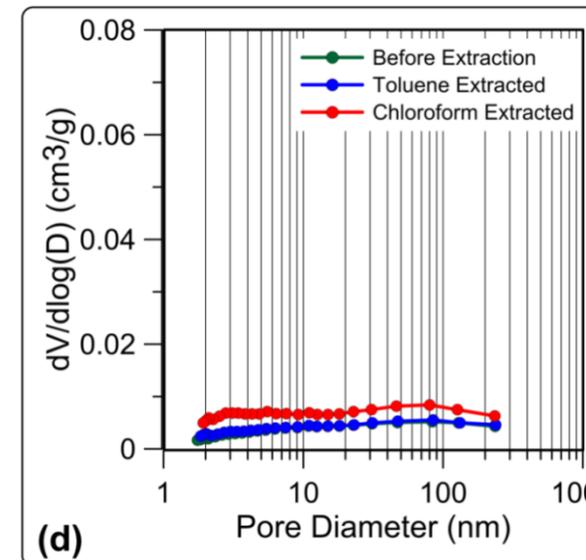
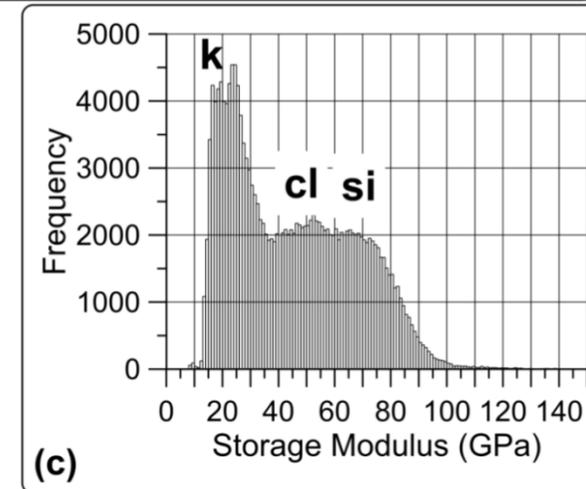
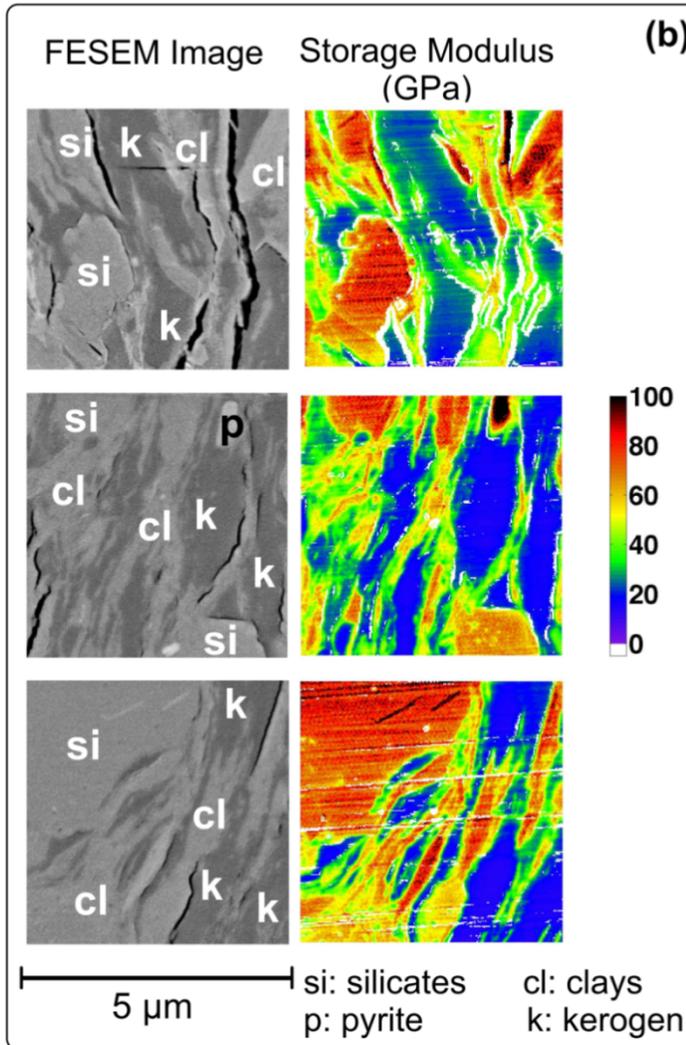
Immature Sample

TOC = 17.7 (wt%)

HI = 633 (mg HC/g TOC)

Max Measured Porosity = 3.7% (a)

Max BET SSA = 5.6 (m<sup>2</sup>/g)



$$E_k = 15 - 20 \text{ GPa}$$

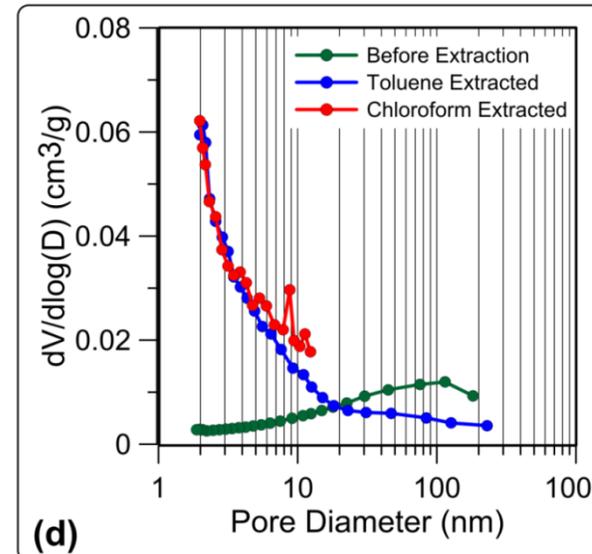
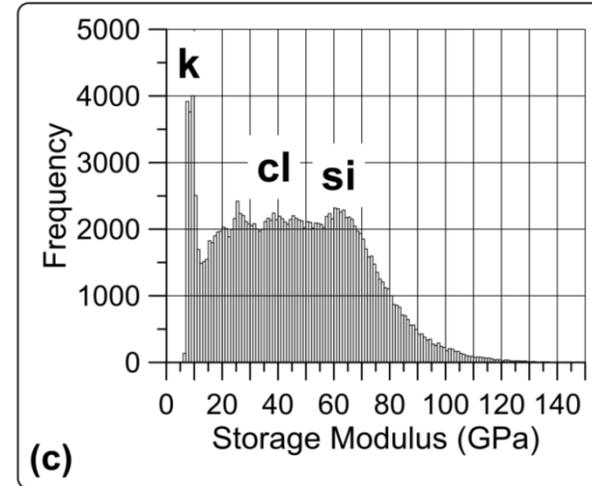
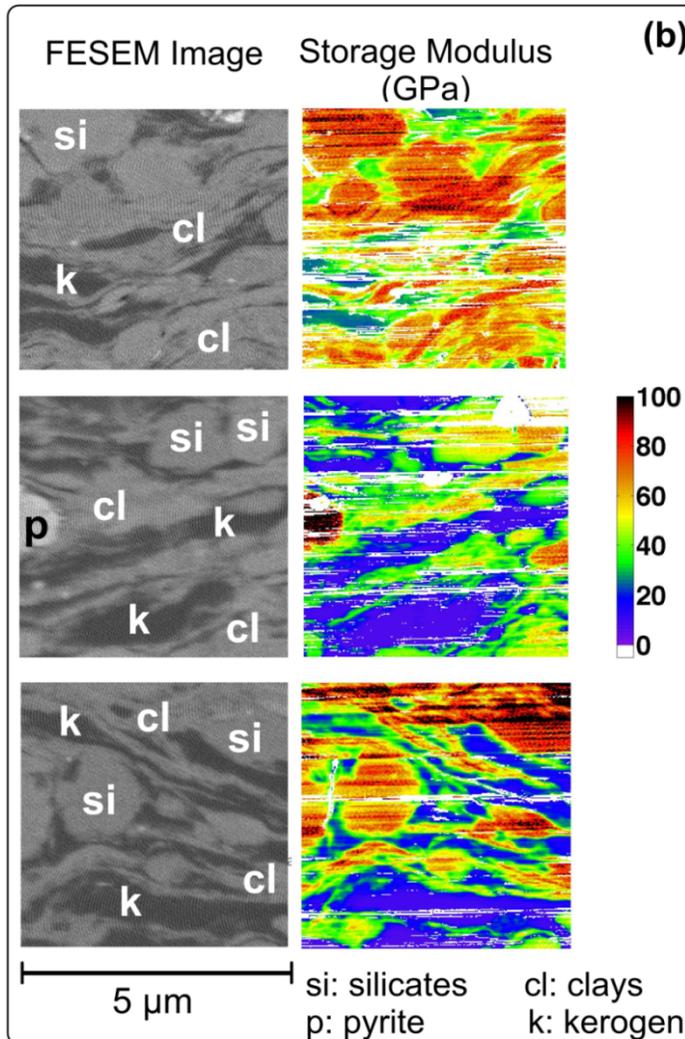
# NANOMECHANICAL MODULUS: OIL WINDOW

Zargari et al., 2016

Oil Window

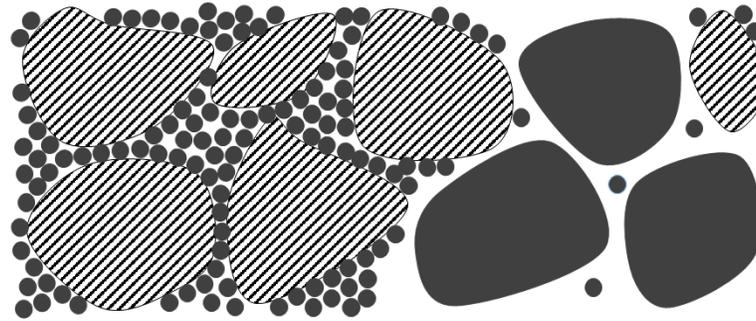
TOC = 21.7 (wt%)  
 HI = 257 (mg HC/g TOC)

Max Measured Porosity = 6.9%  
 Max BET SSA = 53 (m<sup>2</sup>/g)



$$E_k = 7 - 10 \text{ GPa}$$

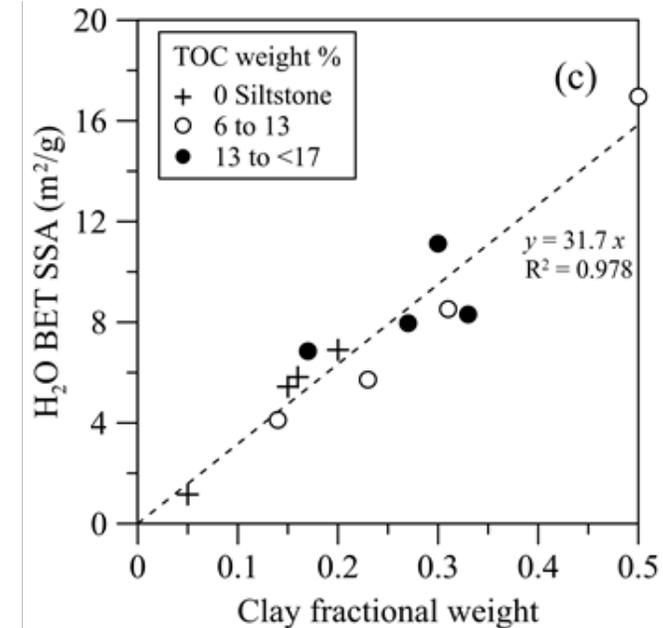
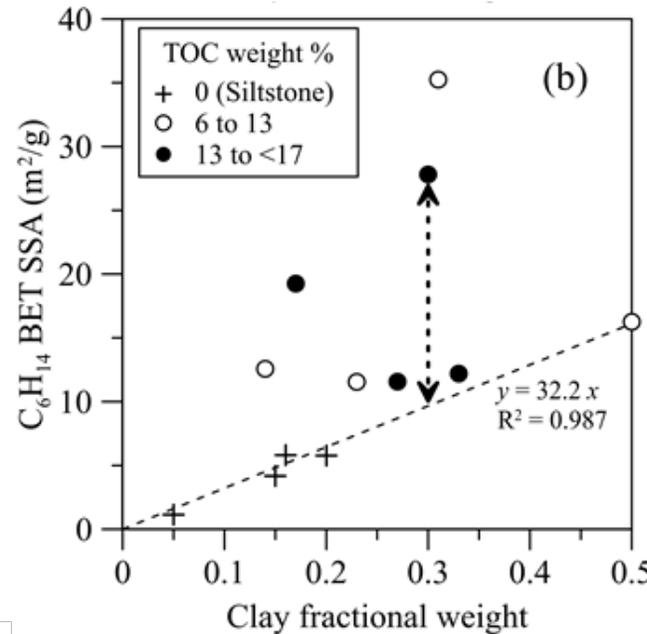
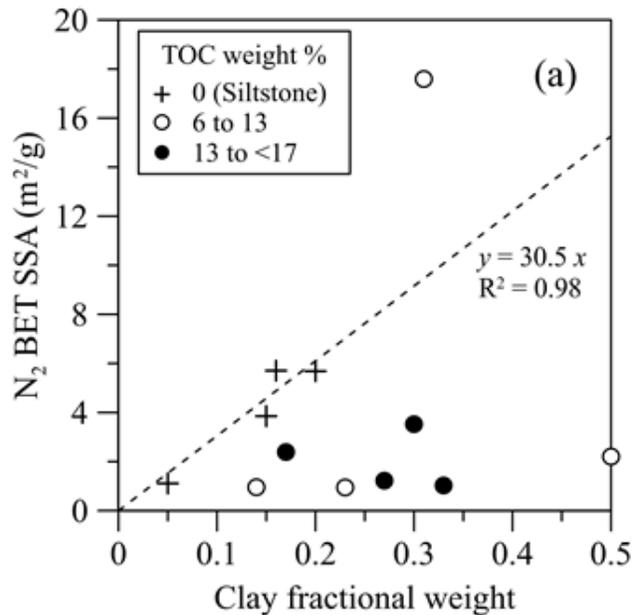
# SELECTIVE ADSORPTIVES FOR ASSESSING ORGANIC MATTER PORES SURFACE AREA



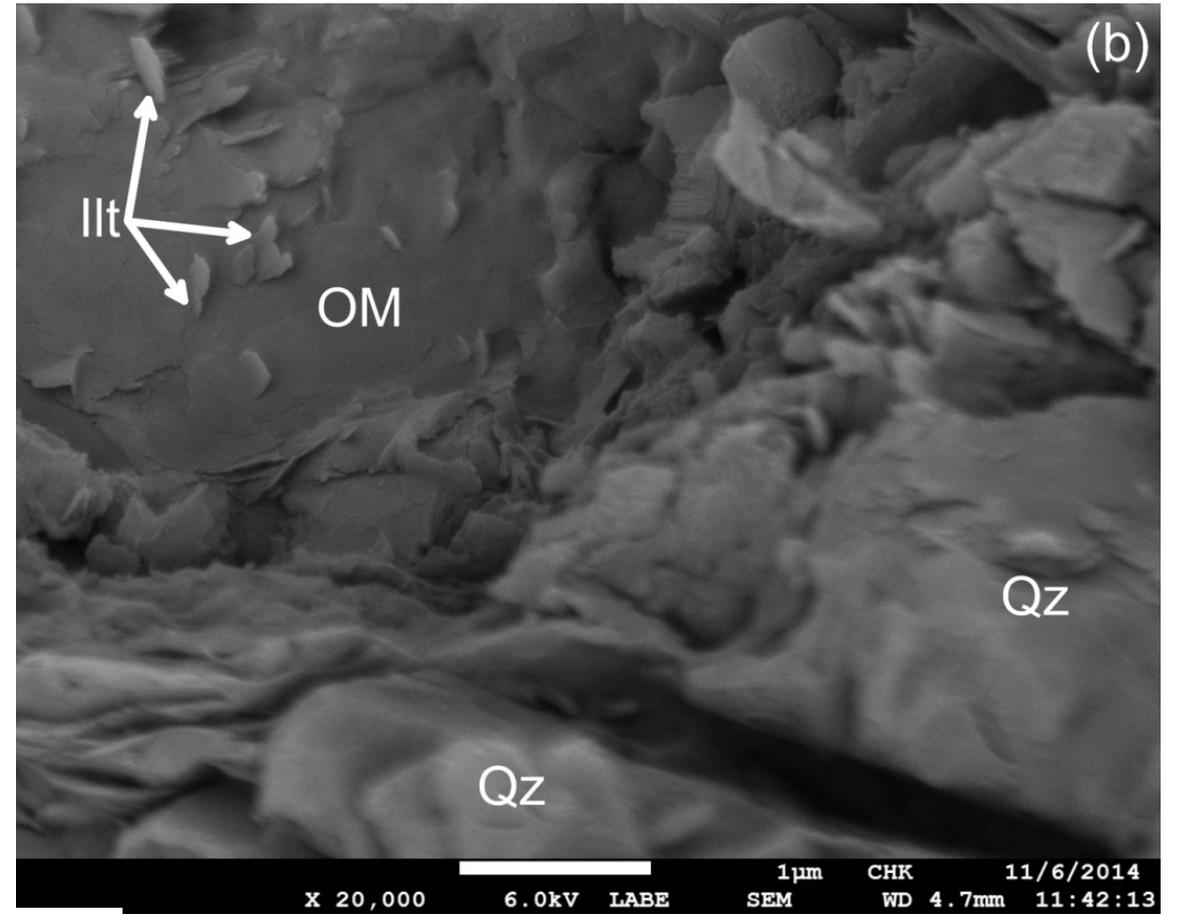
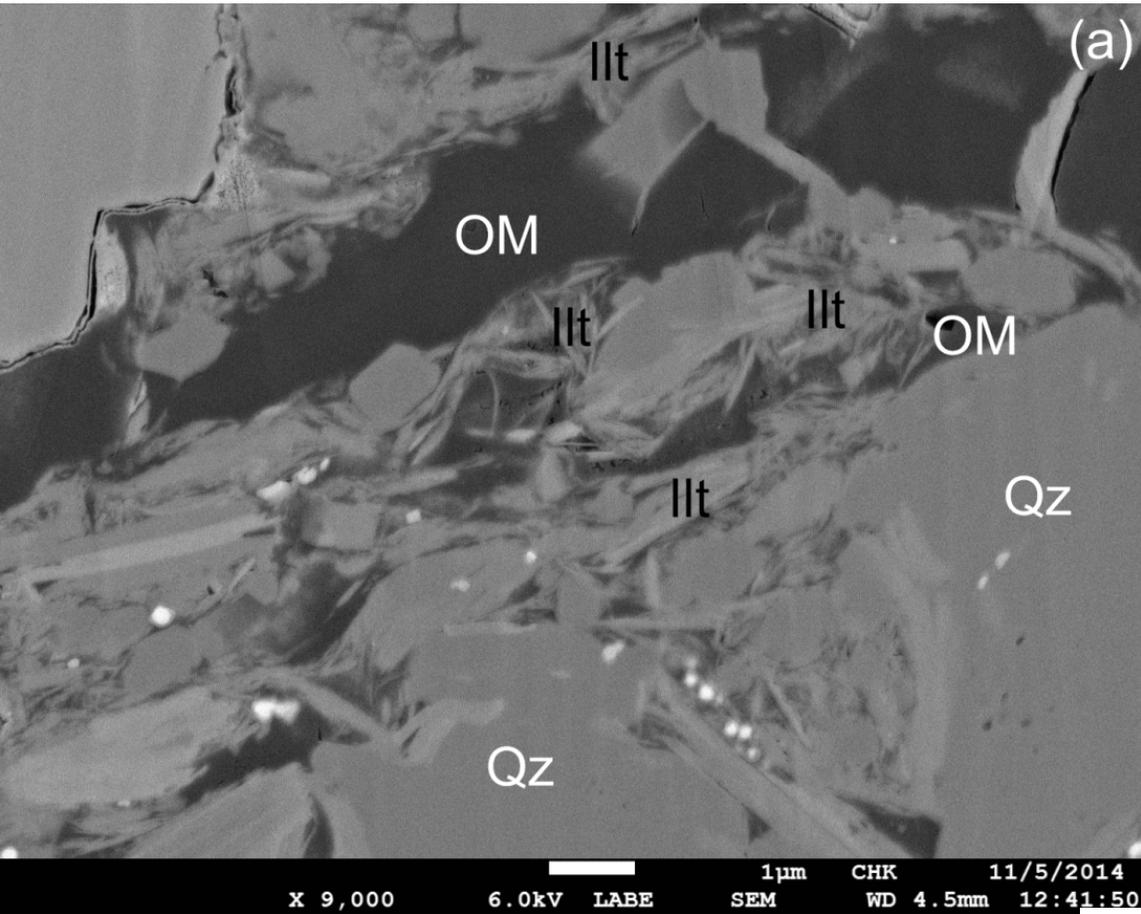
Hydrophilic pores

Hydrophobic pores

*Kumar et al., submitted*



# COATED CLAYS AND BLOCKED PORES



Silurian

*Kuila, 2013; Saidian et al., 2015*



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# EFFECT OF FLUIDS

Clark and Tittman, 1980

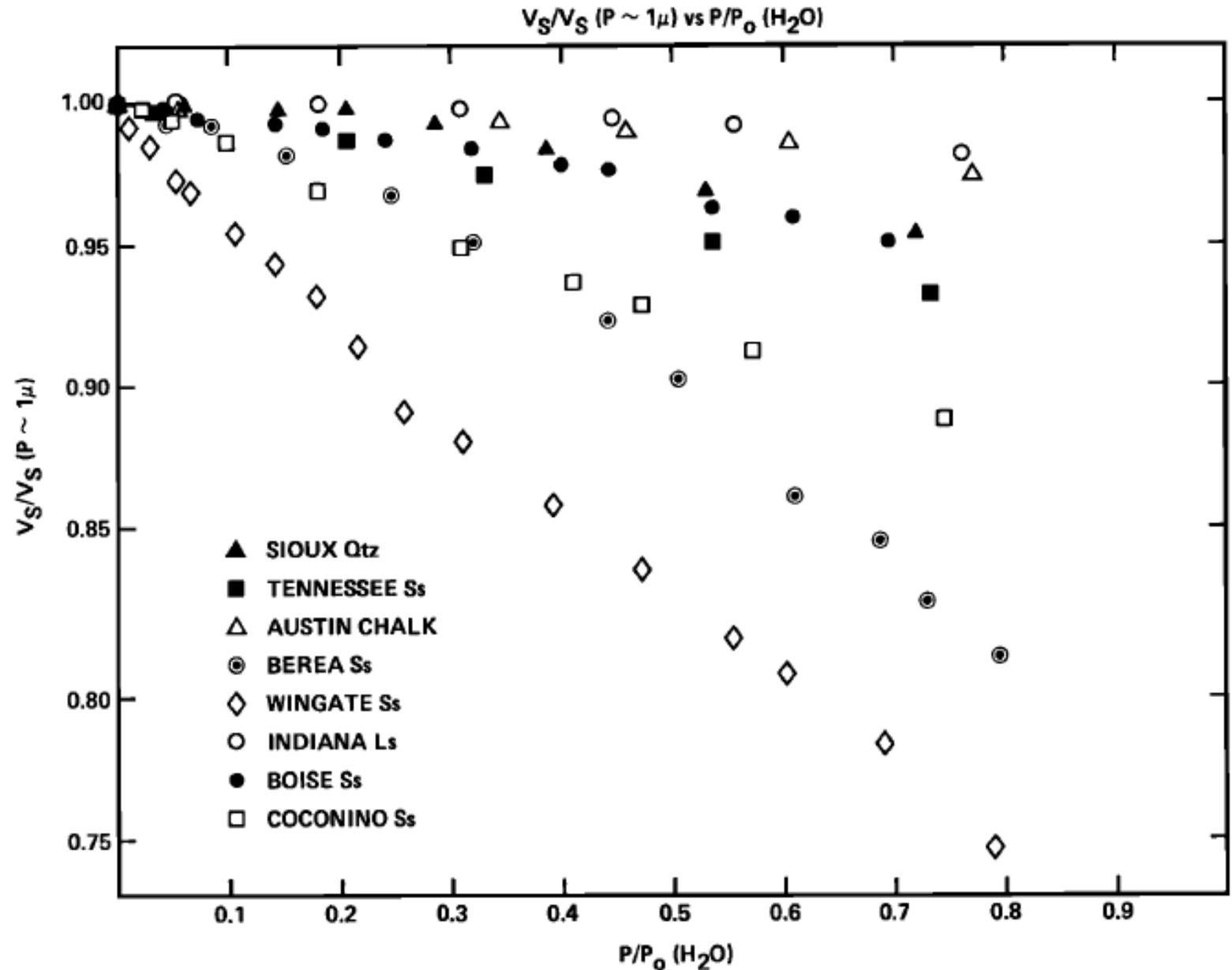
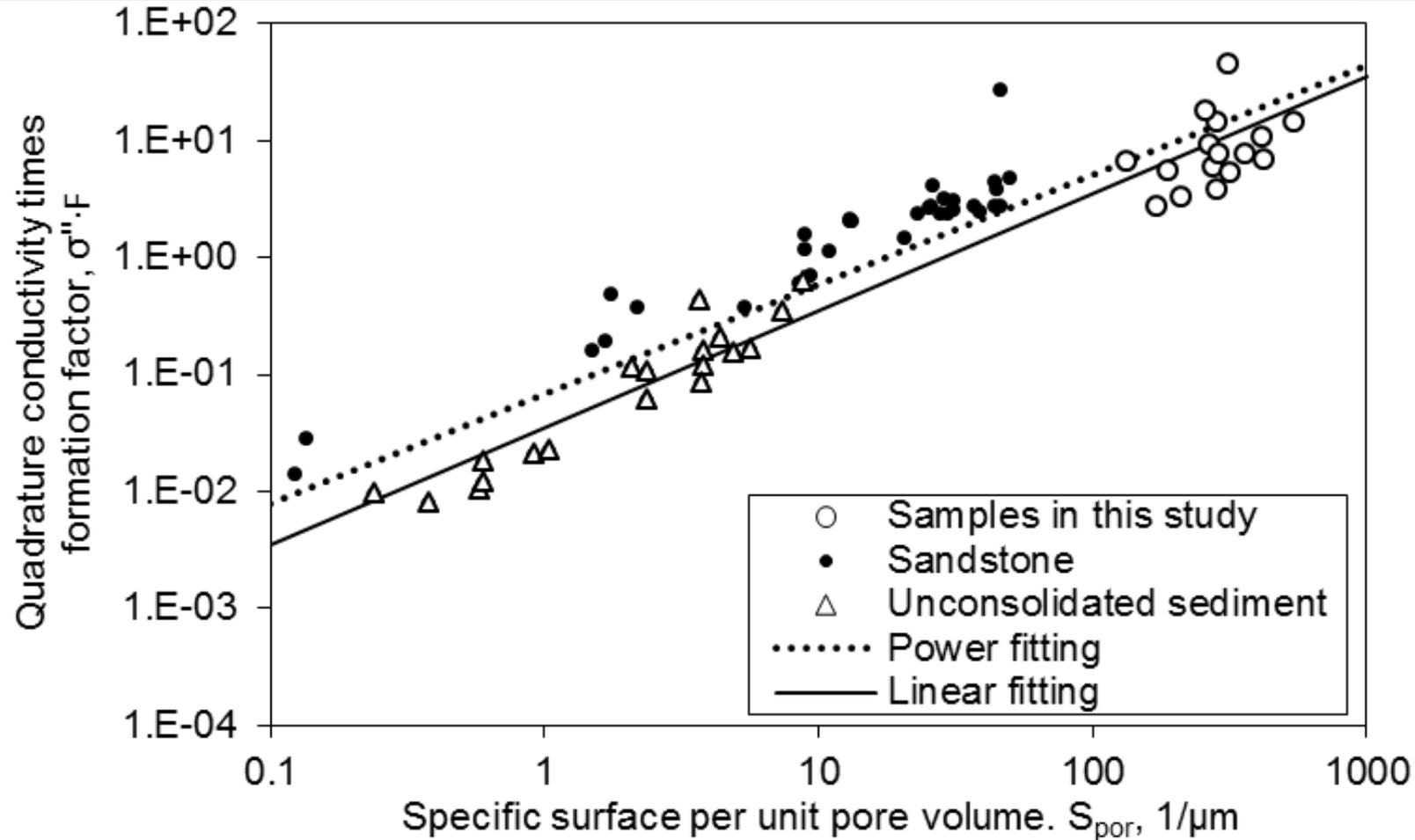


Fig. 7. Shear velocity versus the relative partial pressure of water for the sandstones, the Indiana Limestone, and the Austin Chalk. The velocity is normalized by dividing by the velocity measured in a vacuum of 1 μ.



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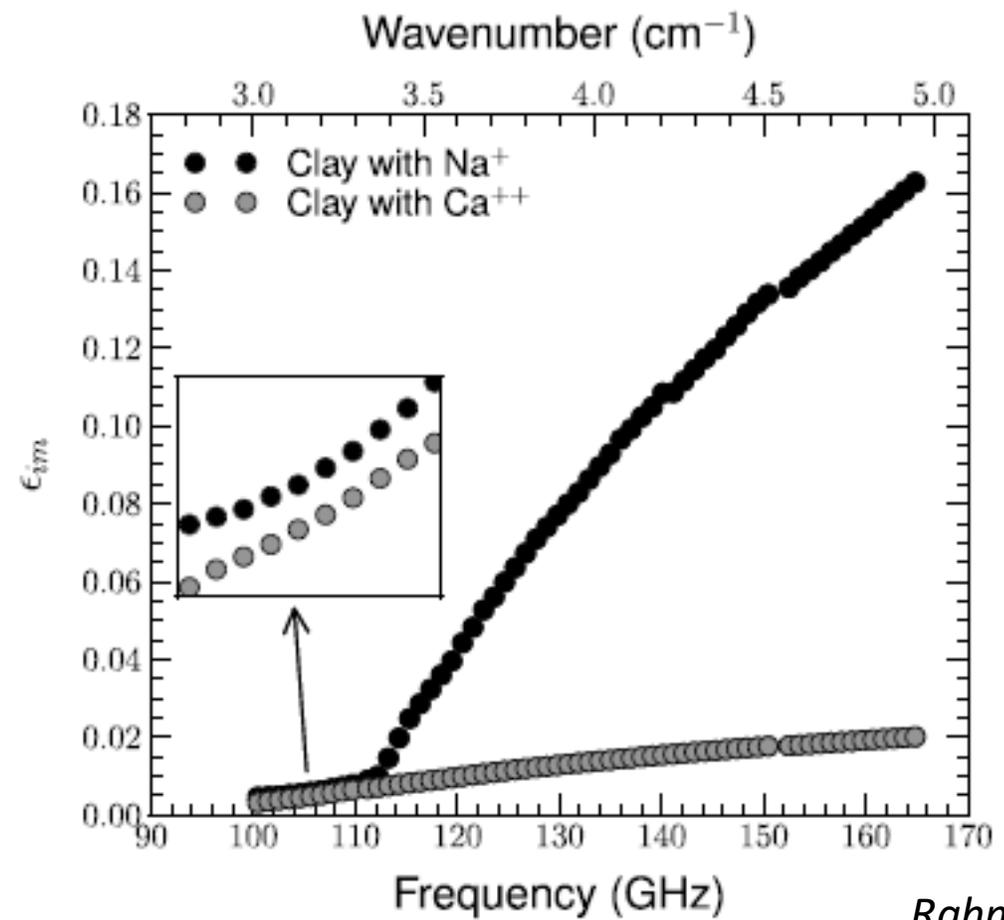
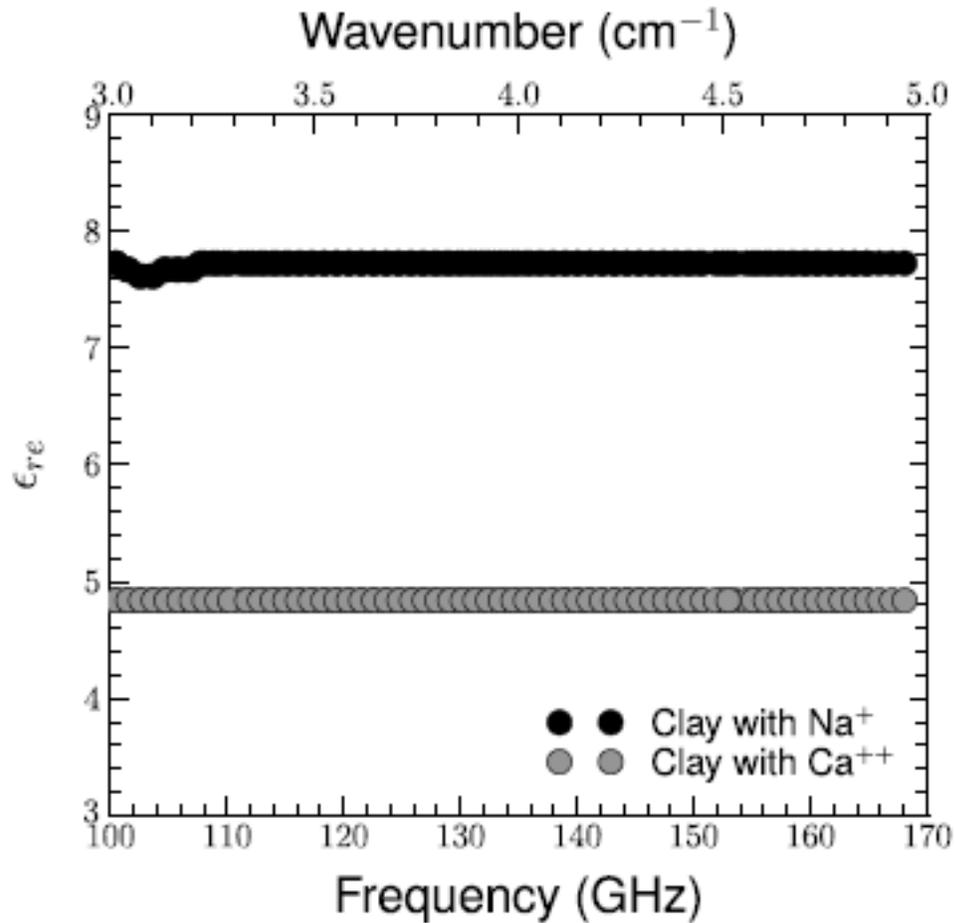
# SPECIFIC SURFACE AREA CONTROLS ON SIP



*Niu et al., submitted*



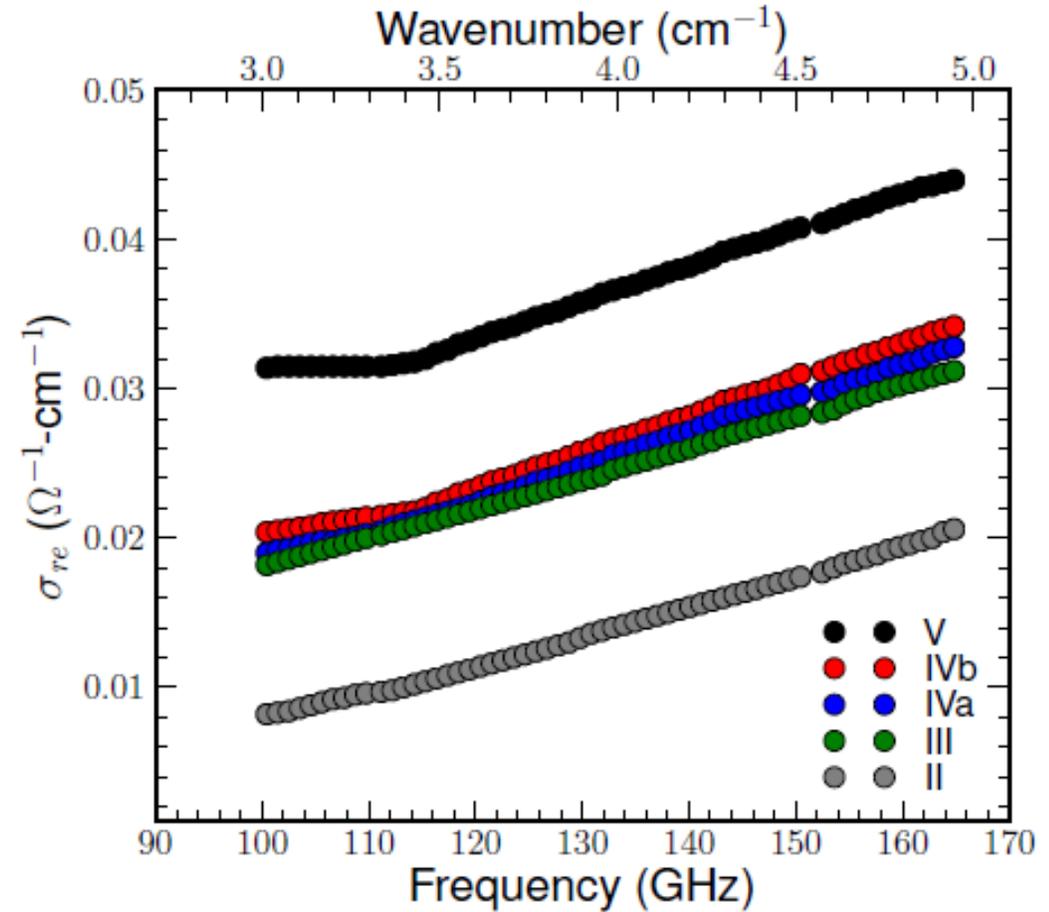
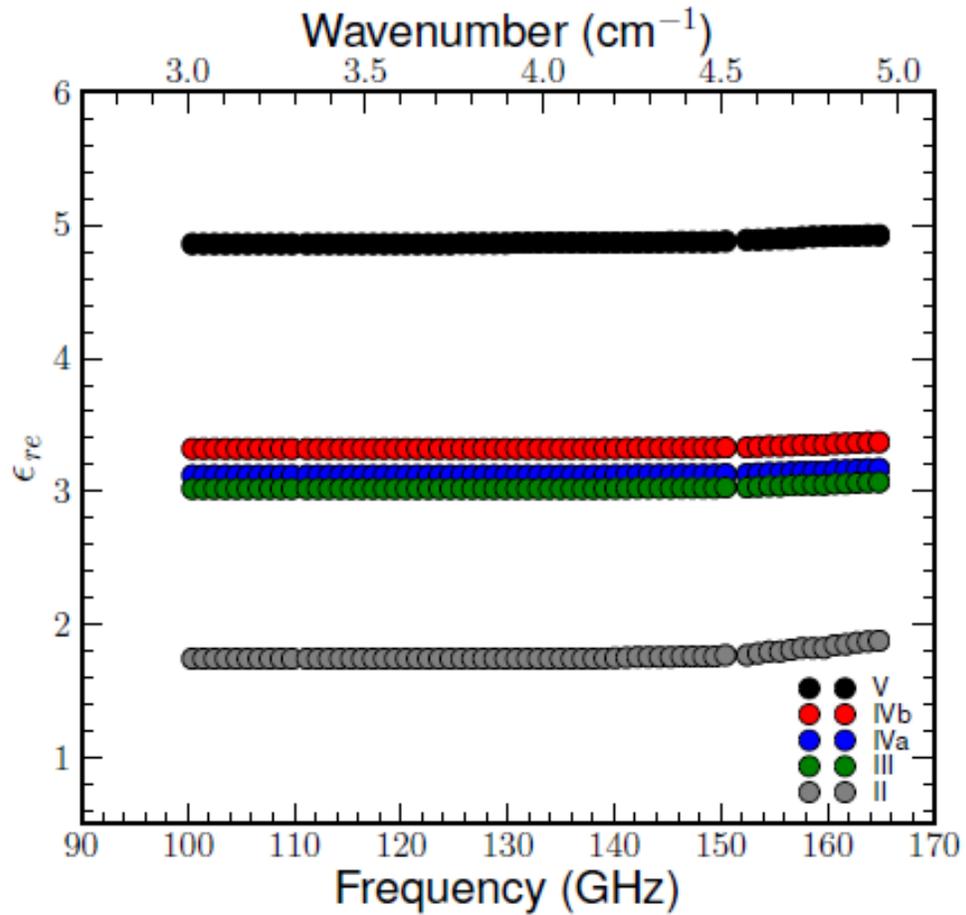
# DIELECTRIC CONSTANT OF HOMOIONIC SMECTITES



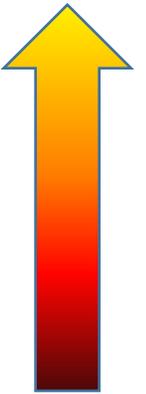
Rahman et al., 2015

$\text{Na}^+$  smectite: higher specific surface area (SSA) and dominant 1–3 nm pores  
 $\text{Ca}^{++}$  smectite: has predominantly larger pores between 50 and 100 nm

# DIELECTRIC CONSTANT OF ORGANIC MATTER



Maturity



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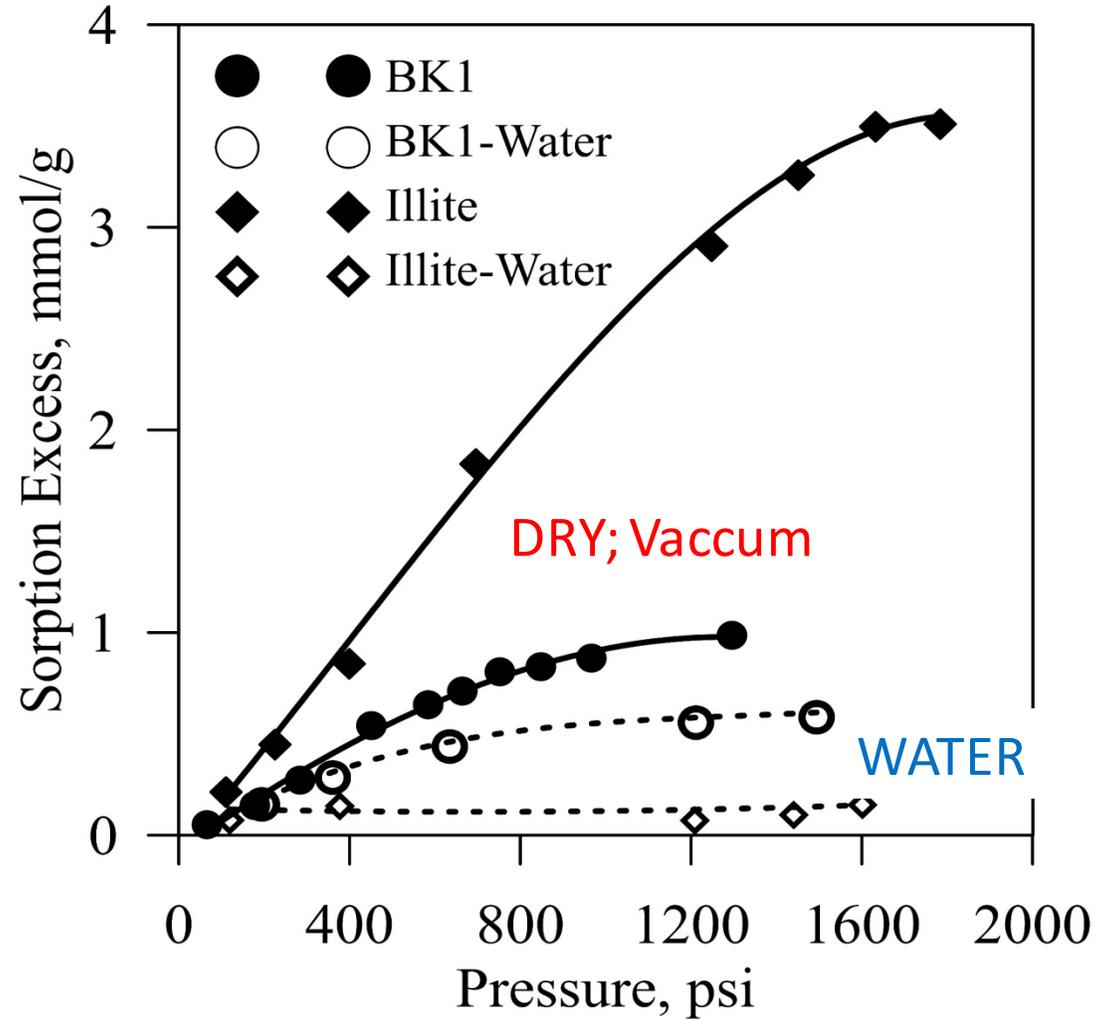
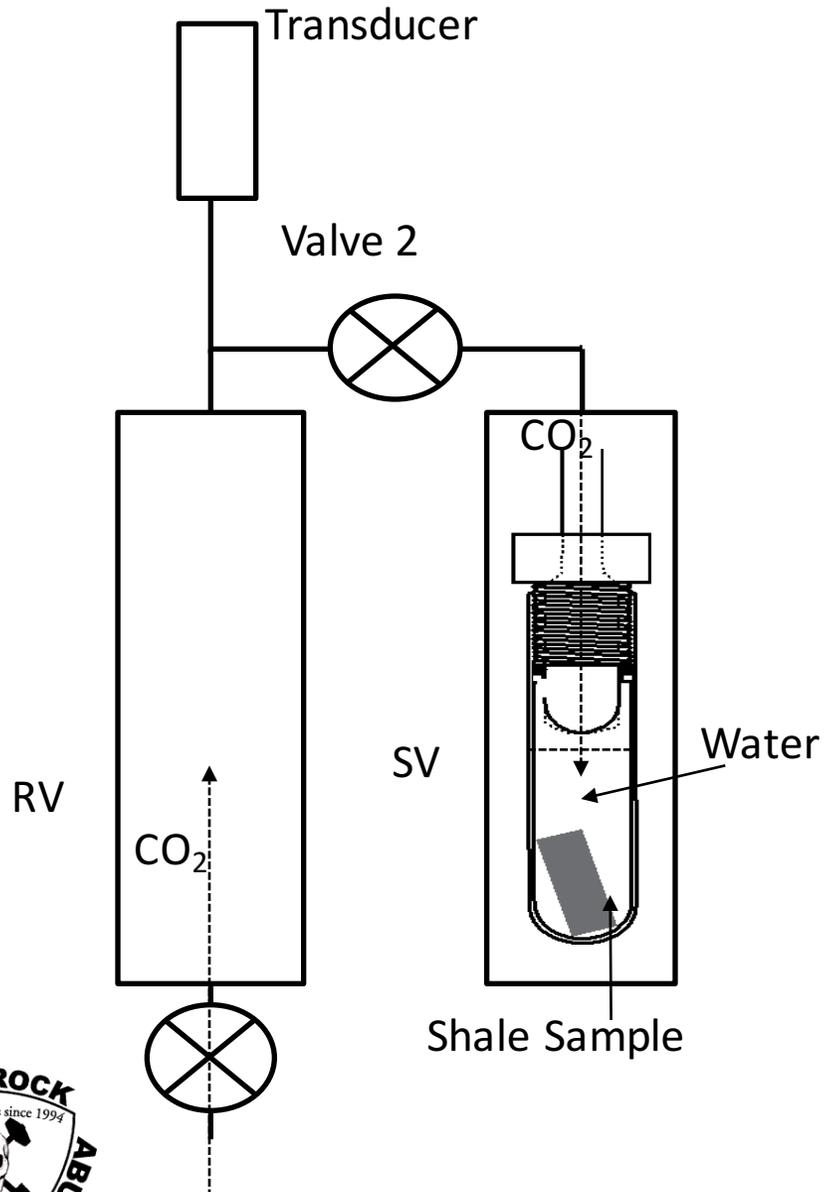
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Rahman et al., submitted



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# SUPER-CRITICAL CO<sub>2</sub> IN WATER IMMERSED ORGANIC SHALE



BK1 Maturity: Oil Window; TOC-12%, Illite-25%



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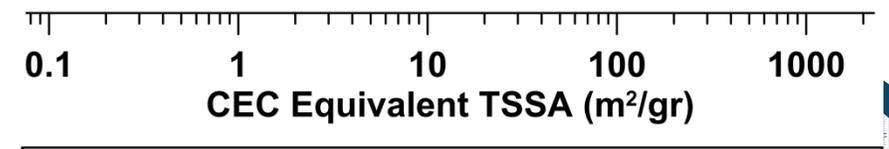
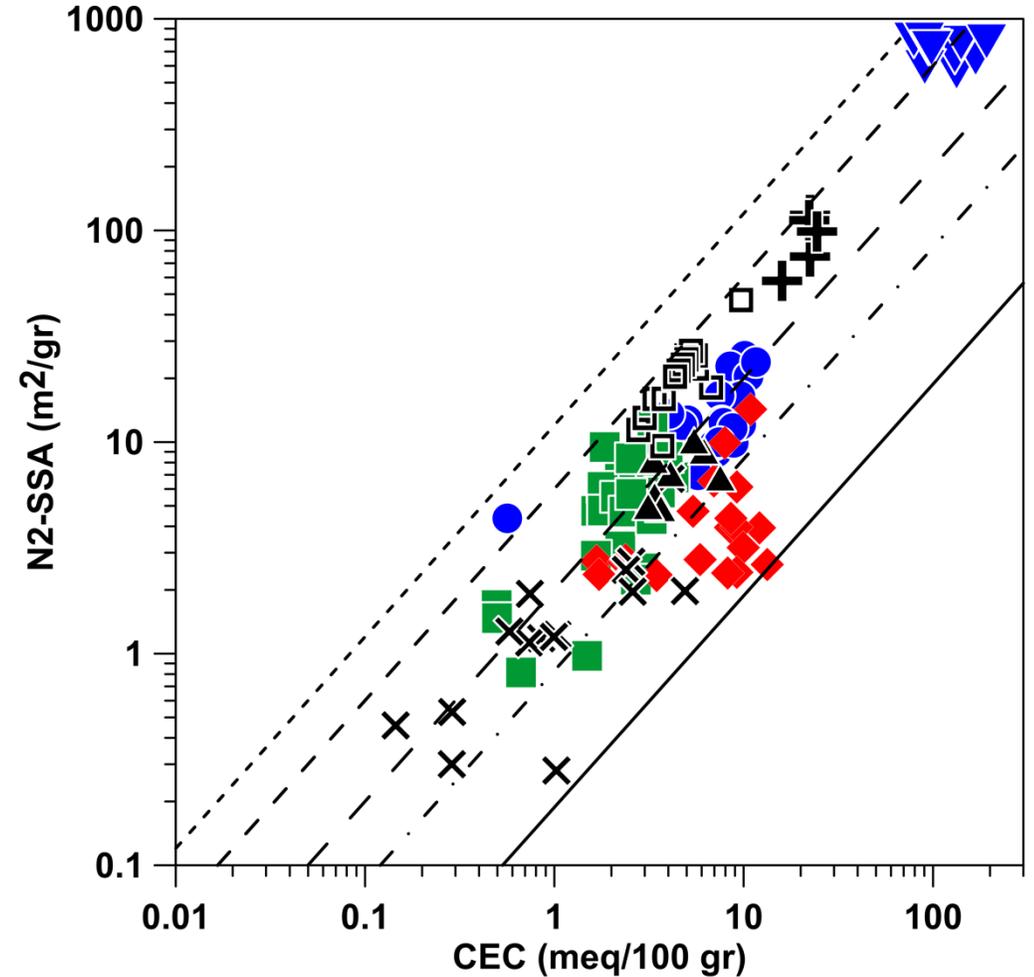
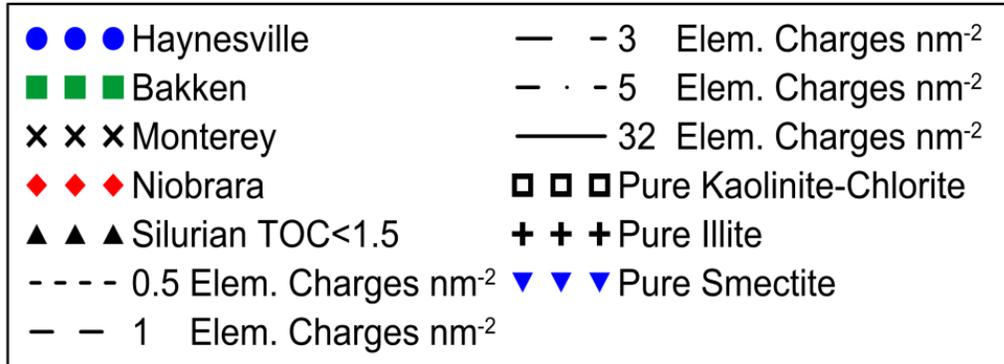


# CONCLUSIONS

- Fluid coverage in poly-mineratic rocks is controlled by:
  - Mineralogy
  - Surface Area
  - Surface Chemistry
- Fluids compete for inorganic and organic constituents
- Preferential fluid coverage depends on mineralogy and fluids polararity
- Fluid coverage affects elastic and electrical properties

# CEC TSSA-N2 SSA CORRELATION

CEC is linearly correlated with smectite content



Saidian et al., 2015

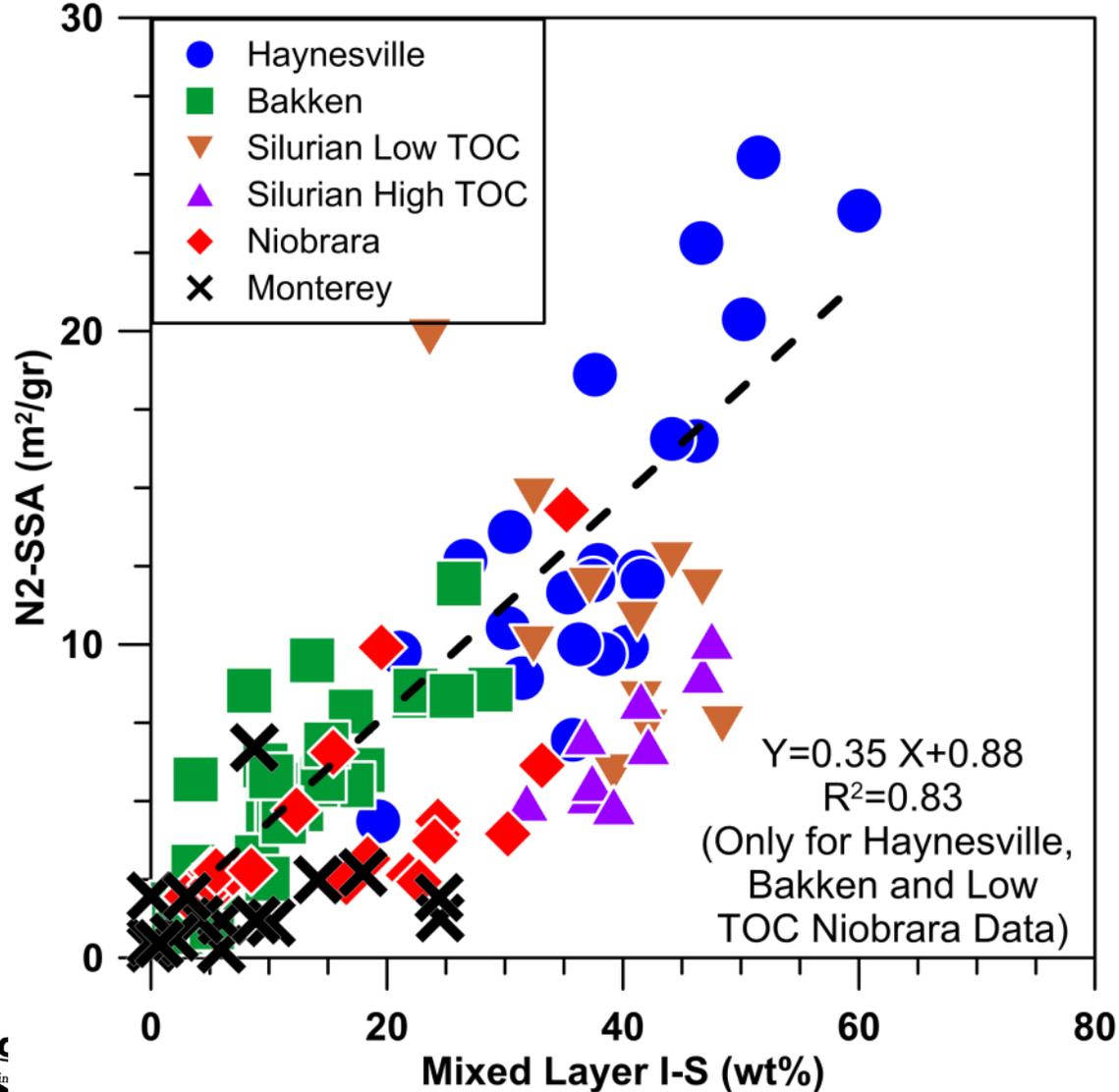
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# CLAY & ORGANIC MATTER EFFECTS ON SURFACE AREA

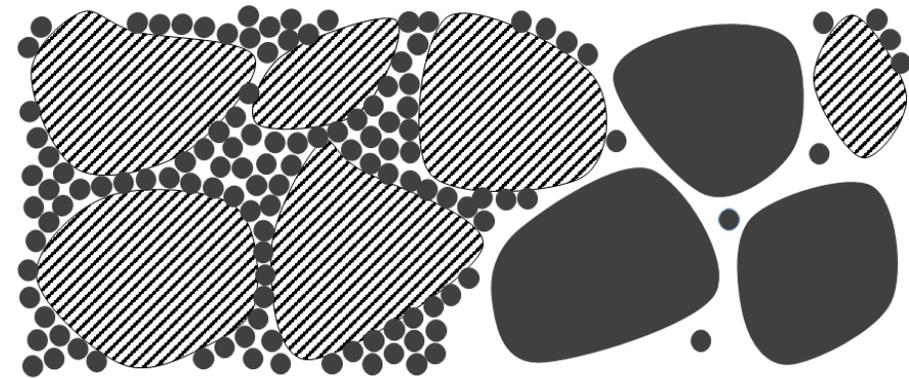
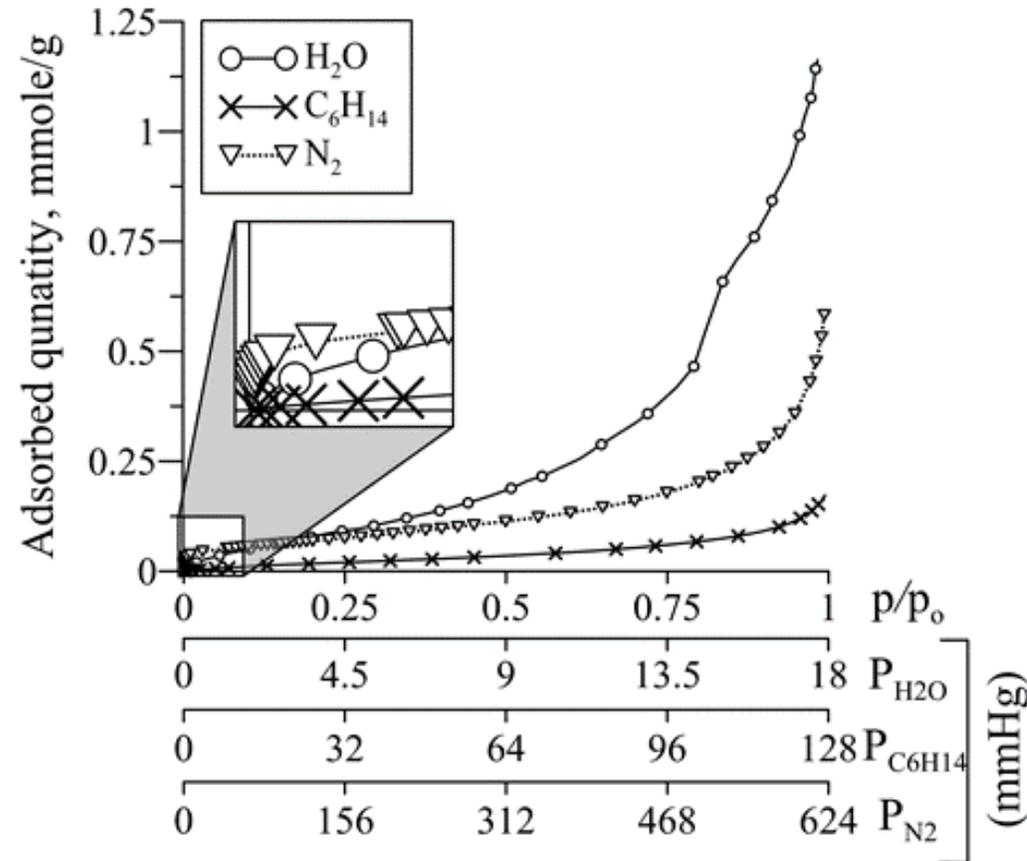


CEC is linearly correlated with smectite content

*Saidian et al., 2015*

# PREFERENTIAL SORPTION OF FLUIDS

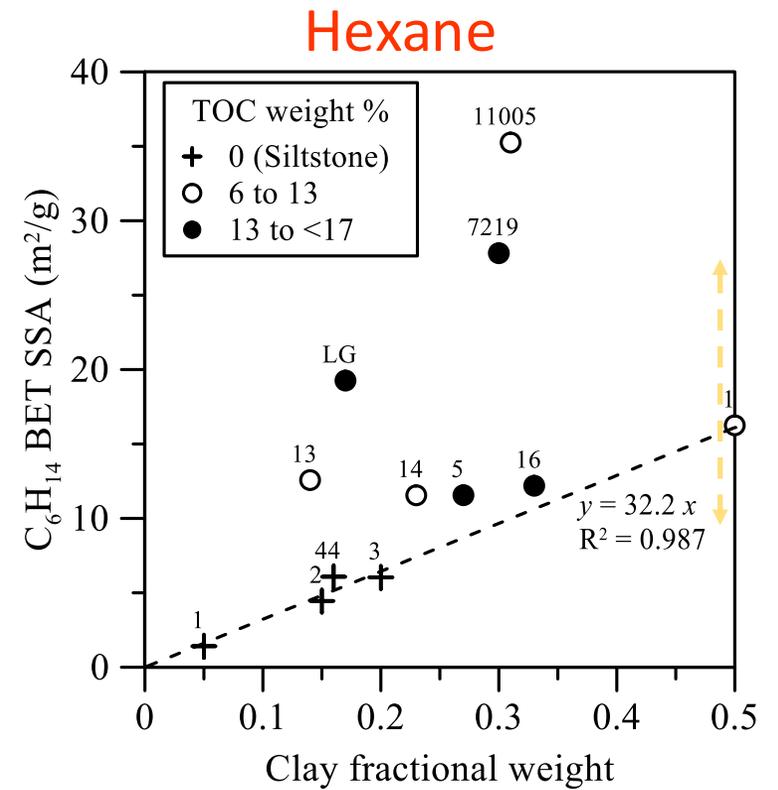
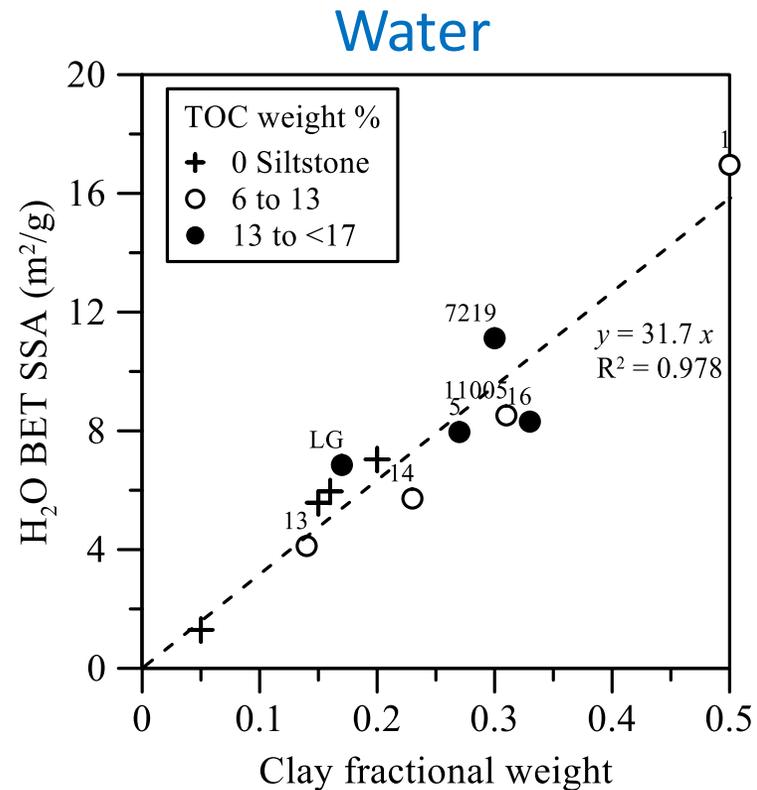
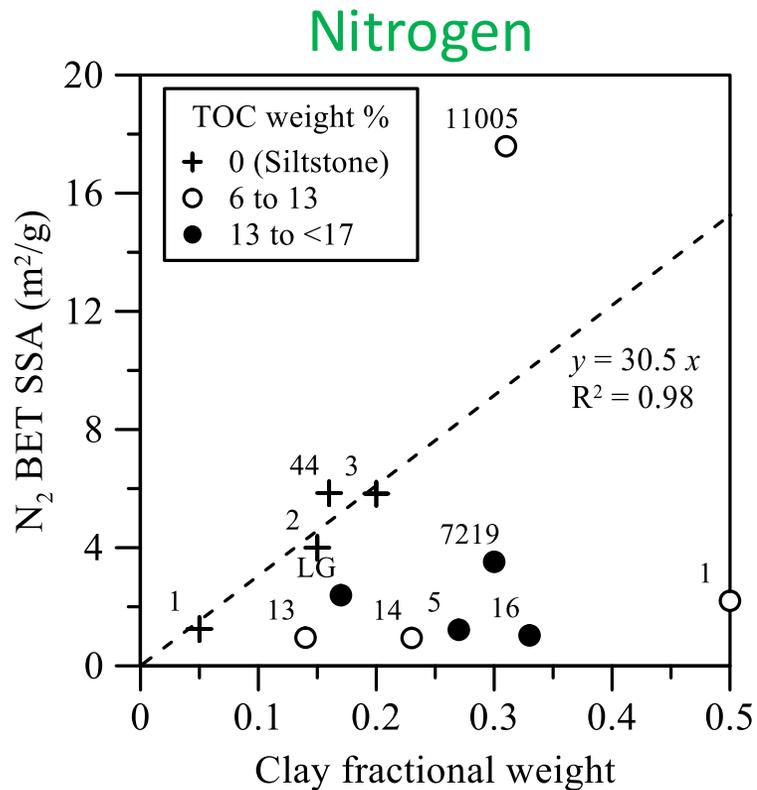
Preferential sorption of fluids depends on polarity of surfaces



- Quantification of hydrophilic and hydrophobic pores of shales

*Kumar et al., submitted*

# SURFACE AREA AND CLAY CONTENT

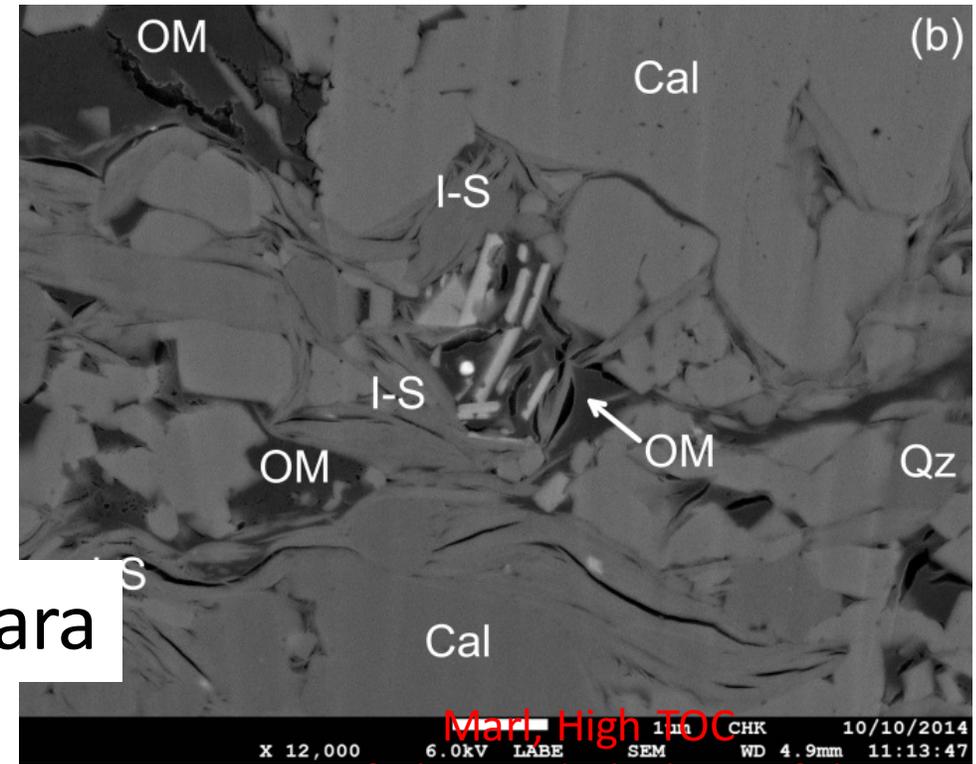
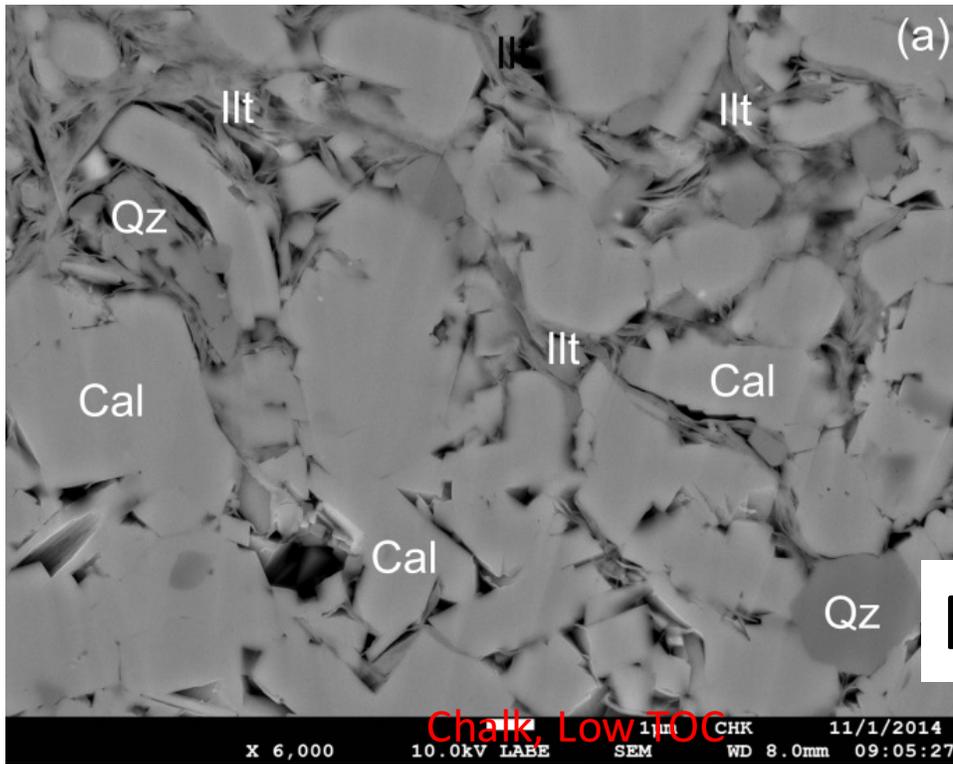


- OM pores are hydrophobic
- OM pore development starts at the onset of oil window
- Presence of **bitumen free OM pores**
- Cryogenic N<sub>2</sub> blocked by nano-sized pores in organic matter

*Kumar et al., submitted*



# WHICH SURFACES ARE EXPOSED

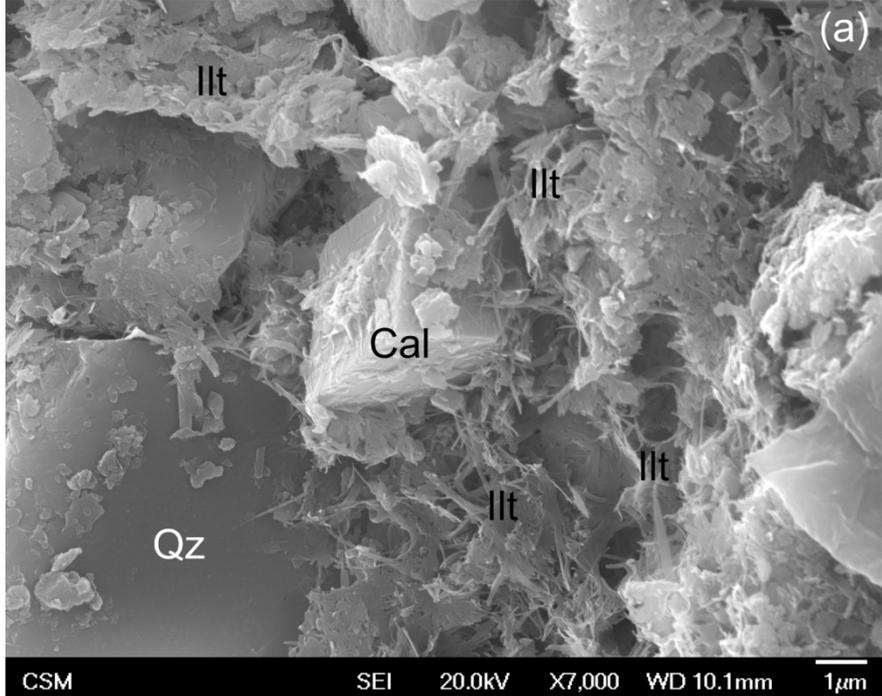


Niobrara

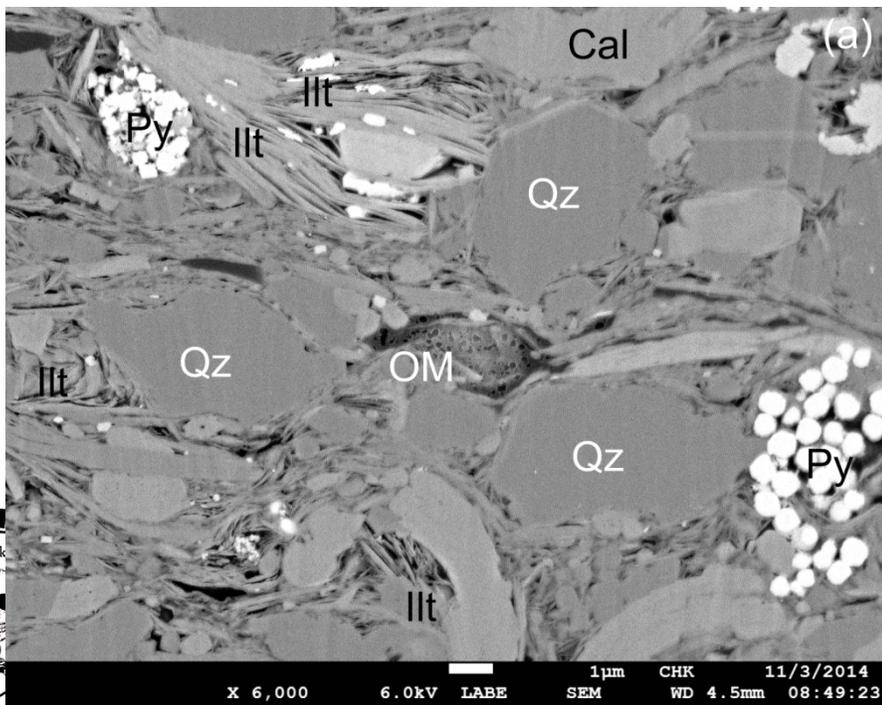
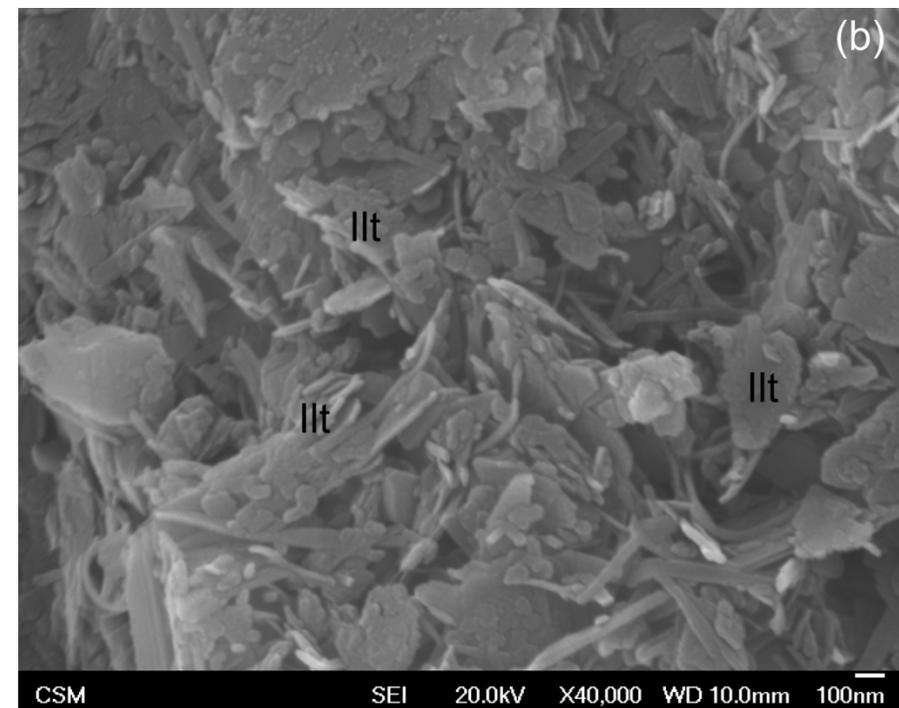
Marl, High TOC

*Kuila, 2013; Saidian et al., 2015*



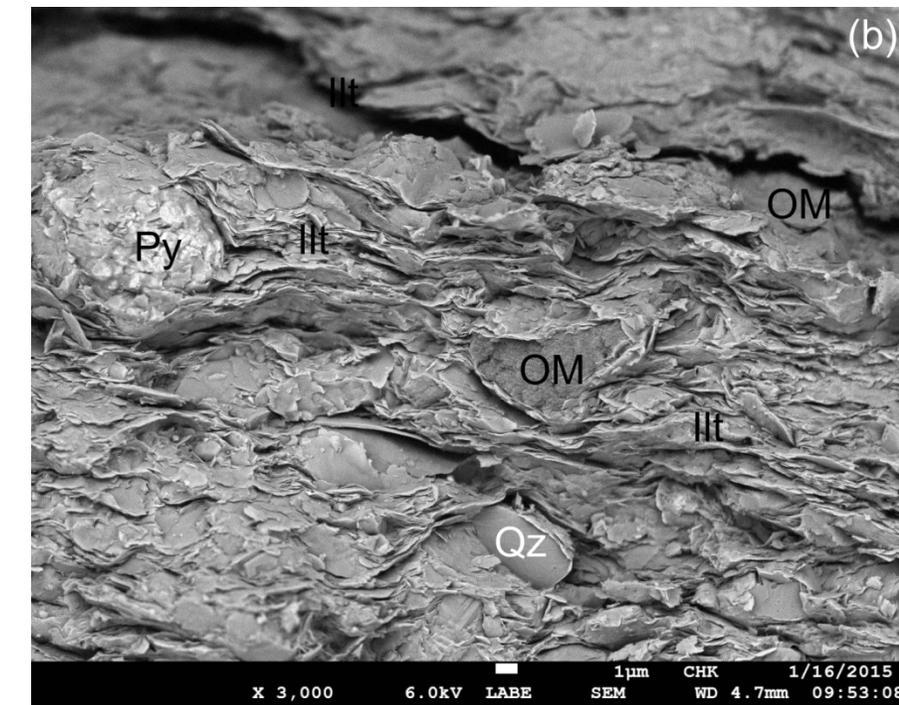


Bakken  
Exposed illite flakes

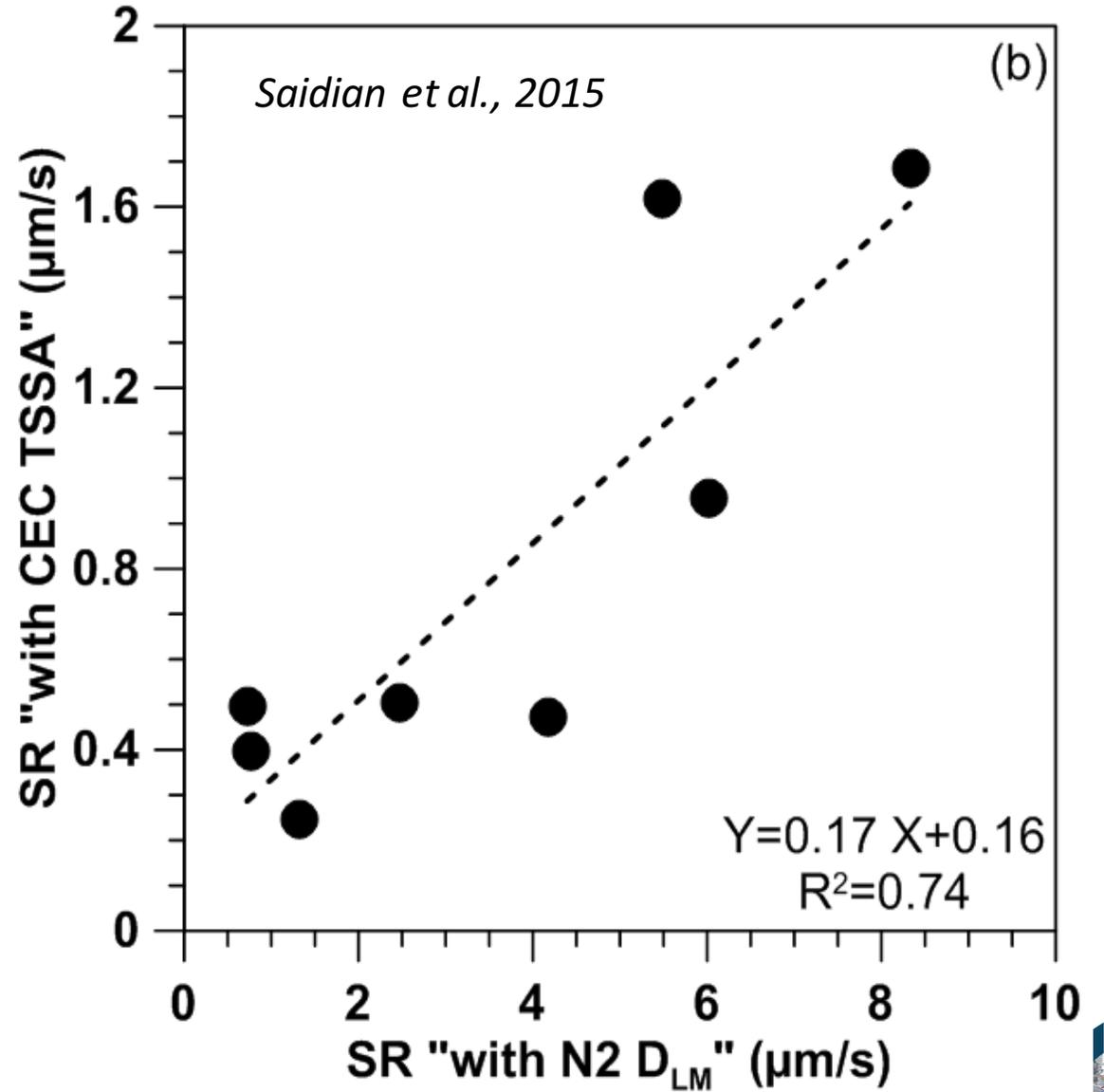
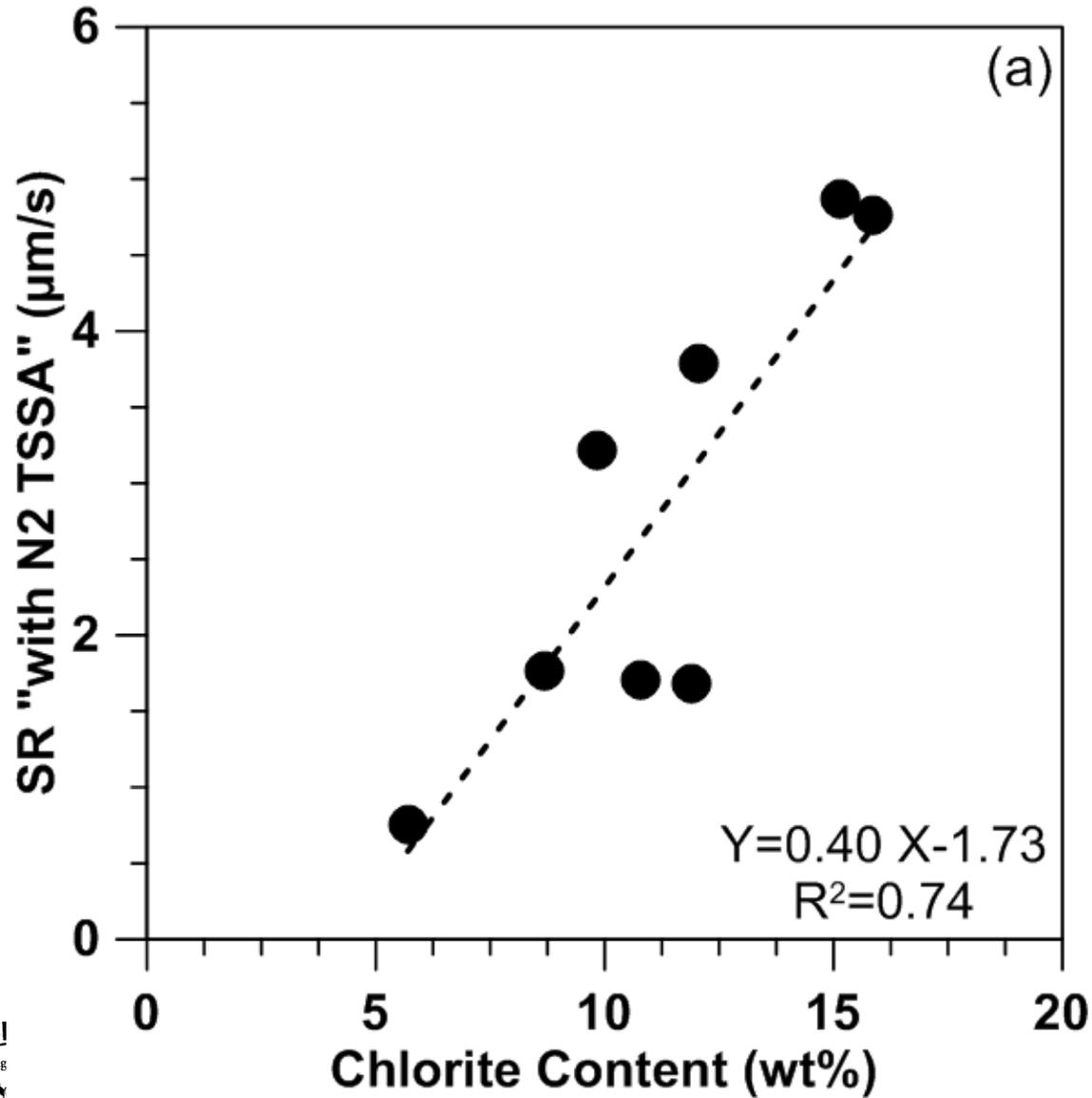


Haynesville  
Exposed illite flakes

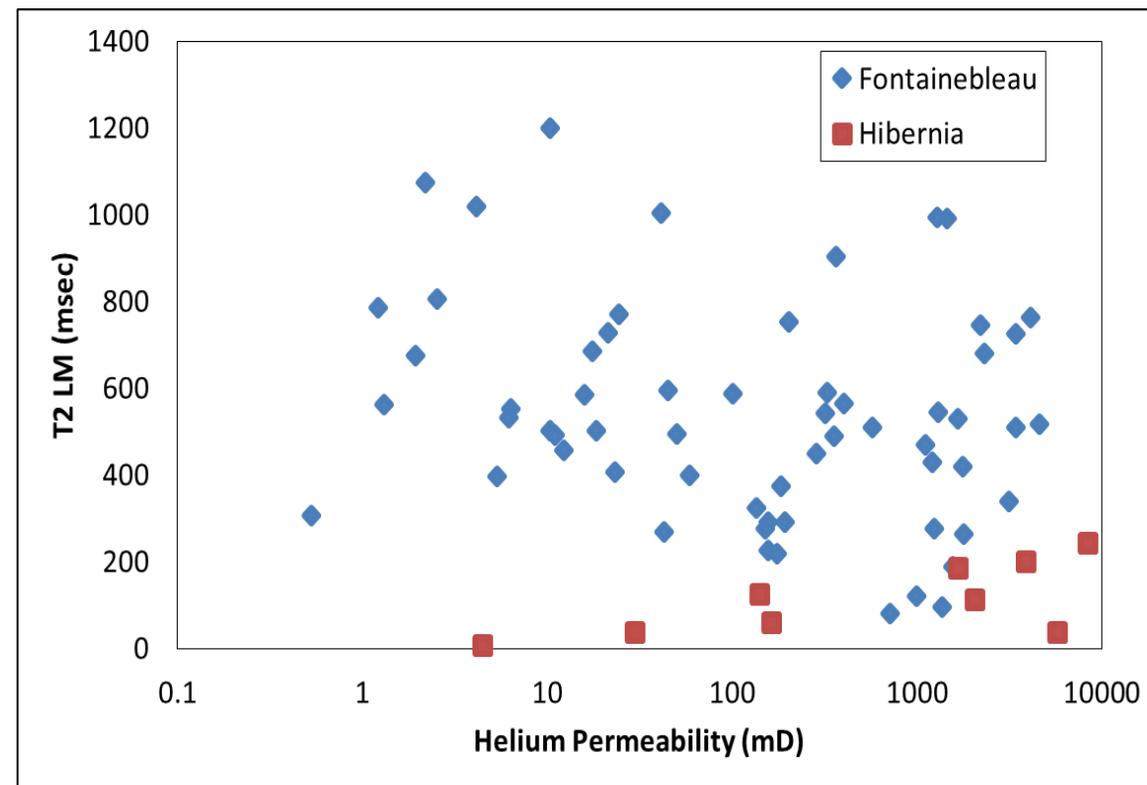
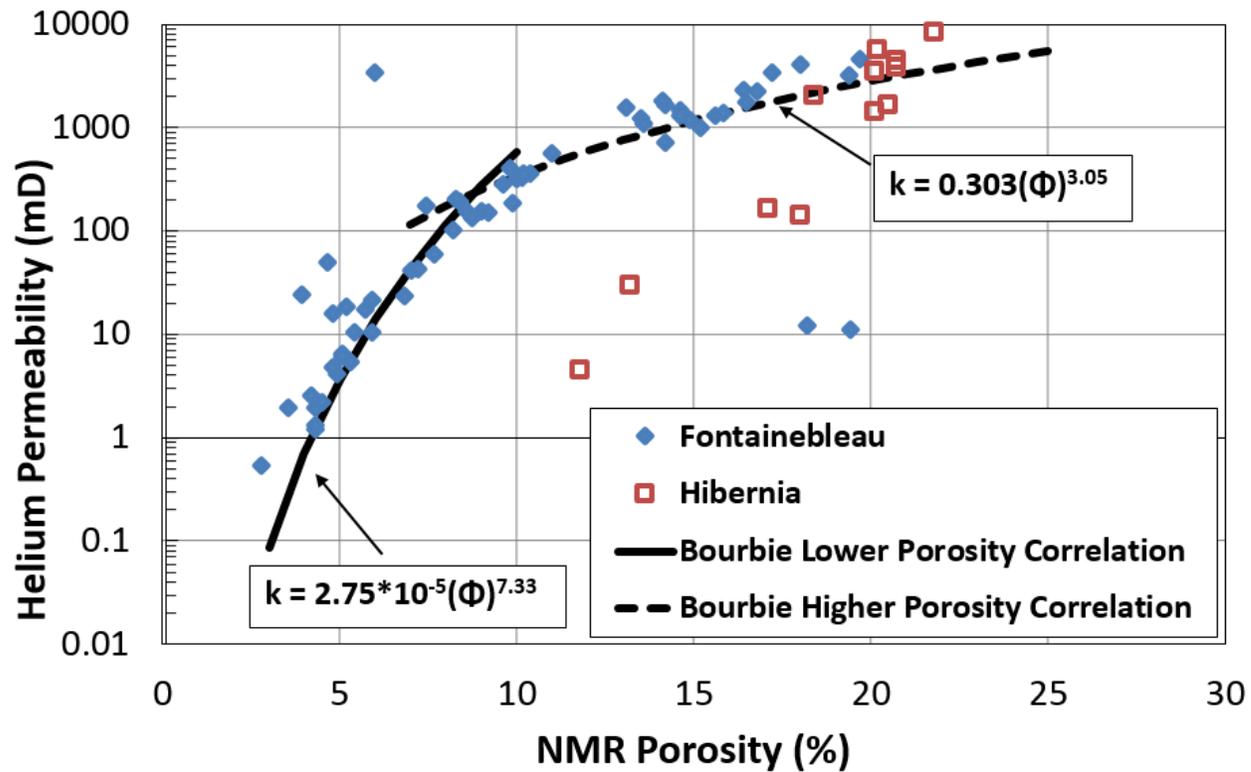
*Kuila, 2013; Saidian et al., 2015*



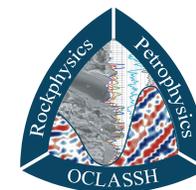
# SURFACE RELAXIVITY AND SURFACE AREA



# PERMEABILITY MODELS

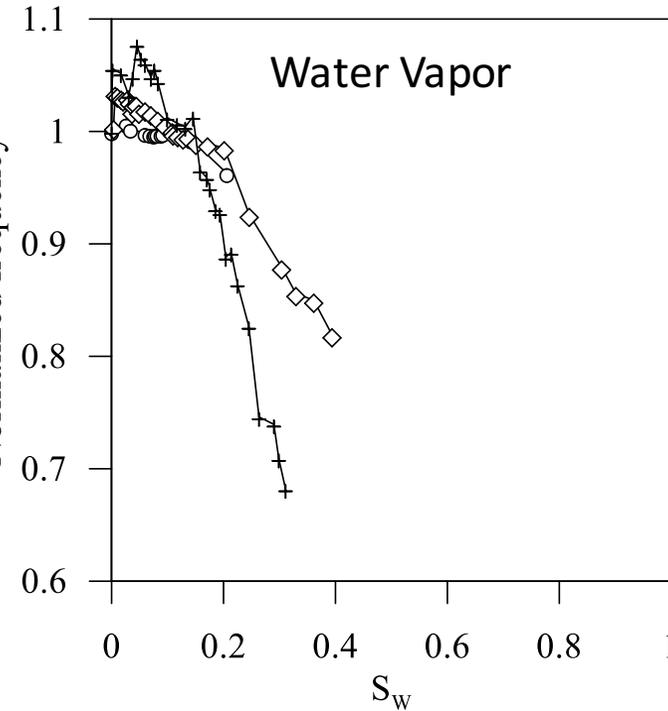
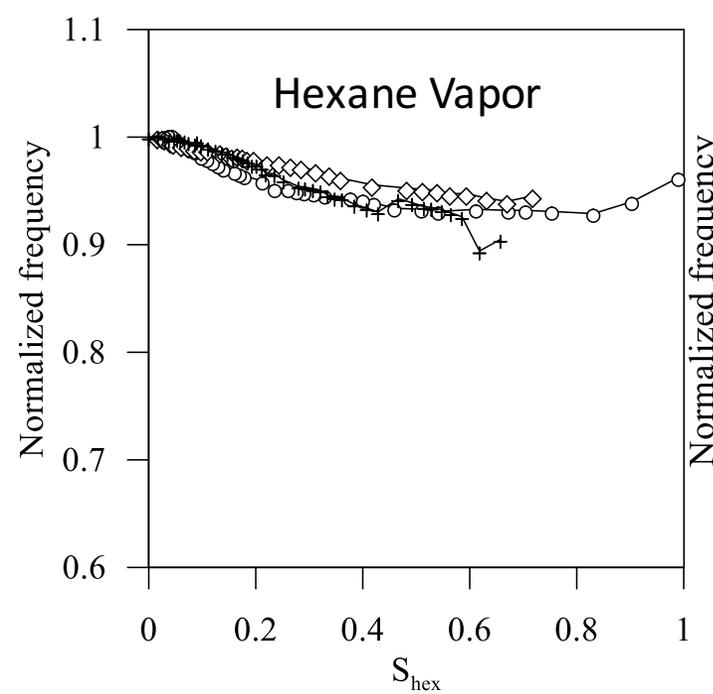
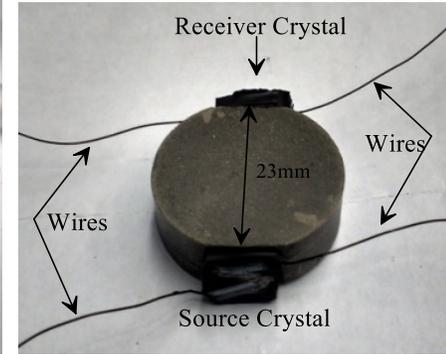
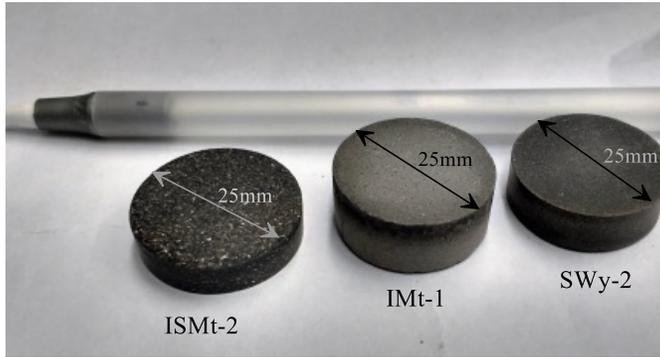
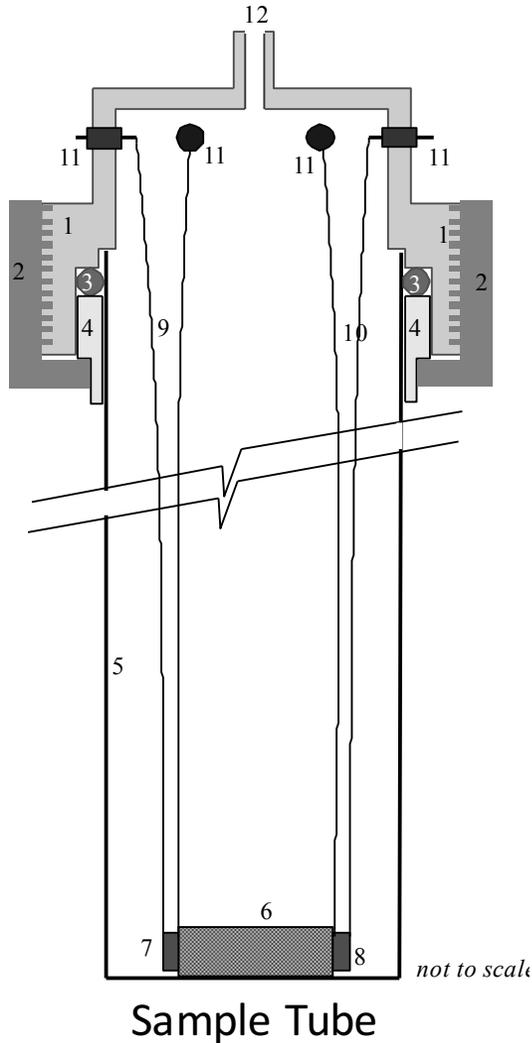


*Livo et al., submitted*



# ACOUSTIC SIGNATURES

## Confined Undersaturated Condensates



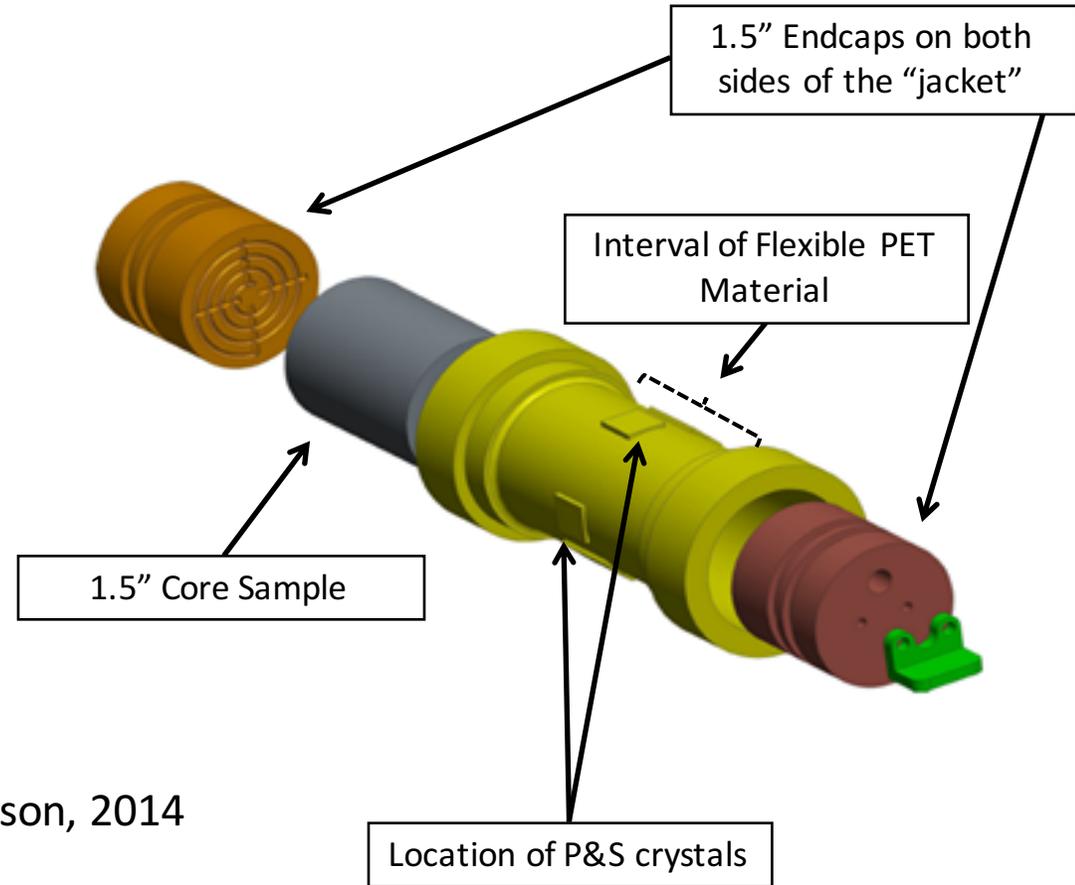
# SIMULTANEOUS ELASTIC AND ELECTRICAL PROPERTY MEASUREMENTS

## Jacket Design:

- Flexible PET jacket
- End pieces for pore fluid lines
- P-wave and S-wave measurements in  $0^\circ$   $45^\circ$  and  $90^\circ$  degrees direction under pressure
- Core sample is **reusable**
- Simultaneous elastic and electrical property measurements

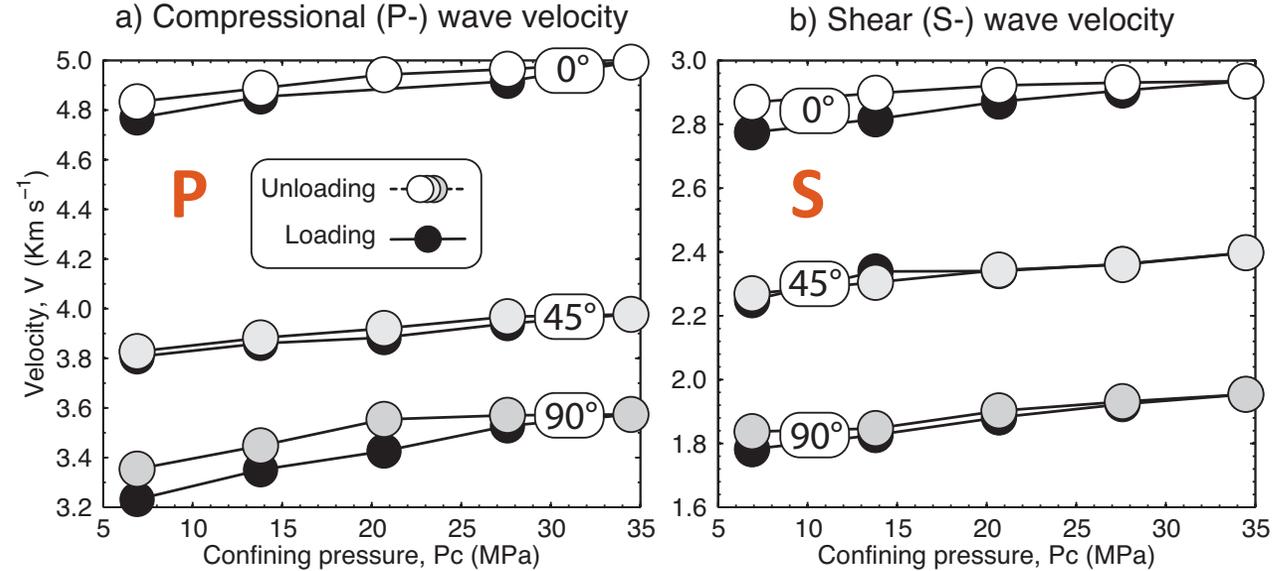
Designed by Prasad, Panfiloff and Larsson, 2014

*Panfiloff, 2015*

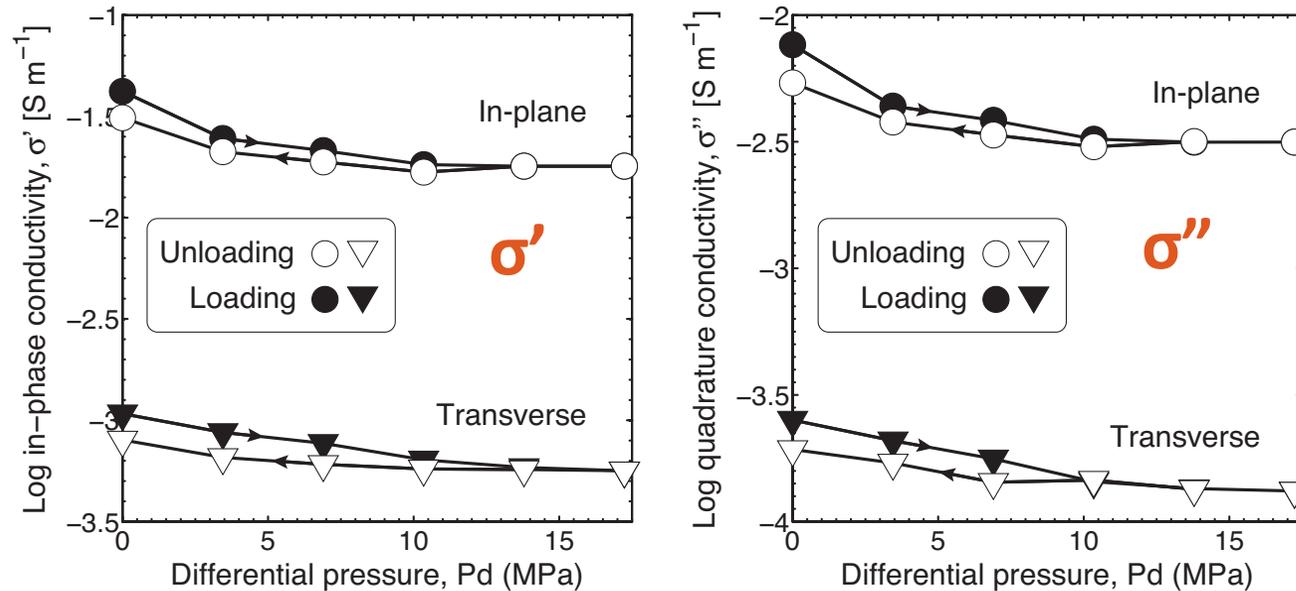


# JOINT ULTRASONIC AND SIP MEASUREMENTS

Ultrasonics



Complex conductivity



Woodruff *et al.*, 2014



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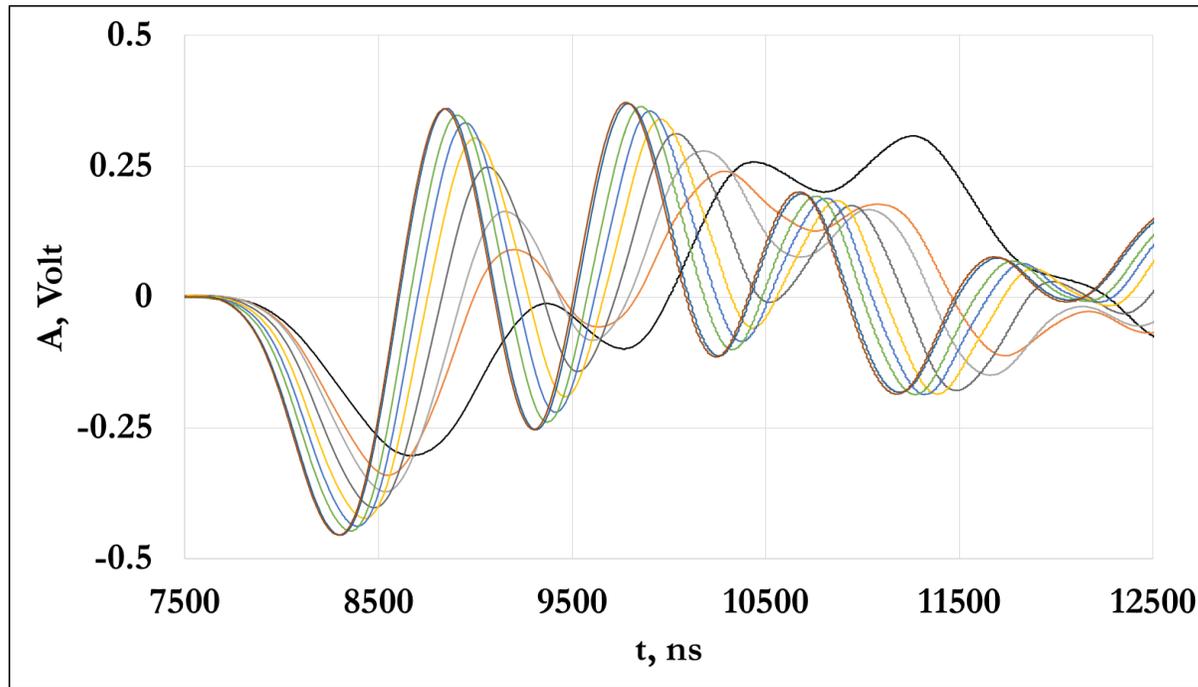
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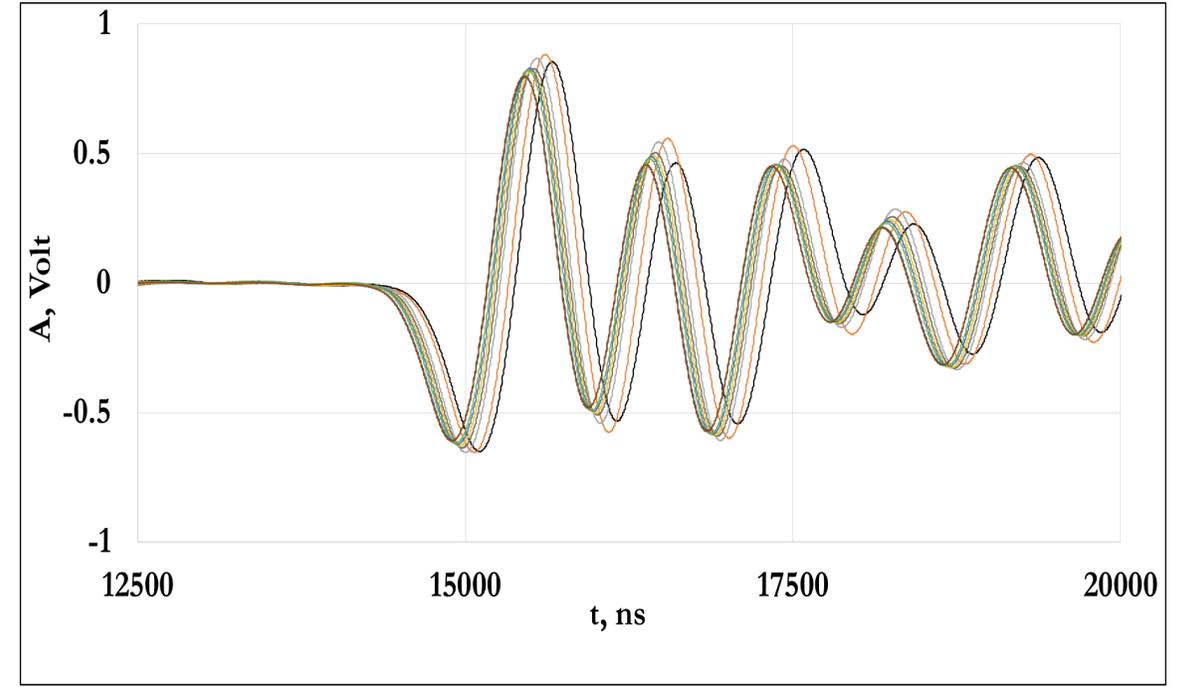


# TYPICAL ACOUSTIC WAVE SIGNALS

## Compressional Waves



## Shear Waves



—1.72MPa —3.44MPa —6.89MPa —10.34MPa —13.79MPa  
—17.24MPa —20.68MPa —24.13MPa —27.58MPa

*Panfiloff (MS cand.); Ou (PhD cand.); Niu (posdoc)*



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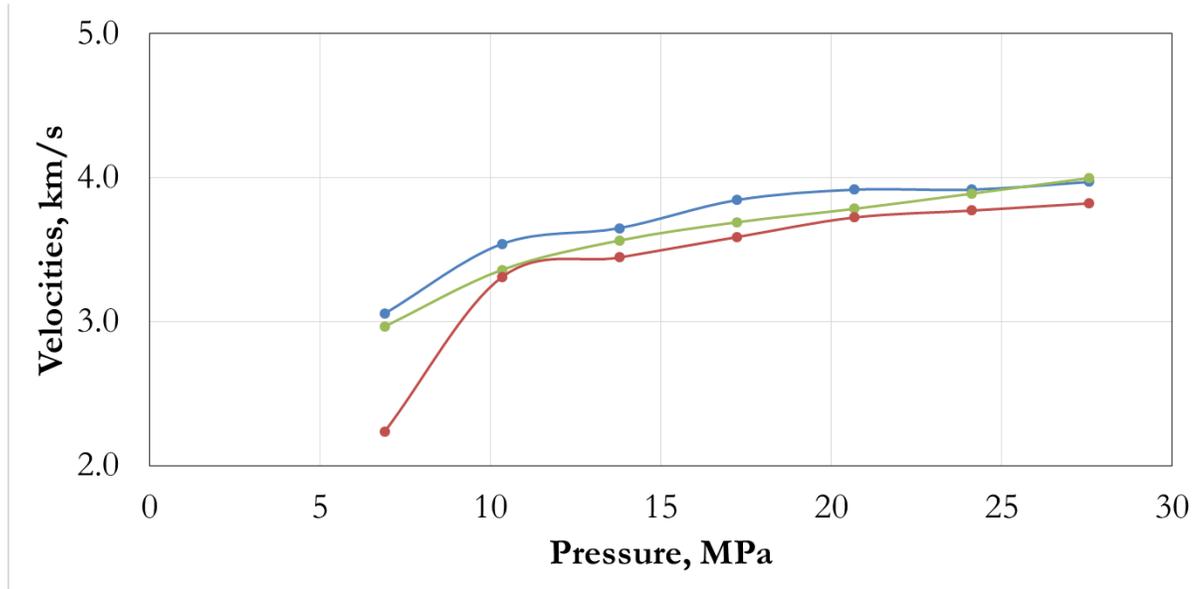
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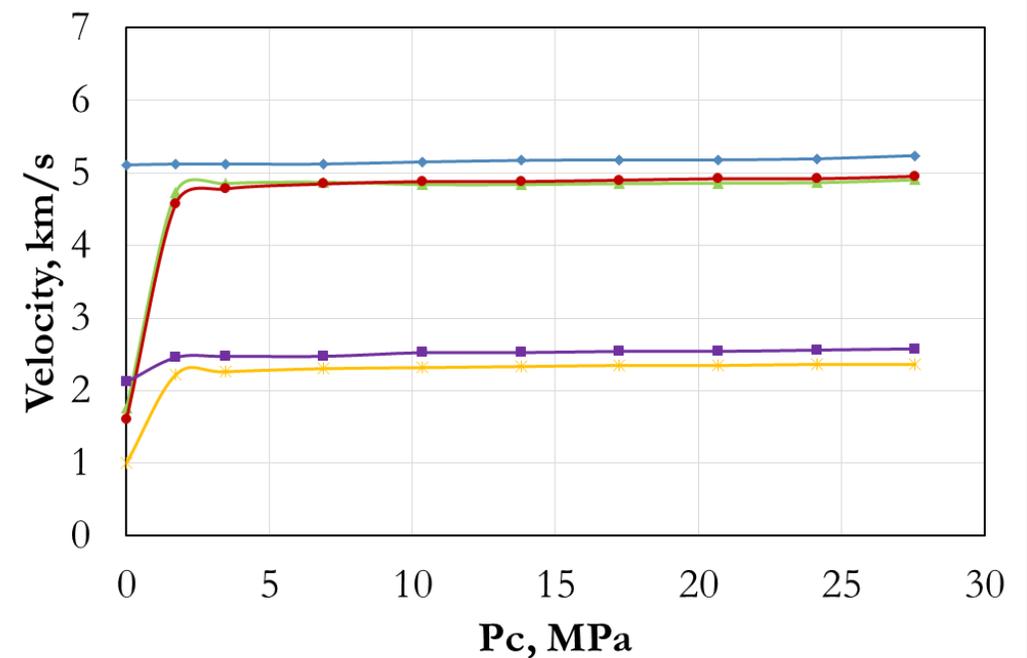
# ACOUSTICS – VELOCITIES

- Pressurized measurement from 0 to 28 MPa (4000psi)
- Velocities as a function of pressure:

Sandstone, Dry



Lower Austin Chalk, Preserved

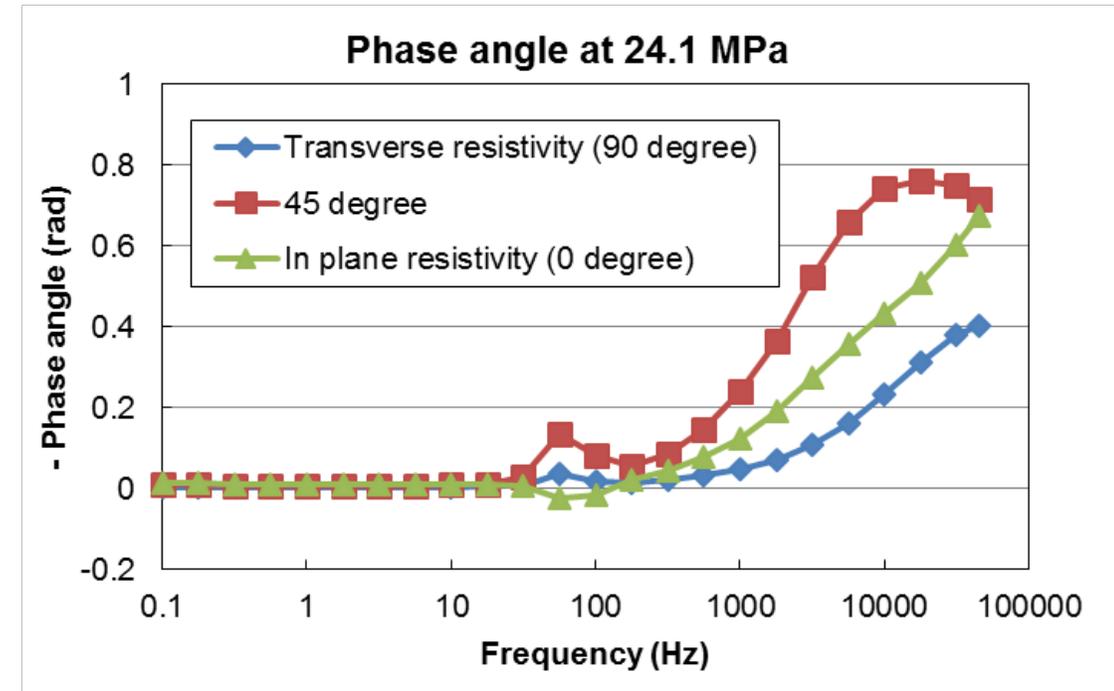
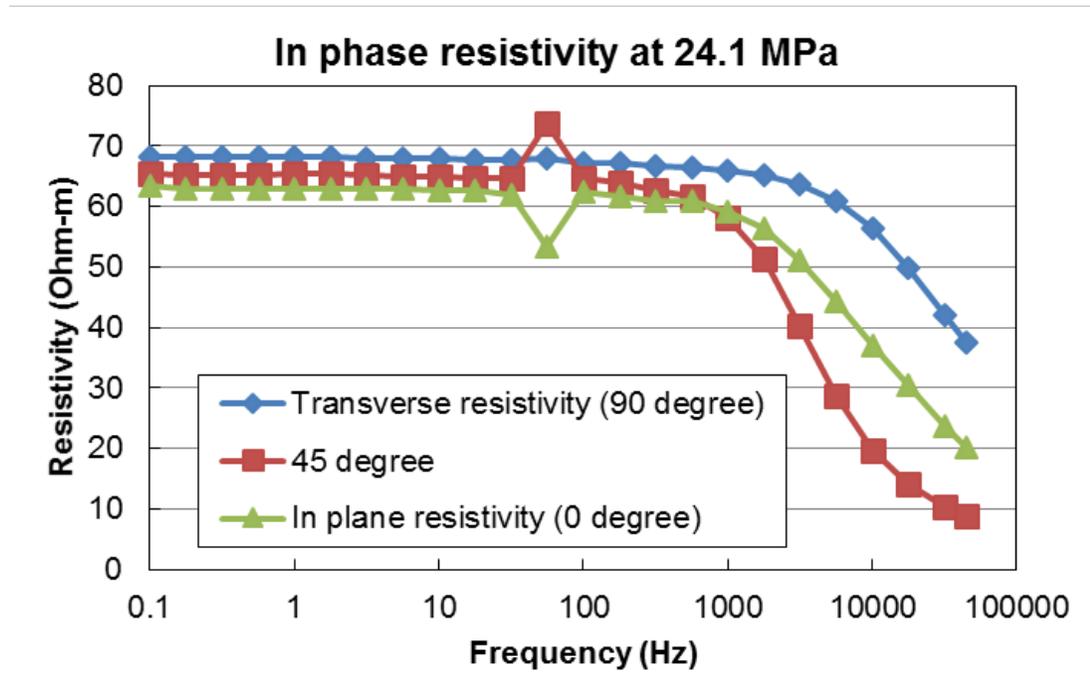


—●— Vp0   
 —▲— Vp45   
 —●— Vp90   
 —■— Vs0   
 —×— Vs45   
 —\*— Vs90



# COMPLEX RESISTIVITY – FREQUENCY DOMAIN

- In phase resistivity and phase angle of **preserved lower Austin Chalk sample** as function of frequency at 24.1 MPa (3000 psi)

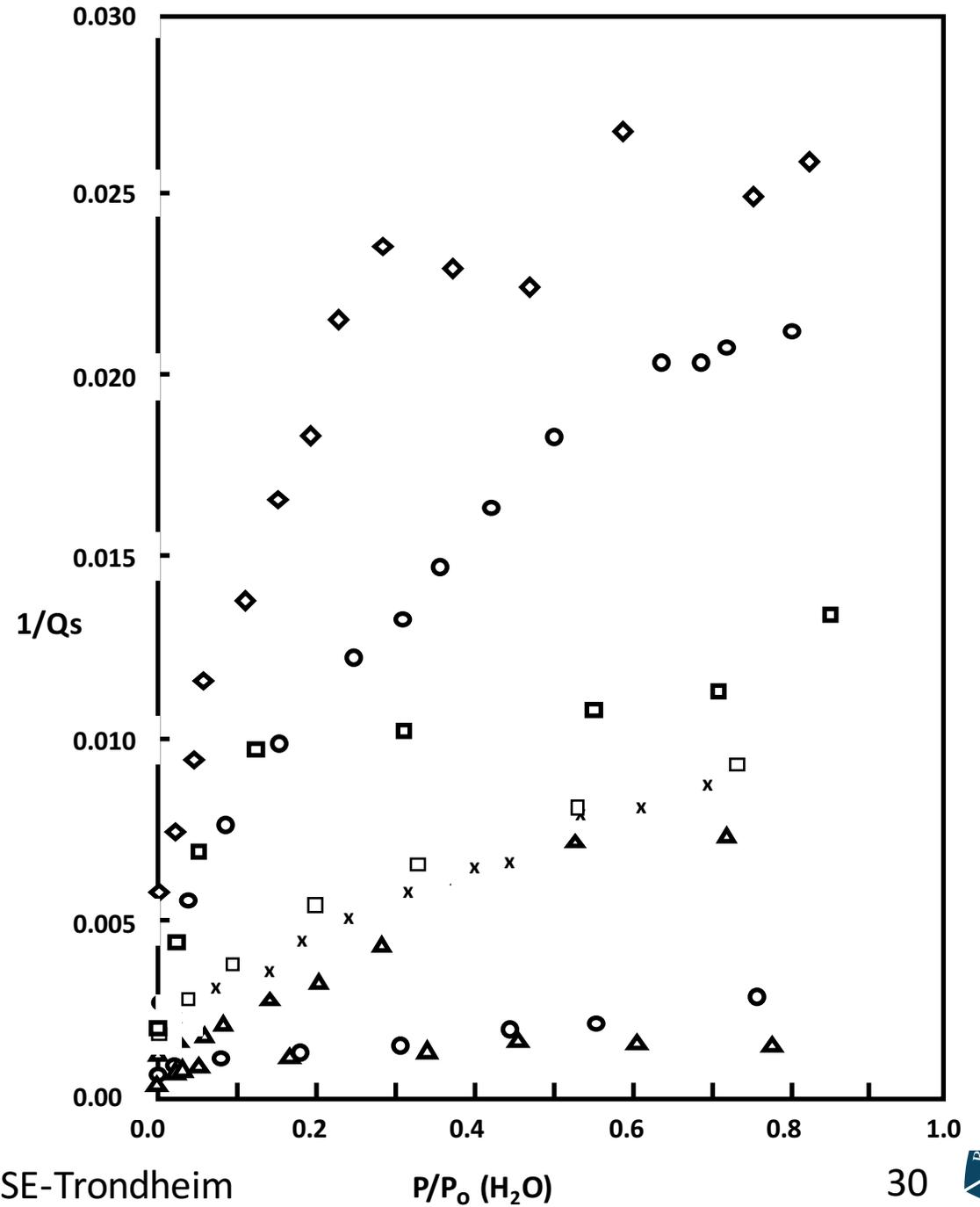


In phase resistivity anisotropy and phase angle anisotropy increase at high frequency (>1 kHz)

# EFFECT OF FLUIDS

-  Sioux Qtz
-  Tennessee Ss
-  Austin Chalk
-  Berea Ss
-  Wingate Ss
-  Indiana Ls
-  Coconino Ss
-  Boise Ss

Clark and Tittman, 1980



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# CSM CAPABILITIES

## 1. SEISMIC & ELECTRICAL PROPERTIES

- Multi-frequency anisotropic acoustic and electrical property measurements under pressure
- Multi-frequency acoustic measurements (max. 150,000 psi, 1000 °C)
- Uniaxial load frames and numerous ultrasonic equipment to measure at high P&T conditions

## 2. FLOW PROPERTIES

- Nano-Darcy permeability measurements
- Conventional poro-perm measurements
- Centrifuge to measure capillary pressures (in collaboration)

## 3. PORE SCALE MEASUREMENTS

- 2-MHz NMR system to measure cores
- Various types of porosity measurements





# SEM EQUIPMENT



## 4. QUANTITATIVE ANALYSES (including those with other departments)

- Scanning acoustic microscope up to 250 MHz (up to 10  $\mu\text{m}$  resolution)
- Micro-CT scanner (up to 10  $\mu\text{m}$  resolution)
- SEM; ESEM; FE-SEM, Nano-indentation system, ion mill (Material Science)
- QEMSCAN, SEM, XRD, Rock-Eval, and optical microscopy, (Geology)
- Open Column Liquid Chromatography (Petroleum Engineering)
- NMR, FTIR, GCMS; MBMS (Chemistry and Chemical Engineering)

## 5. PORE SCALE MEDDLING

- Subcritical sorption equipment with various gases, including moisture
- Equipment for high pressure sorption under construction
- Equipment for high pressure sorption under construction
- Pressure pulsing system (under construction)

CO / CO<sub>2</sub> Flooding system



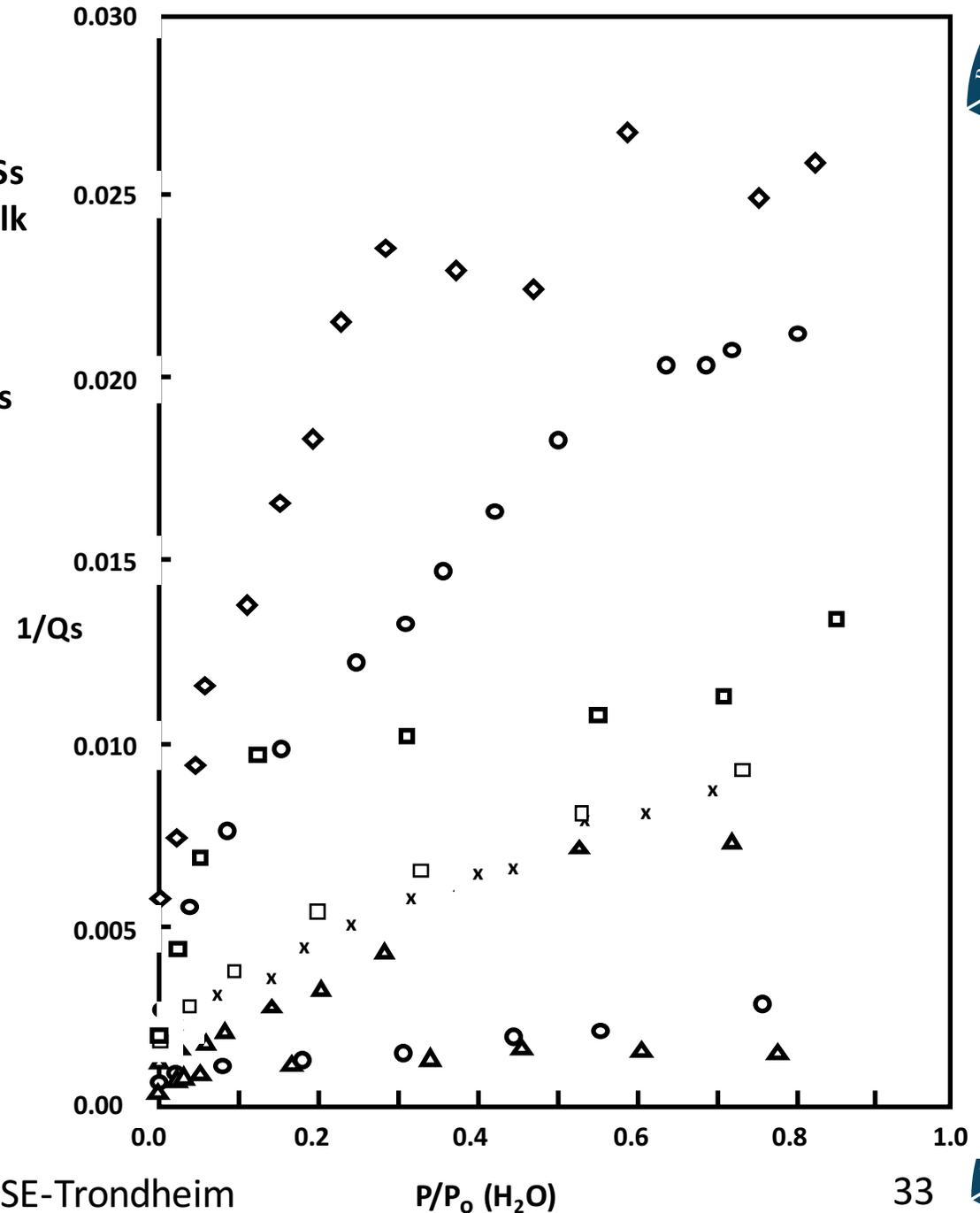


# EFFECT OF FLUIDS

Clark and Tittman, 1980

- Sioux Qtz
- Tennessee Ss
- Austin Chalk
- Berea Ss
- Wingate Ss
- Indiana Ls
- Coconino Ss
- Boise Ss

- Sioux Qtz
- Tennessee Ss
- Austin Chalk
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- Boise Ss



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$P/P_0$  (H<sub>2</sub>O)

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# BACKGROUND

- Carbon capture and storage in deep geological settings
- Caprock seals and prevents buoyant migration of CO<sub>2</sub>
  - Permeability of caprock ~ Nanodarcy
  - Permeability of tight-gas shales ~ Nano to Microdarcy
- CO<sub>2</sub> injection changes the state of stress in reservoir rocks and in caprocks
- **Could faults or fractures develop in caprocks that allow CO<sub>2</sub> transport and escape?**





# HYPOTHESIS AND OBJECTIVES

## *Hypothesis:*

- Mechanical damage to shales not necessarily = high permeability and high leak rates

## *Objectives:*

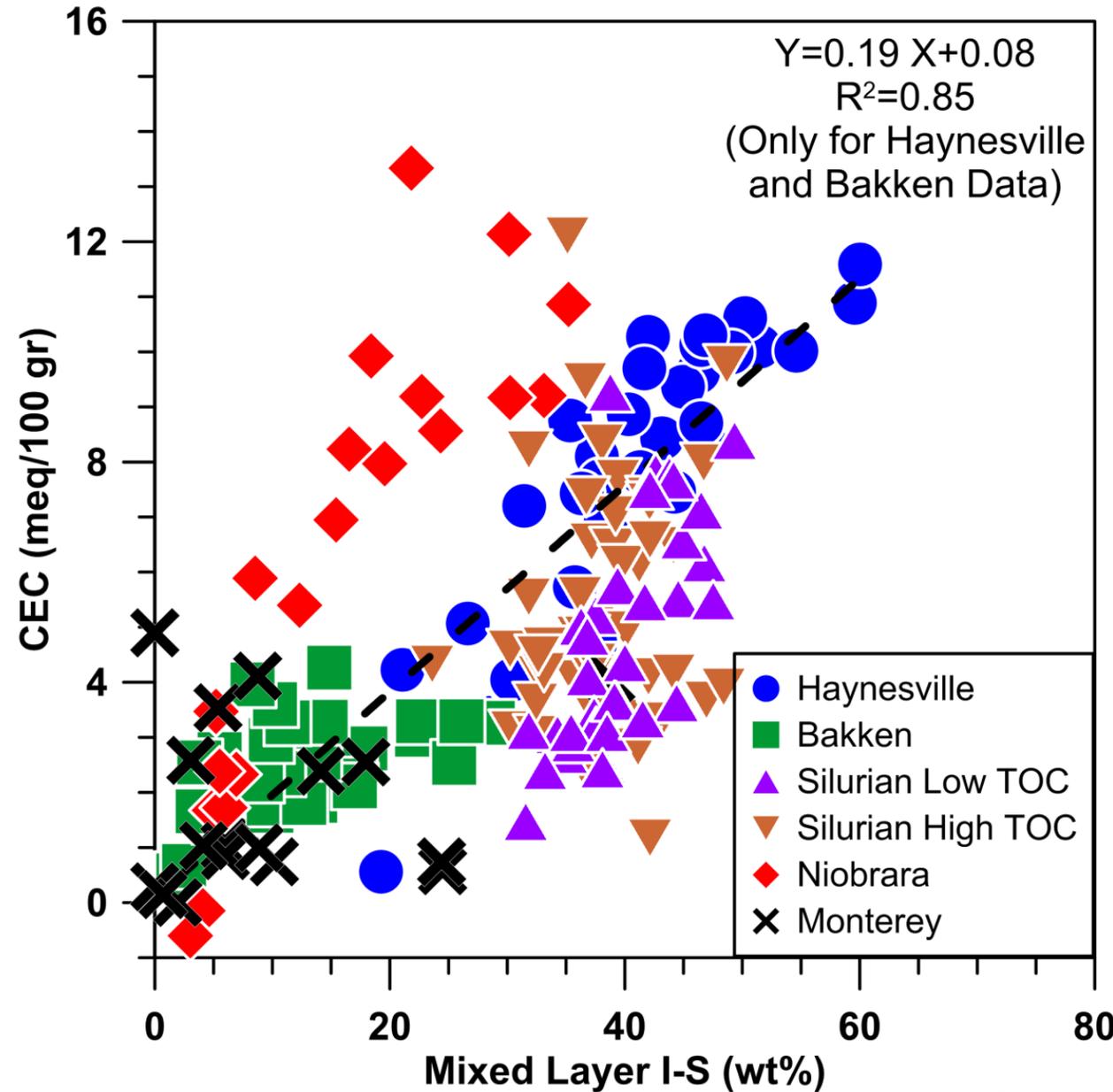
- Determine the behavior of intact and fractured caprocks when exposed to supercritical CO<sub>2</sub> at elevated pressures
- Quantify adsorption, strain and acoustic properties of shales with sorbed CO<sub>2</sub>
- Provide framework for monitoring, verification and accounting (MVA) efforts of CO<sub>2</sub> sequestration and its effect on caprock



# EFFECT OF CLAY AND ORGANIC MATTER

Prasad\_ROSE-Trondheim

*Saidian and Prasad, 2015*



April 2016

