# Characterizing and quantifying $CO_2$-fluid-shale interactions and pore changes

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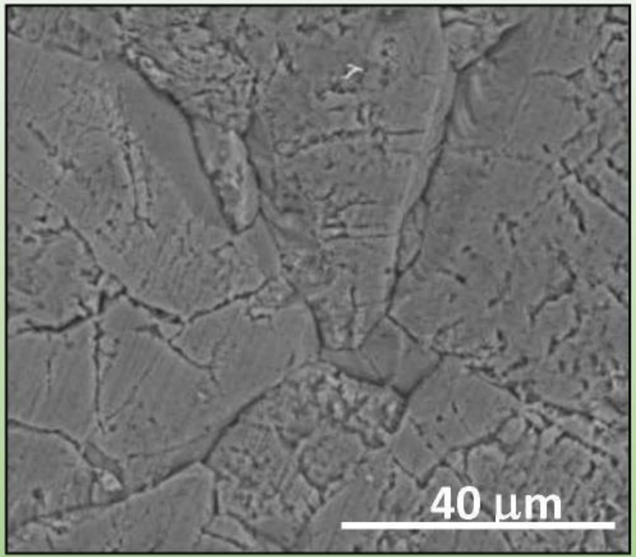
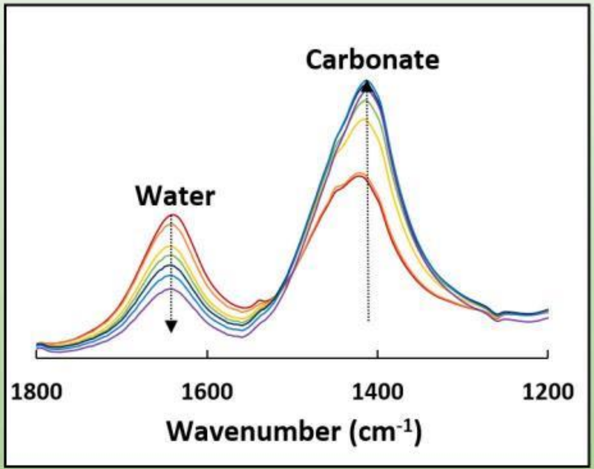
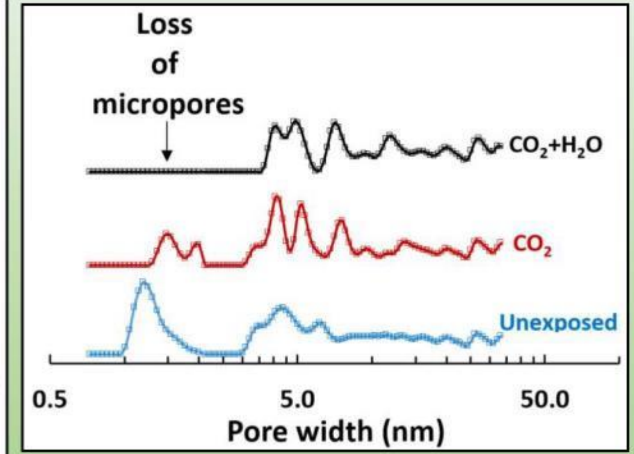
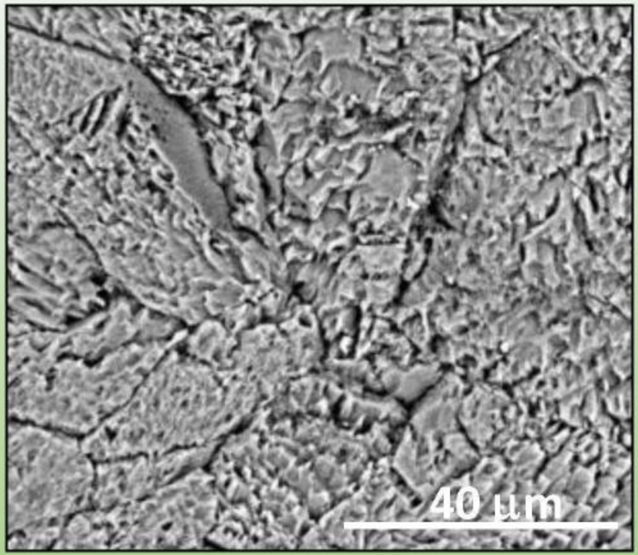
March, 31st 2019



# History of DOE $CO_2$ Storage Methods

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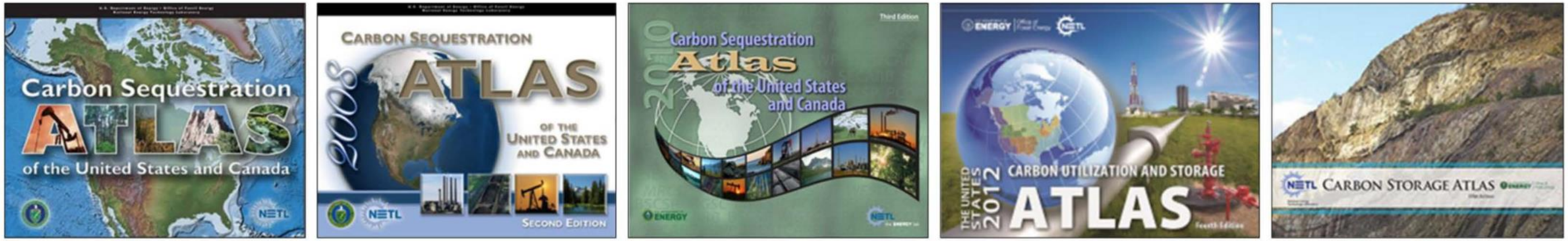
**Carbon Sequestration Atlas of the United States and Canada**




2007 – 2008 – 2009 – 2010 – 2011 – 2012 – 2013 – 2014 – 2015 – 2016 – 2017 – 2018 – 2019

- **2007–2008:** Method Development through RCSP's Working Groups
- **2011:** Initial Methodology for Saline, Coal, and Oil and Gas Reservoirs[1] (*Cited 127 times; Impact Factor of 3.7*)
- **2012:** Saline Method Comparative Analysis[2] (*cited 7 times; Impact Factor of 2.5*)
- **2013:** Saline Method Statistical Comparison[3] (*cited 25 times impact Factor of 3.7*)
- **2014:** Initial Methodology for Shale[4] (**cited 12 times** Impact Factor of 1.1)
- **2014:** Stochastic Modeling of Sedimentary Formations[5] (***cited 8 times;*** *Impact Factor of 6.1*)
- **2016:** Shale Method[6] (*cited 18 times; Impact Factor of 3.7*)
- **2016:** Saline Method Refinement[7] (*cited 8 times (Impact Factor of 3.7)*)
- **2016:** Development of $CO_2$-SCREEN Tool[8]
- **2017:** Shale Efficiency Factors[9] (*cited 3 times; impact Factor of 3.7*)
- **2018:** $CO_2$-SCREEN Oriskany Example[10] (*cited 1 time (Impact Factor of 3.7)*)
- **2019:** ROZ Storage Method & Efficiency Factors
- **2019:** Shale flow regimes

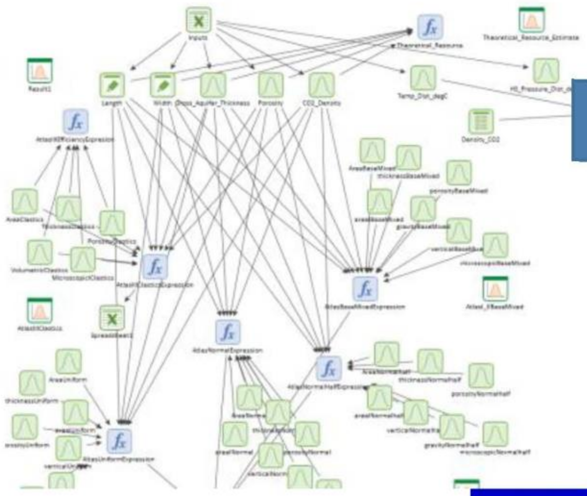
# A. Prospective $CO_2$ Storage in Shale Formations

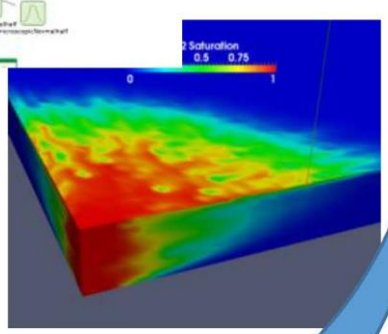
$$G_{CO_2} = A_t E_A h_g E_h \left[\rho_{CO_2} \phi E_\phi + \rho_{sCO_2} (1-\phi) E_S\right]$$

**Net effective formation volume**

**Efficiency of storage as free gas**

**Efficiency of storage in sorbed phase**

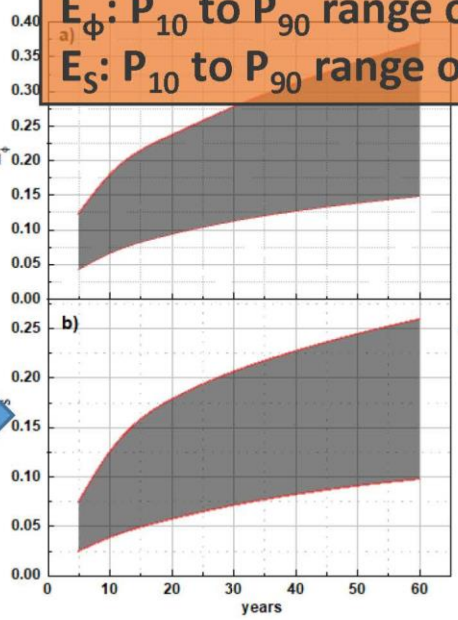





**$E_\phi$: $P_{10}$ to $P_{90}$ range of 0.15 to 0.36**
**$E_S$: $P_{10}$ to $P_{90}$ range of 0.11 to 0.24**

$E_\phi$

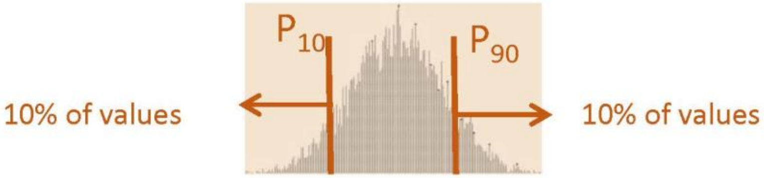
$E_S$




Log-odds stochastic approach

$E_A$ $E_h$ $E_\phi$ $E_S$

$$\frac{1}{(1+e^{(-E_A)})} * \frac{1}{(1+e^{(-E_h)})} * \frac{1}{(1+e^{(-E_\phi)})} * \frac{1}{(1+e^{(-E_s)})}$$



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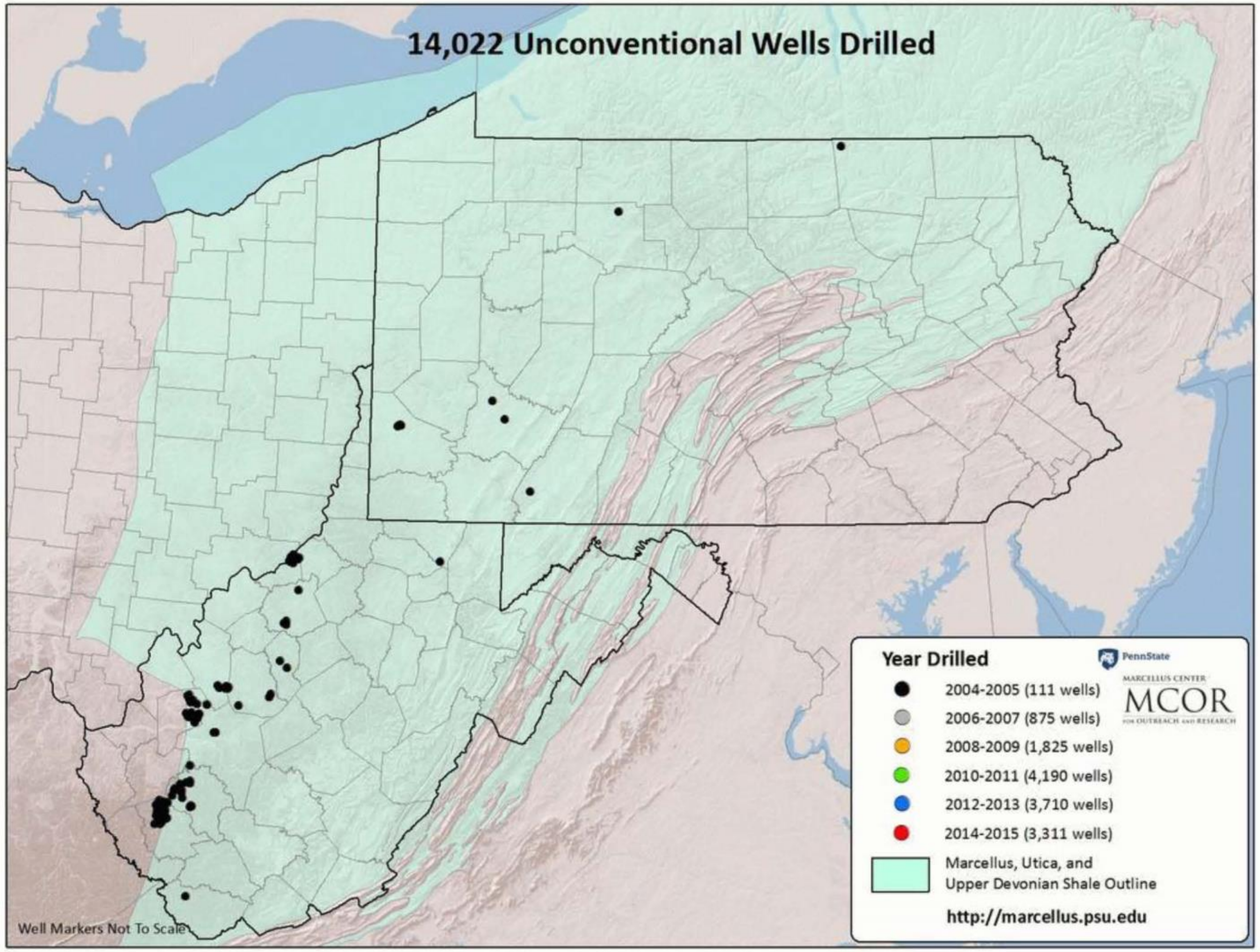
# Lower 48 states shale plays

# Motivation

- **How does fracturing fluid alter hydrocarbon production and $CO_2$ storage?**
- **Can $CO_2$ be used as a fracturing agent?**
- **Can $CO_2$ and surfactants extract hydrocarbons?**

- Hydraulic fracturing is implemented to produce hydrocarbons (over 14,000 permitted wells in Pennsylvania between 2004 and 2015
- 47 to 91% of the fracturing fluid remains in the subsurface
- Fracturing fluid can alter petrophysical characteristics:
  - Surface area
  - Porosity
  - Mineralogy
  - Permeability

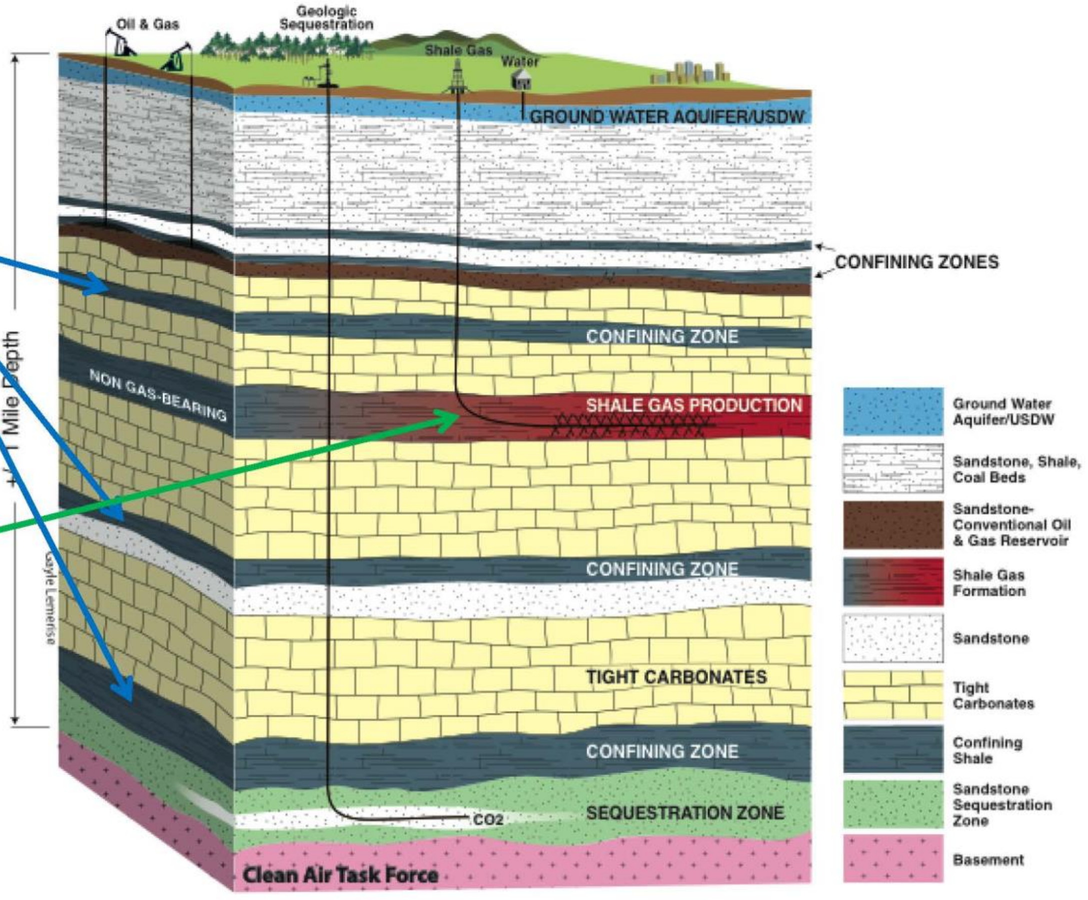


# Shale Formations in Relation to GCS

Shales as Seals

Shales as Storage Reservoirs

Hydrocarbon Production




http://www.catf.us/blogs/ahead/2012/06/07/fracking-and-geologic-carbon-storage-can-safely-coexist/

# Criteria for Storing $CO_2$ in Shale

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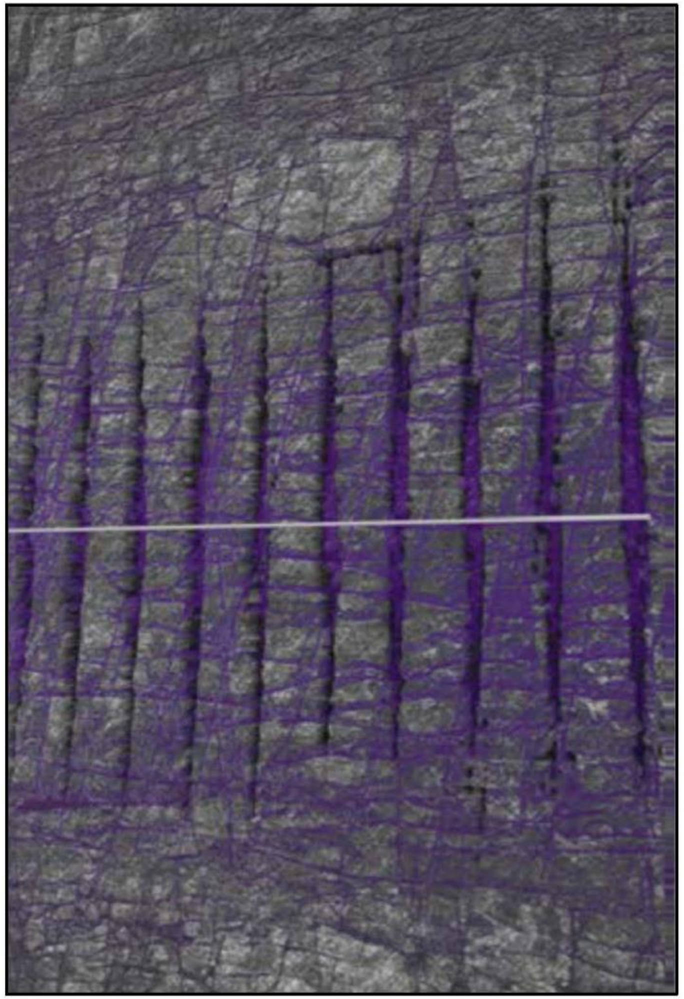
- The portion of shale formation being assessed for storage must be at depths sufficient for $CO_2$ to exist as a dense supercritical or liquid state (~800 m)
- An appropriate seal system must exist above the storage formation
- Hydrocarbons must have been produced from the shale formation via horizontal drilling and high-volume **hydraulic fracturing**

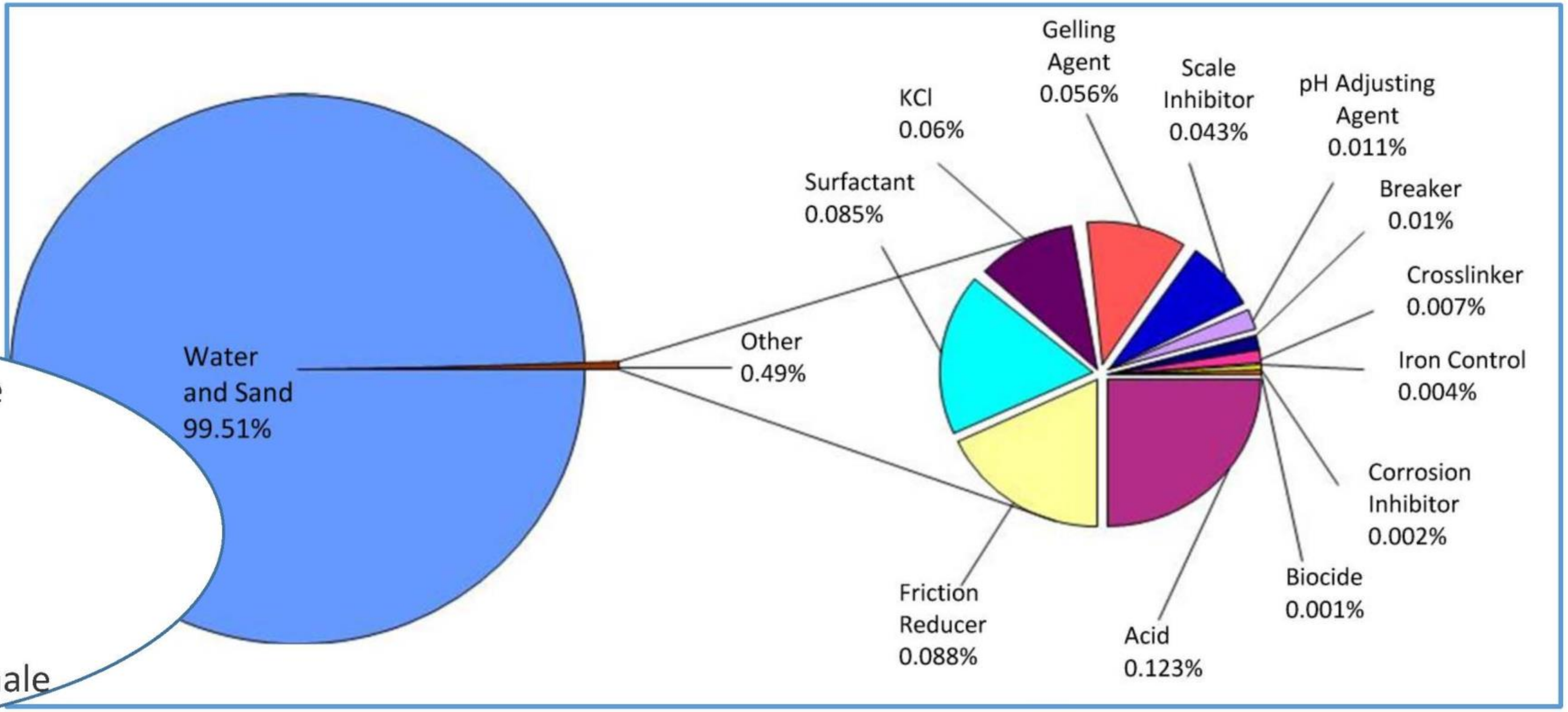




Levine et al., 2016; Sanguinito et al., 2018

# Geochemical Reactions in Shale

- **How does $CO_2$ interact with fracturing fluid left behind in shale and as a potential fracturing agent?**




1. Fracturing Fluid – Shale
2. $CO_2$-Shale
3. $CO_2$-Water-Shale
4. $CO_2$-Fracturing Fluid-Shale

- *Examining petrophysical characteristics including <u>reaction mechanism, precipitation, dissolution, surface area, porosity, permeability, and mineralogy</u> of the host formation*

# Research Capabilities

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Feature Relocation SEM/EDS


Static batch reactors for long-term experimentation

BET Pore Size Analysis


Quantitative Adsorption Isotherms

*In-situ* Fourier Transform Infrared Spectroscopy

NIST SAXS

# Samples



- **Utica Shale**
  - Stream outcrop (US-1)


US-1: Canajoharie, NY

- **Marcellus Shale**
  - Stream outcrop (MS-1)
  - Quarry exposure (MS-4)



MS-1: Le Roy, NY

MS-4: Seneca Falls, NY

- **Eagle Ford Shale**
  - Kocurek Industries (EF-1)

EF-1: Kocurek Industries

- **Barnett Shale**
  - Kocurek Industries (BS-1)

BS-1: Kocurek Industries

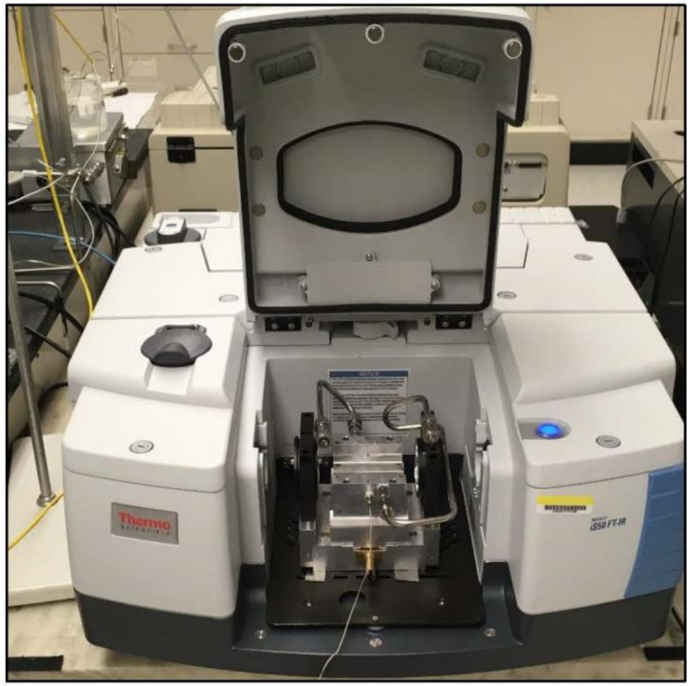
- **Clays**
  - Kaolinite
  - Illite
  - Illite-Smectite
  - Chlorite

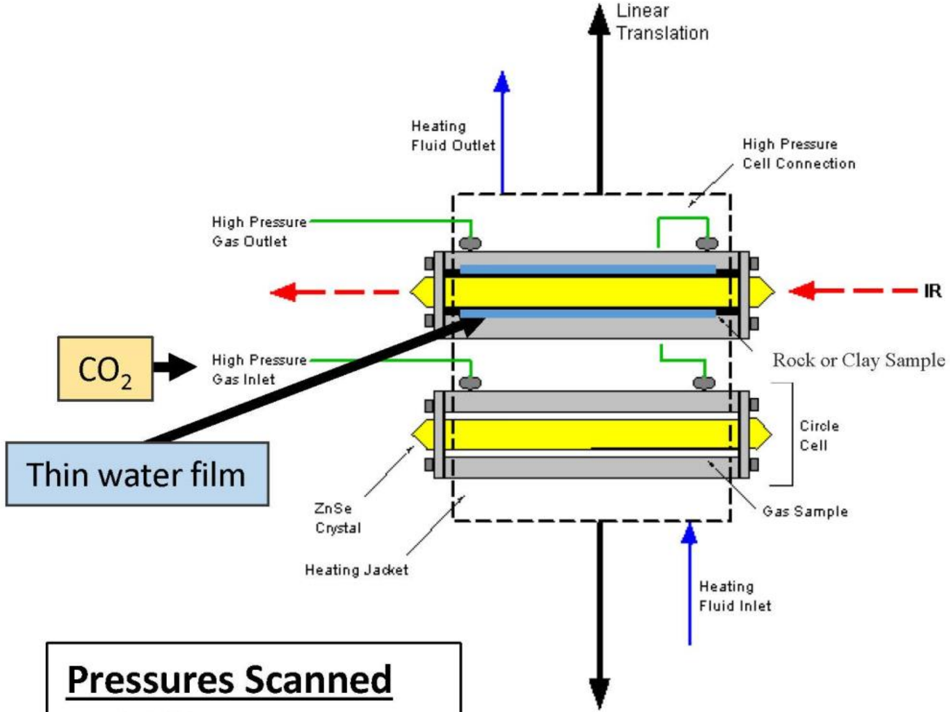
- **Kerogen**
  - Extracted from the New Albany Shale

# Fourier Transform Infrared Spectroscopy

## Conditions

- $CO_2$-Shale Interface
  - Samples prepared in methanol to avoid water film
  - 40°C and scanned at stepwise pressures from 0 to 1200 psig
- $CO_2$-Fluid-Shale Interface
  - Samples prepared in Millipore water to create water film
  - 40°C and scanned at stepwise pressures from 0 to 1200 psig






**Pressures Scanned**
- 0 PSI
- 50 PSI
- 100 PSI
- 400 PSI
- 800 PSI
- 1200 PSI

# IR Results: Dry $CO_2$

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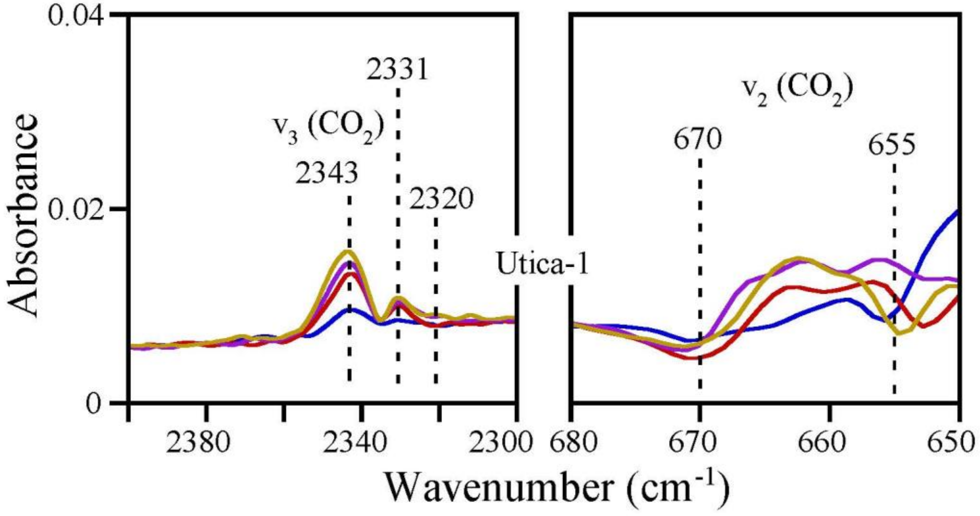
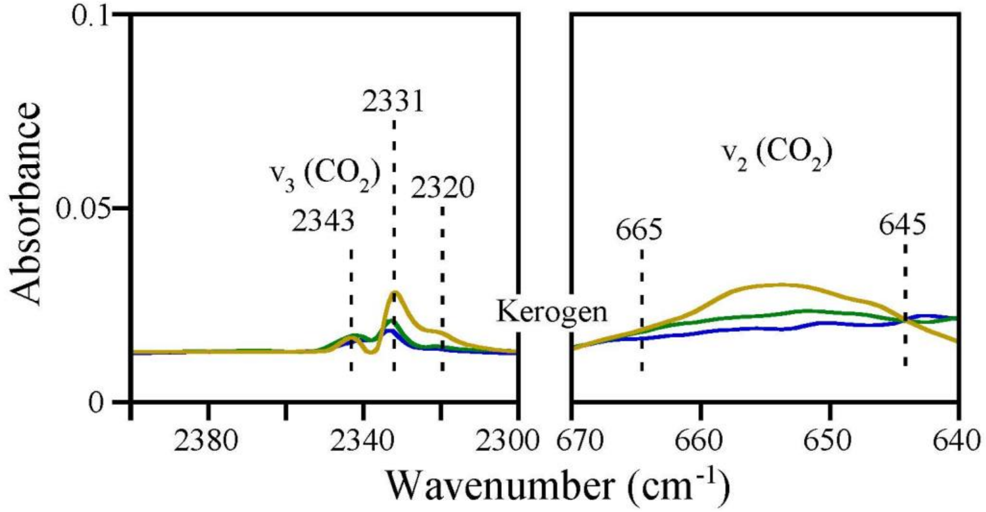
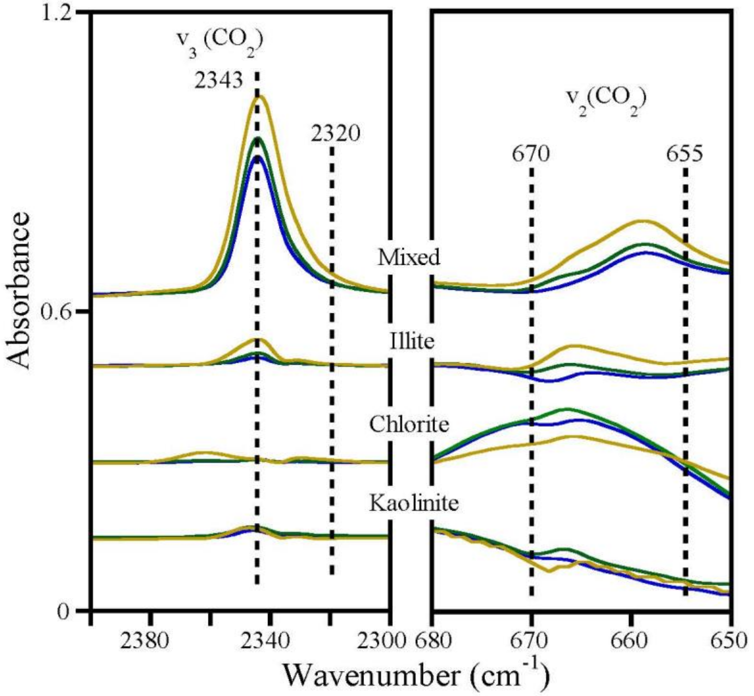


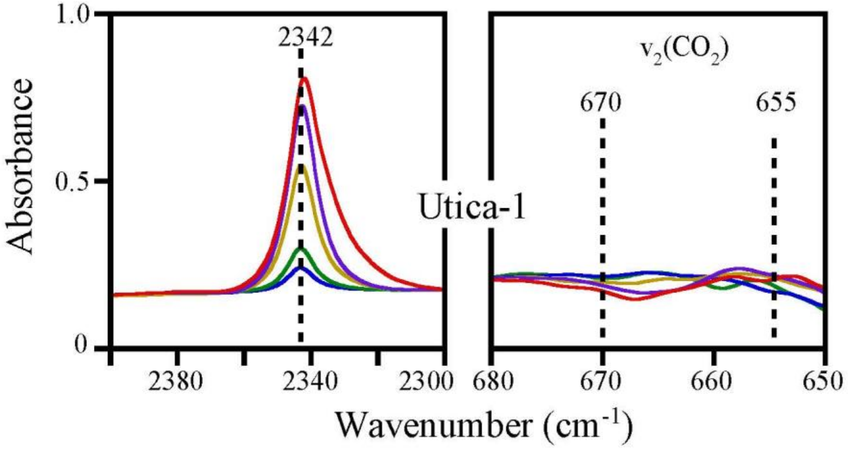



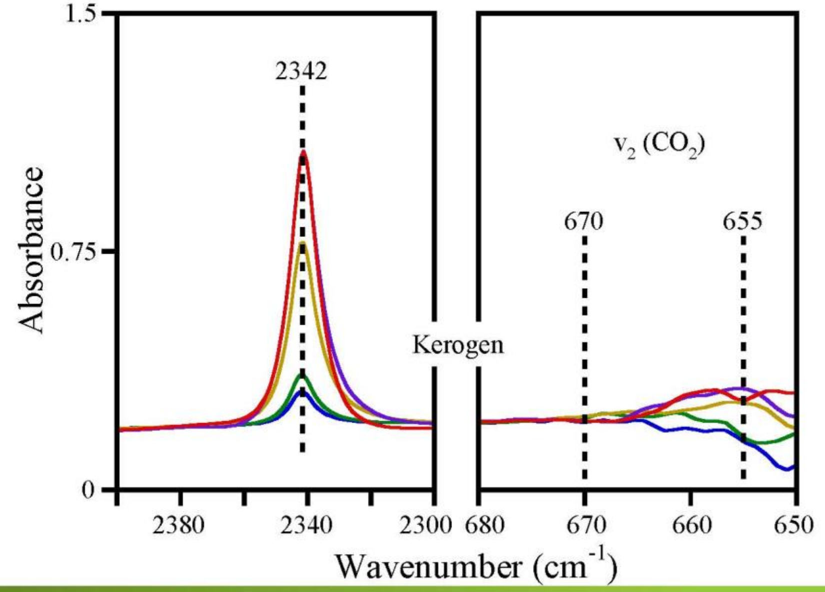



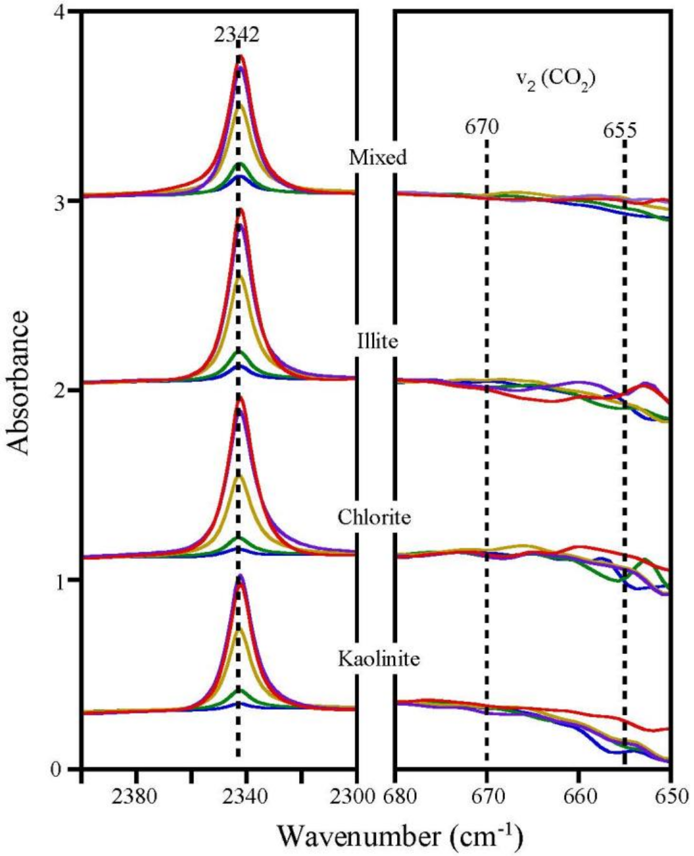

**$CO_2$ sorption occurs in:**
- Micro-porosity of the organic fraction
- Surfaces and internal layers of clay minerals

| Sample | IR Frequency ($cm^{-1}$) | Spectral Assignment |
|---|---|---|
| Utica Shale | 2343, 2331 | Organic and Inorganic |
| Illite-Smectite | 2343 | Inorganic |
| Illite | 2343 | Inorganic |
| Chlorite | 2343 | Inorganic |
| Kaolinite | 2343 | Inorganic |
| Kerogen | 2331 | Organic |

# IR Results: Water + $CO_2$



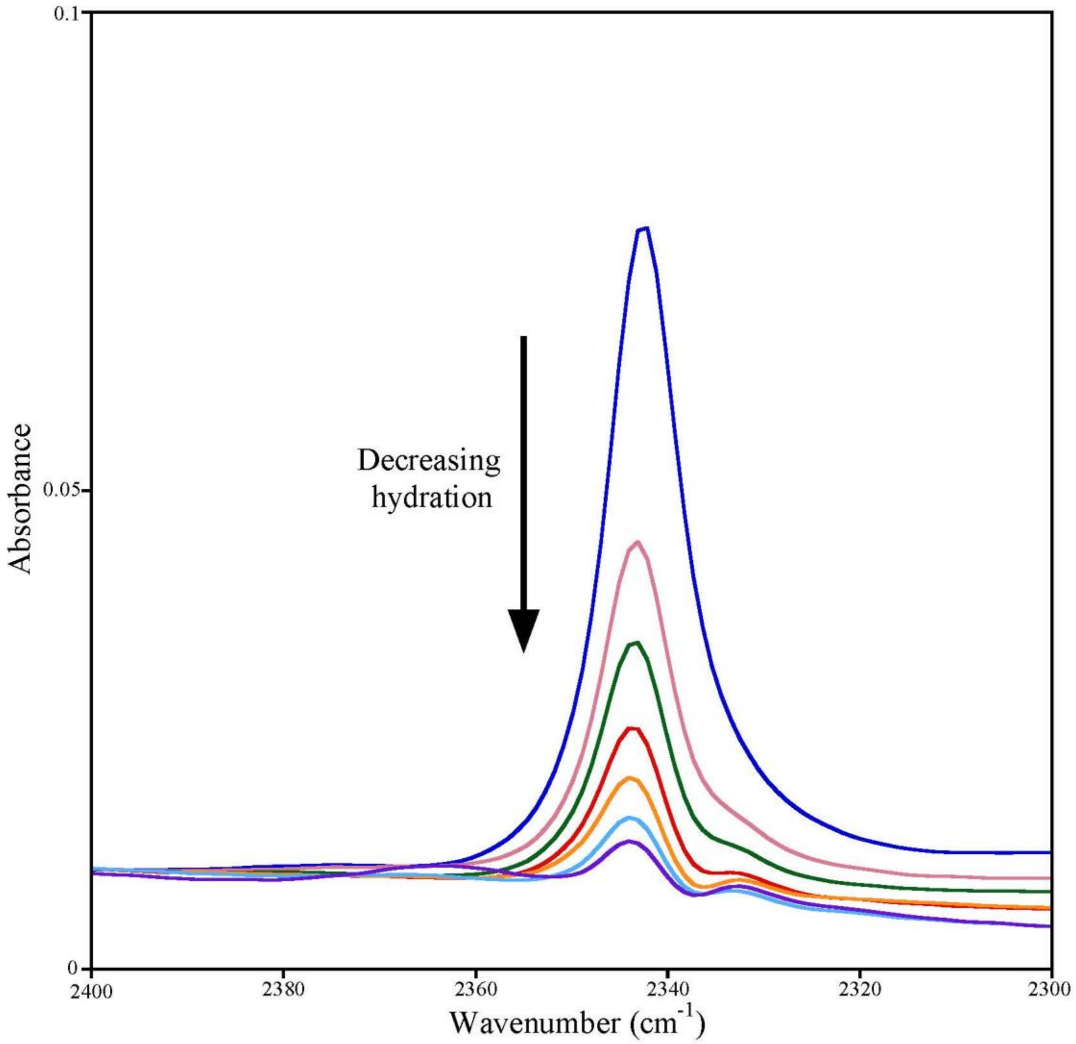




$CO_2$ dissolution in water occurs regardless of sample material

| Sample | IR Frequency ($cm^{-1}$) | Spectral Assignment |
|---|---|---|
| Utica Shale | 2342 | $CO_2$ Dissolution |
| Illite-Smectite | 2342 | $CO_2$ Dissolution |
| Illite | 2342 | $CO_2$ Dissolution |
| Chlorite | 2342 | $CO_2$ Dissolution |
| Kaolinite | 2342 | $CO_2$ Dissolution |
| Kerogen | 2342 | $CO_2$ Dissolution |

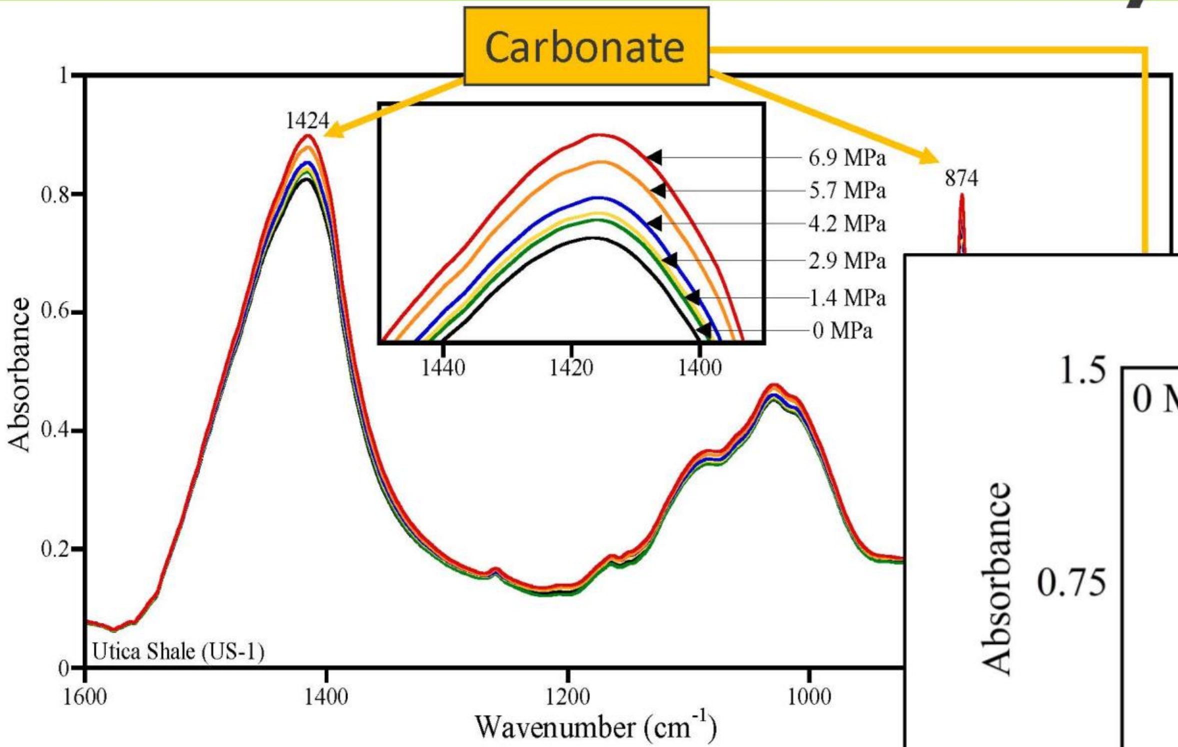
# IR Results: Wet to Dry




**Slowly dried sample while collecting IR Scans**

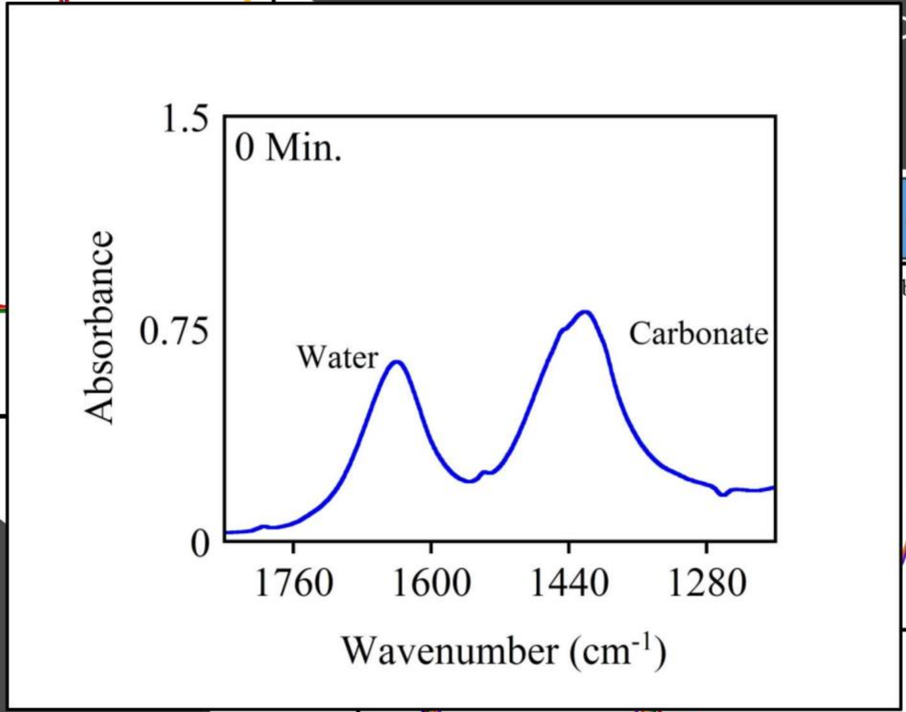
- **Wet Peak**
  - Symmetrical centered around 2342
- **Dry Peak**
  - Centered around 2343 with a shoulder and second peak centered around 2331

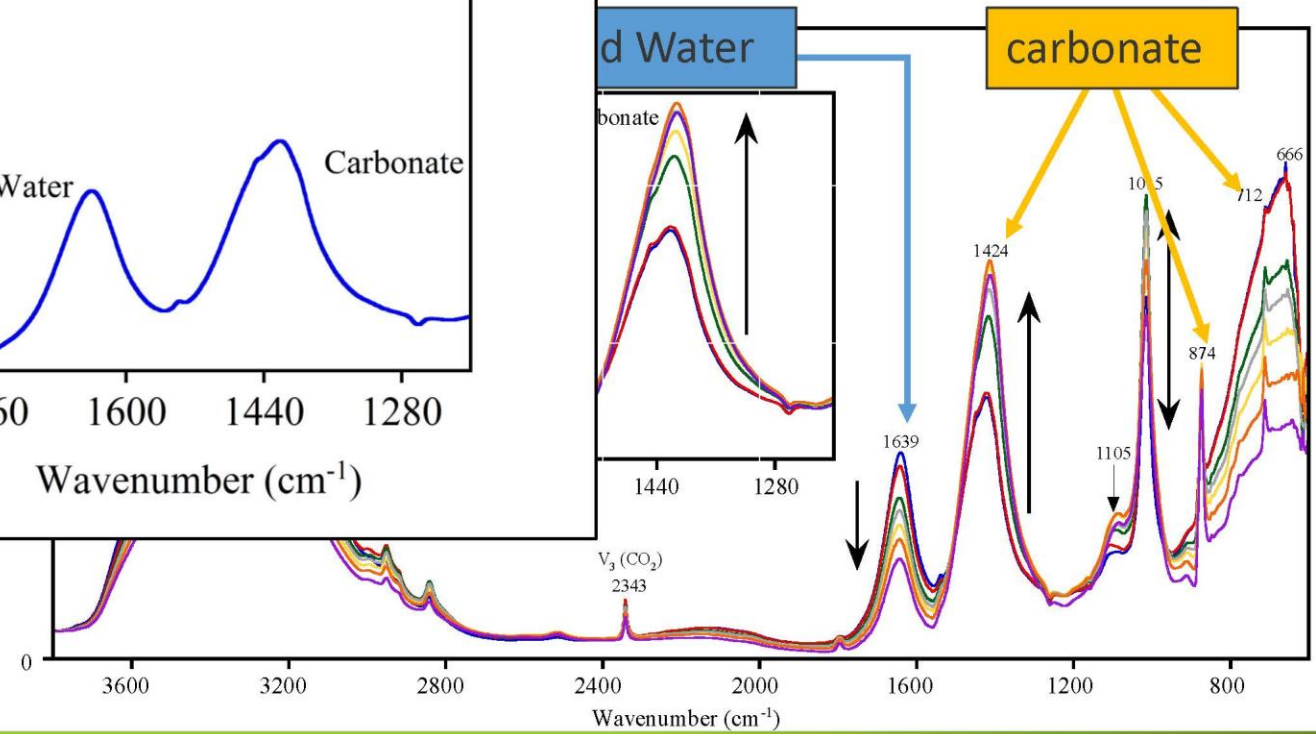
# IR Carbonate Chemistry




## $CO_2$-Shale

- Overall - intensity of the carbonate
creased with pressure
observed




## $CO_2$-Fluid-Shale

- Indicate carbonate formation and dissolution and mineral dissolution

# Feature Relocation SEM

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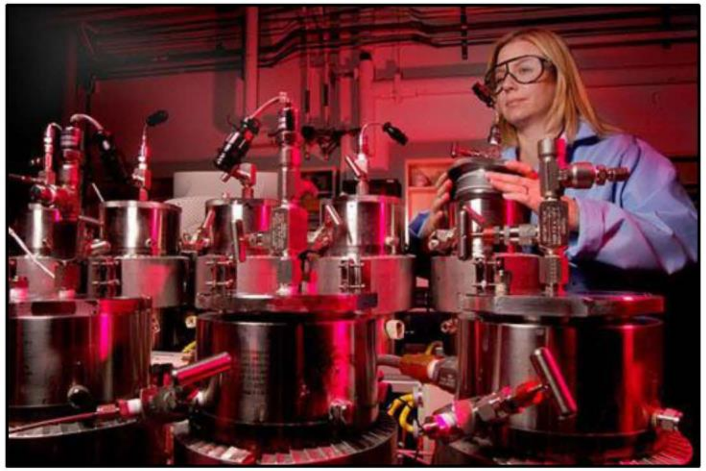
## Procedure



- Multiple sites selected and imaged on pre-exposed shale sample
- Sample placed in an autoclave that was pressurized with dry $CO_2$ for 14 days (40°C and 1500 PSI)
- Initial sites were relocated and reimaged
- Sample placed in an autoclave with Millipore water and pressurized with dry $CO_2$ for 14 days (40°C and 1500 PSI)
- Initial sites were relocated and reimaged

# SEM Results: Utica Shale

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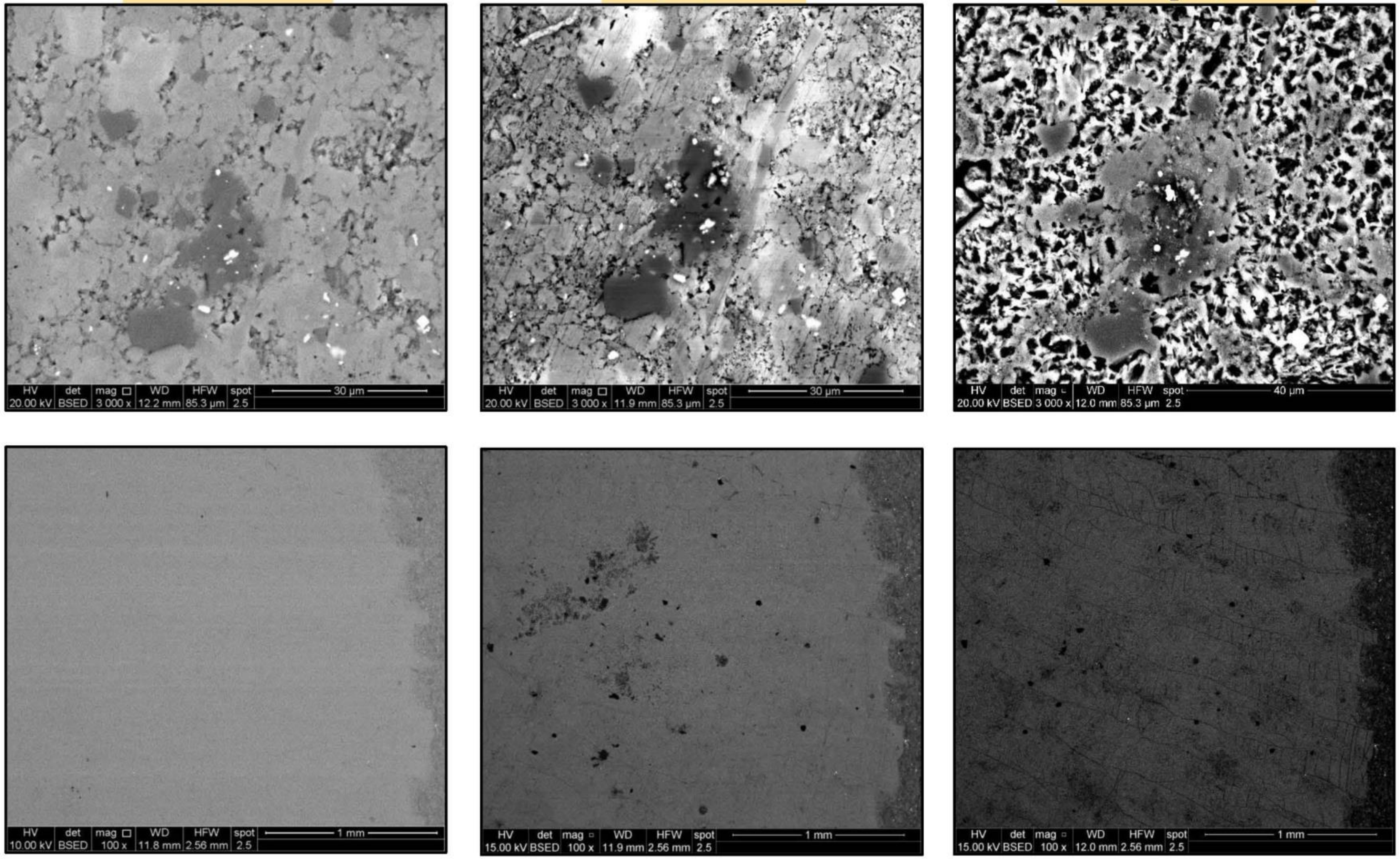
Pre-Exposure | $CO_2$ Exposure | Wet $CO_2$ Exposure

Site 1

Site 2



| Sample ID | Total Carbon | |
|---|---|---|
| | Carbon (%) | Std. Dev. |
| US-1 | 9.86 | 0.08 |
| MS-1 | 6.64 | 0.21 |
| MS-4 | 14.7 | 0.2 |

| Sample ID | Total Inorganic Carbon | |
|---|---|---|
| | Carbon (%) | Std. Dev. |
| US-1 | 9.41 | 0.14 |
| MS-1 | 0.13 | 0.06 |
| MS-4 | 5.5 | 0.06 |

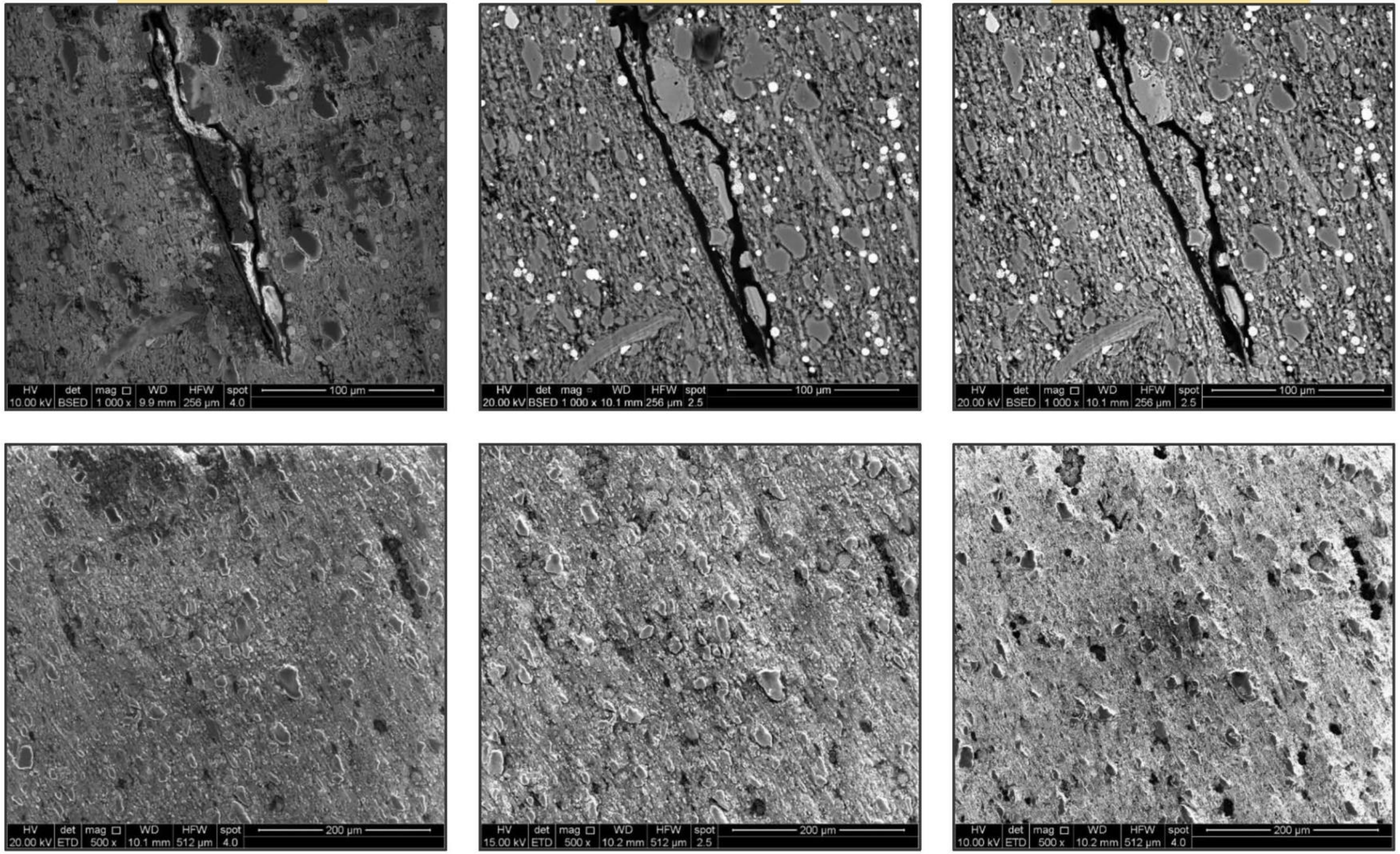
| Sample ID | Total Organic Carbon | |
|---|---|---|
| | Carbon (%) | Std. Dev. |
| US-1 | 0.45 | 0.17 |
| MS-1 | 6.51 | 0.22 |
| MS-4 | 9.2 | 0.6 |

# SEM Results: Marcellus Shale

Pre-Exposure | $CO_2$ Exposure | Wet $CO_2$ Exposure

Site 1

Site 2




| Sample ID | Total Carbon | |
|---|---|---|
| | Carbon (%) | Std. Dev. |
| US-1 | 9.86 | 0.08 |
| MS-1 | 6.64 | 0.21 |
| MS-4 | 14.7 | 0.2 |

| Sample ID | Total Inorganic Carbon | |
|---|---|---|
| | Carbon (%) | Std. Dev. |
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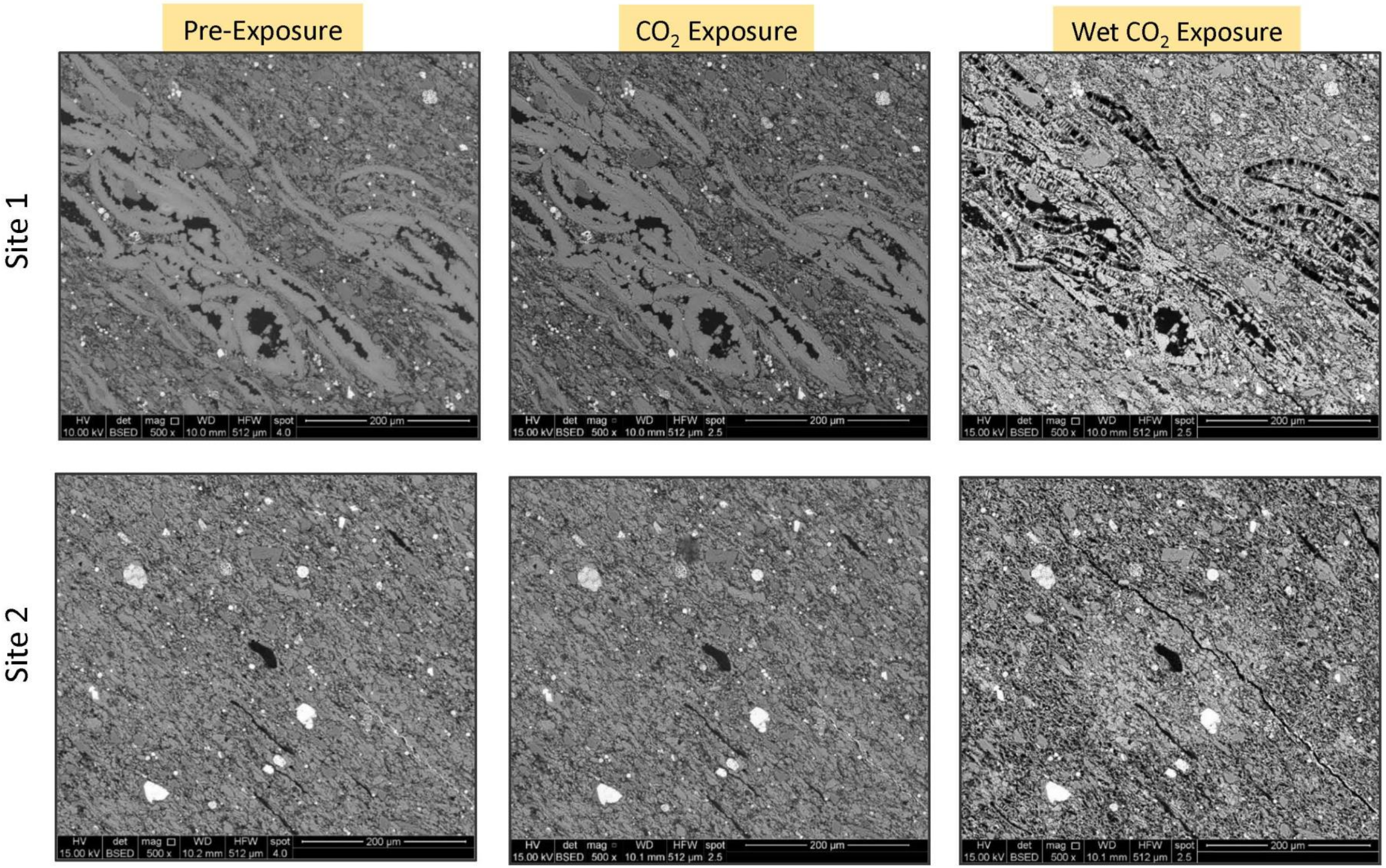
# SEM Results: Marcellus Shale

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# SEM Image Analysis

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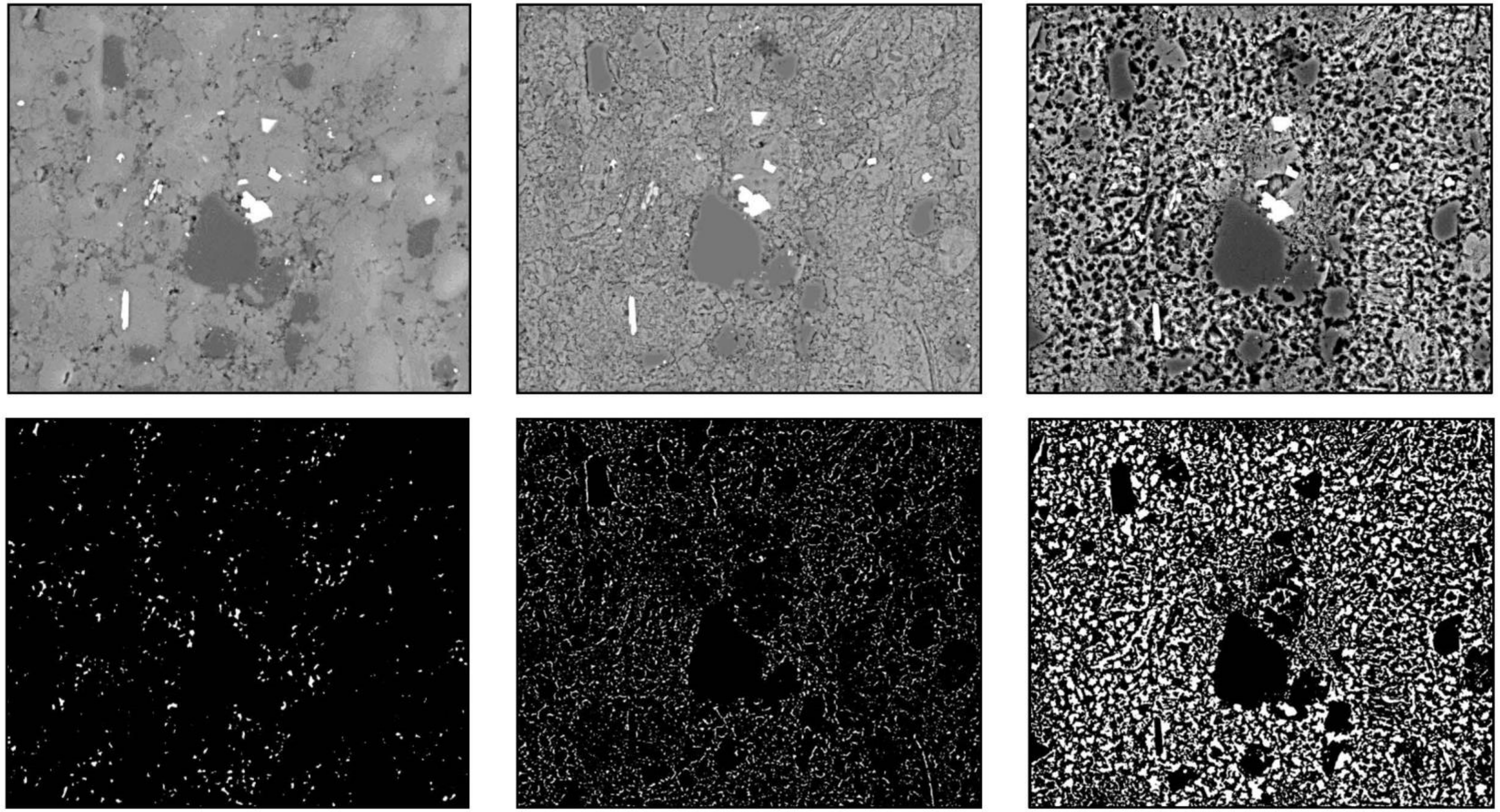
Utica Shale (US-1)

Unexposed | $CO_2$-Exposed | $CO_2 + H_2O$ - Exposed

A

B



Porosity = 1.8% | Porosity = 7.6% | Porosity = 33%

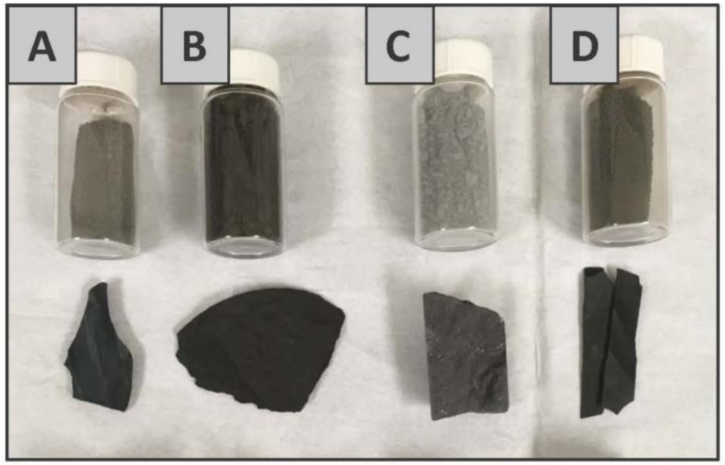
# Pore Size Analysis

**Brunauer-Emmett-Teller (BET)**

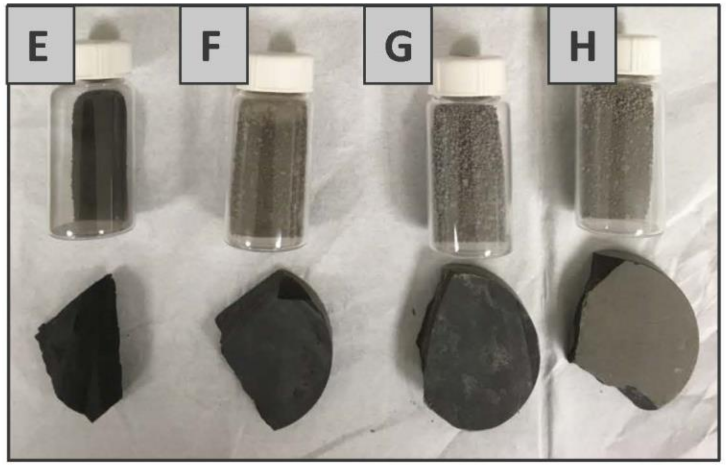
- Autosorb 1-C Analyzer
- CO2 Adsorption
  - 0.3 to 0.8 nm pores
- N2 Adsorption
  - 1 to 35 nm pores

**Mercury Intrusion**

- Hg Porosimeter
  - 3-1,000,000 nm pores




A: Utica Shale (Outcrop)
B: Utica Shale (Prod. Zone)
C: Utica Shale (At Depth)
D: Marcellus Shale
E: Marcellus Shale
F: Eagle Ford Shale
G: Mancos Shale
H: Barnett Shale



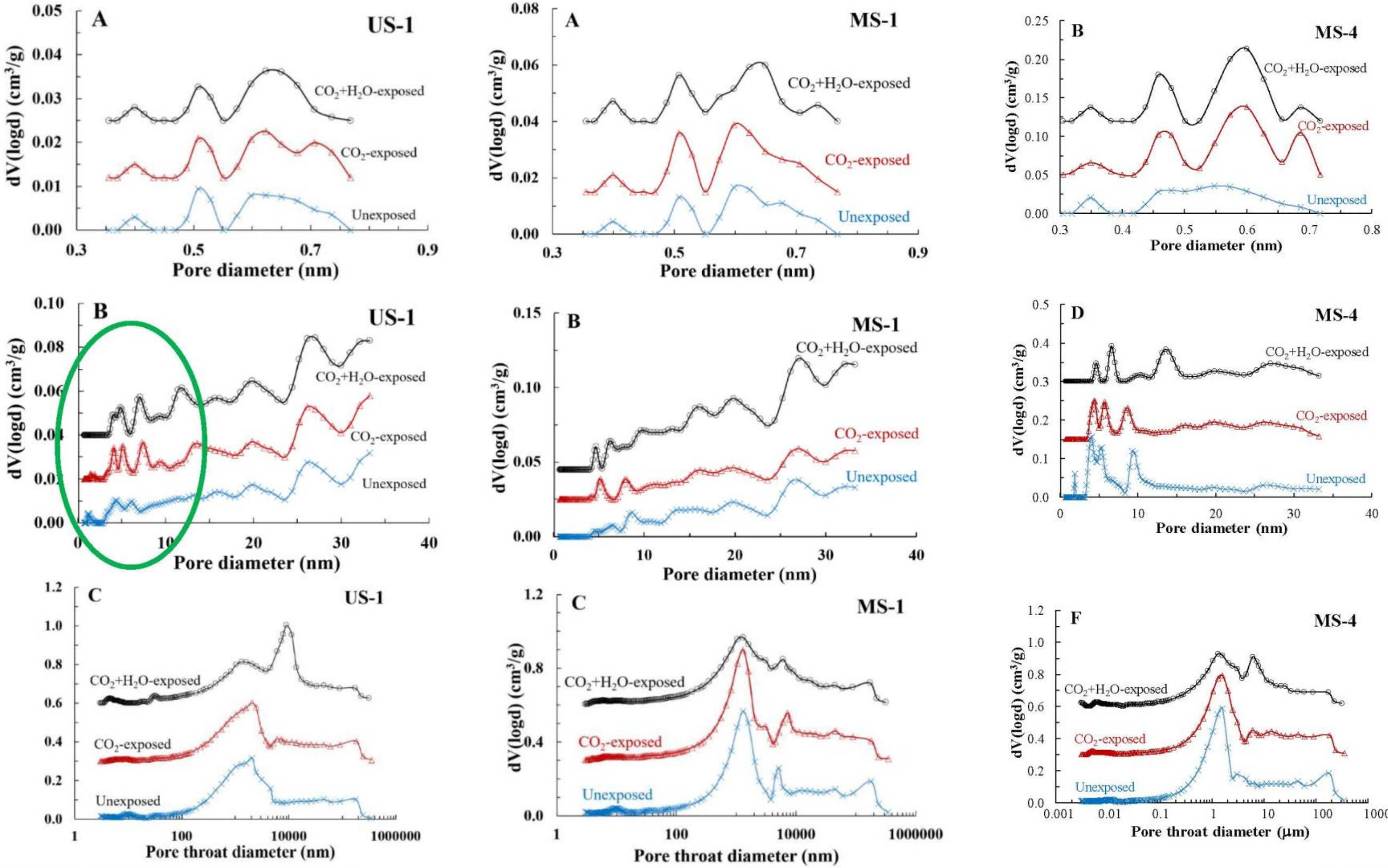
# Pore Size Analysis Results

Utica-1 | Marcellus-1 | Marcellus-4

CO2-PSD

N2-PSD

Hg-PSD




## $CO_2$/Dry Shale:

- Pore size changes from micro- to meso-scale

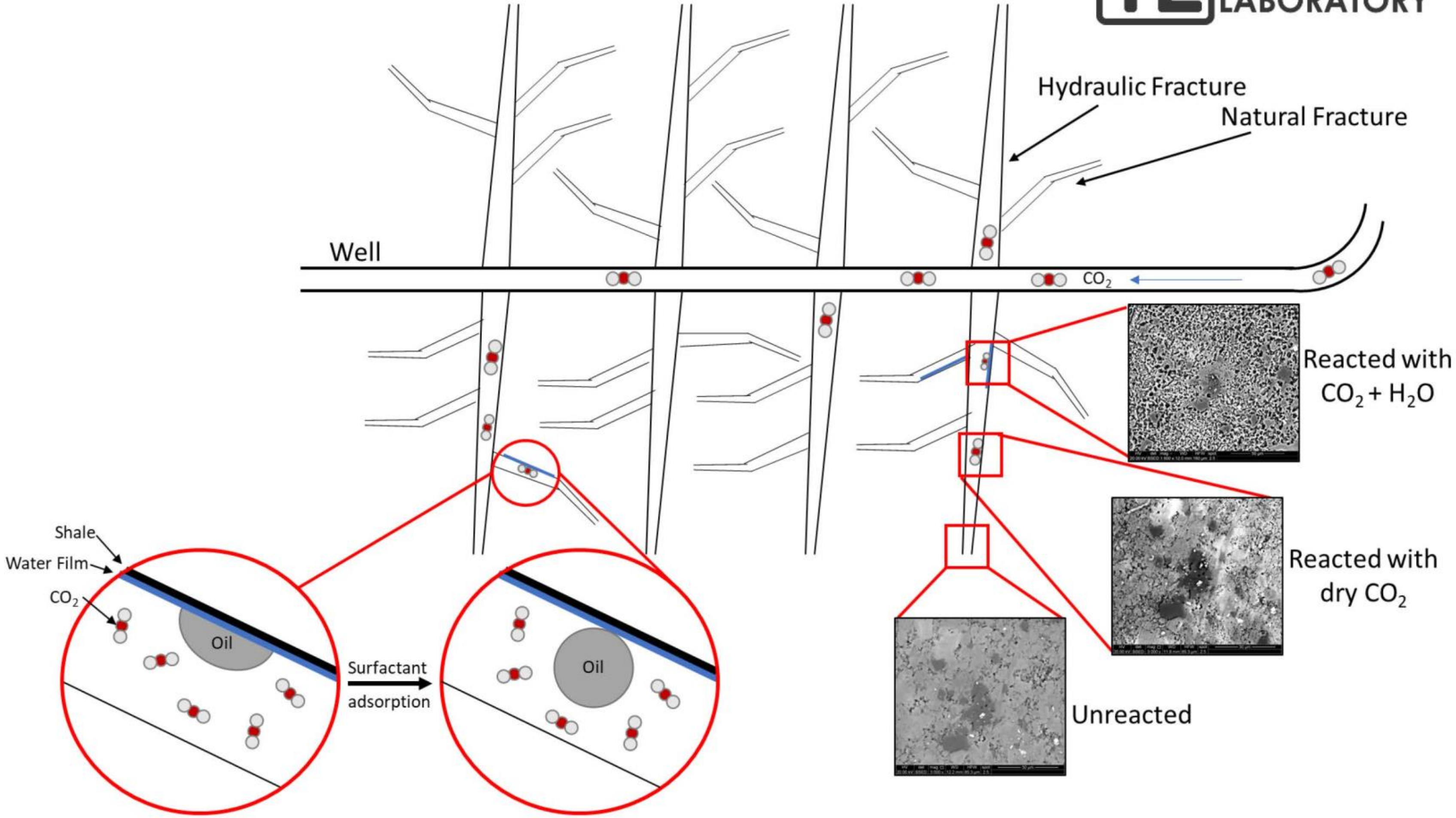
## $CO_2$/Wet Shale:

- Decrease in micro-pores

# Shale-CO2 Interactions and Oil Mobilization

- **Additives dissolved in the $CO_2$ or frack fluid can adsorb on oil-wet shale surfaces and make the surface more oil-phobic, thereby promoting the removal of oil from the shale**

- **Examine effect of chemical reactivity coupled with water issue**




**Without Surfactant**
Shale is originally oil-wet

**With Surfactant**
Shale becomes oil-repellent

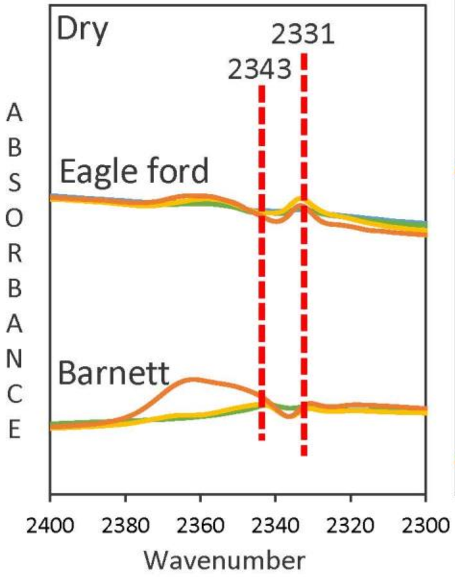
# Key Findings

**NETL discovered that the chemical composition of shale has a major effect on $CO_2$-shale interactions**

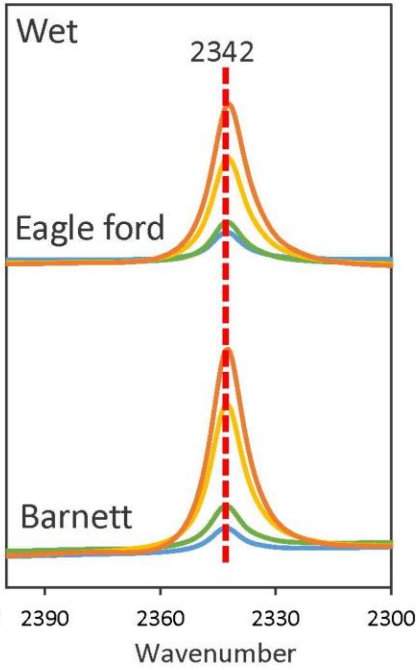
- When *carbonate-rich* Utica Shale samples were exposed to $CO_2$ and water, significant alterations in pore sizes were observed.
  - $CO_2$ and water reactions in carbonate rich shales increases porosity at the meso-scale while decreasing porosity at the micro-scale.

- When *silicate-rich* Marcellus shale samples were exposed to $CO_2$ and water, the pores were unchanged
  - Moderate increases in fracture sizes were observed.

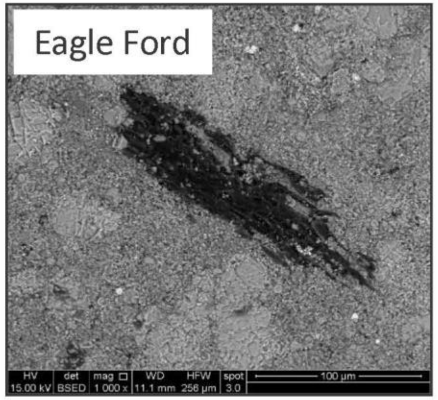
# Eagle Ford and Barnett Preliminary Results




CO$_2$ interaction with clays and kerogen




CO$_2$ Dissolution in water




Before Exposure

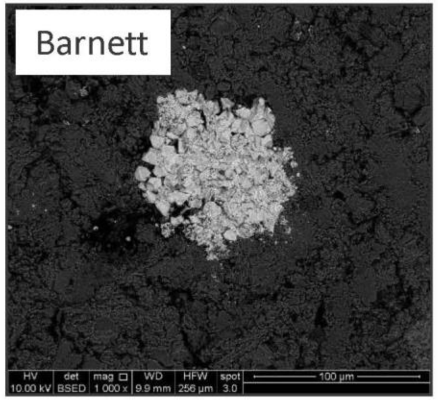



Image Coming Soon

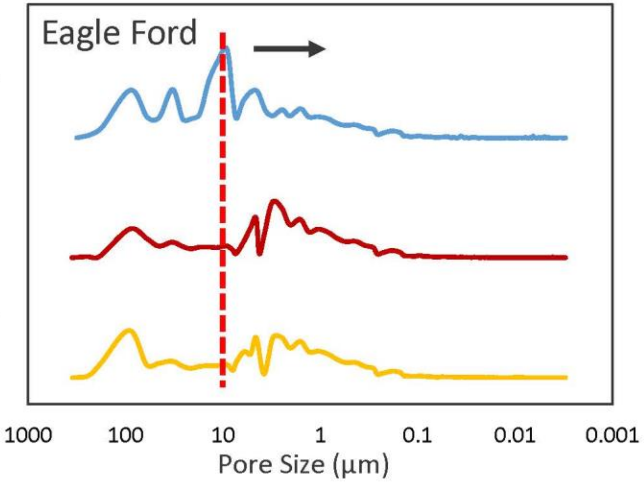
Image Coming Soon

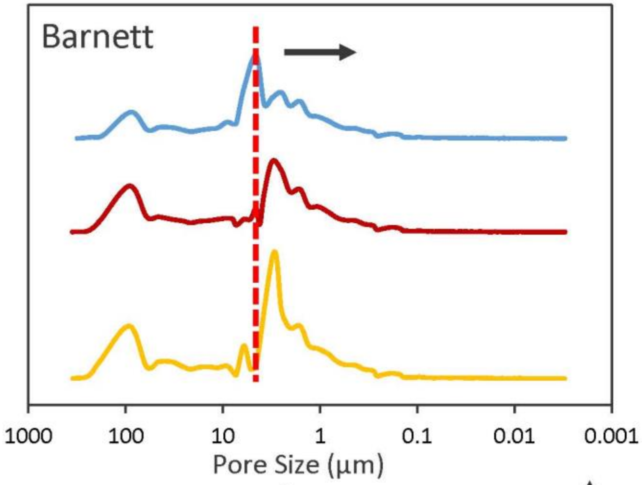
After CO$_2$

After CO$_2$ + H$_2$O

Image Coming Soon

Image Coming Soon




Large Pores = ↓ Small Pores = ↑

**Major Data Gap**: What is the influence of water on oil mobilization via CO$_2$ flooding?

# Next Steps

- Further investigate pore changes and quantify if these *changes impact flow pathways*
  - Pore changes from reaction with
    - $CO_2$
    - $CO_2$/fluid (water, brine, and fracturing chemicals)
  - Flow experiments in progress
- Can SANS provide more details on matrix scale porosity changes?

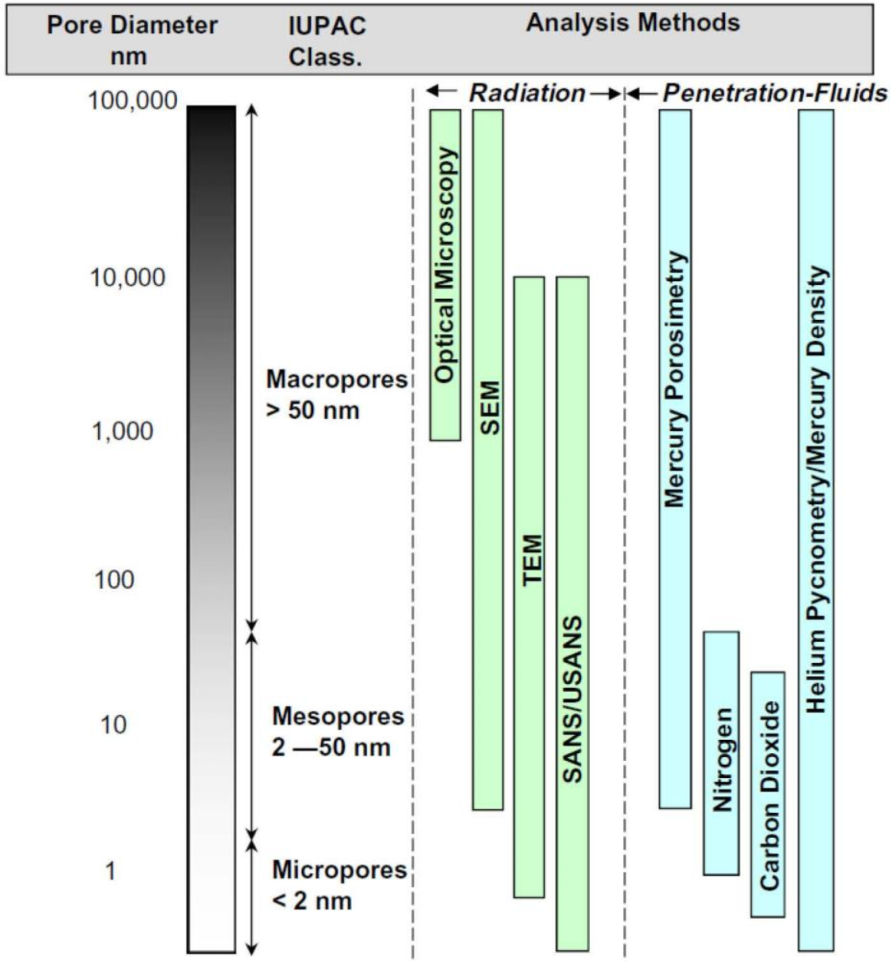
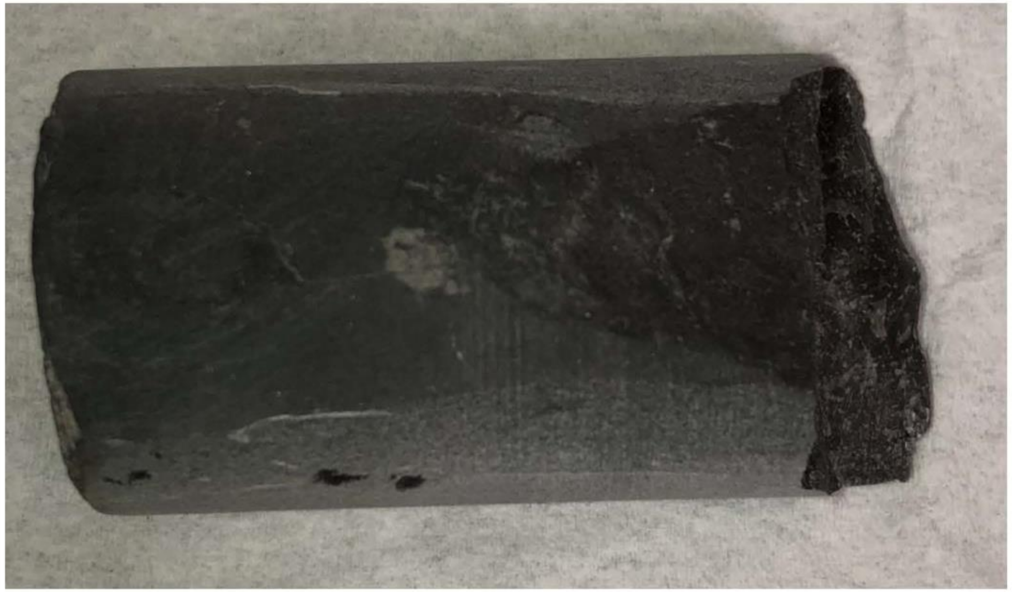


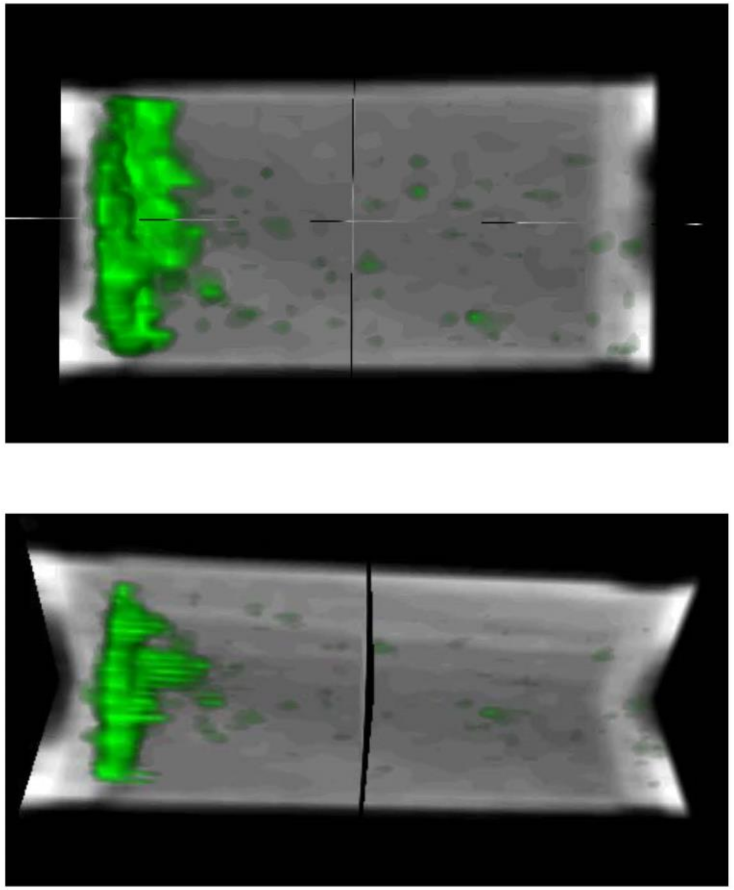

**Fig. 1.** Methods used to estimate porosity and pore size distributions in unconventional gas reservoirs. Modified from Bustin et al. [1].

# $CO_2$-Shale Interactions Affect on Flow

- Core Flow Tests in Progress to evaluate whether pore changes impact flow pathways in the shale matrix



Utica Shale Core

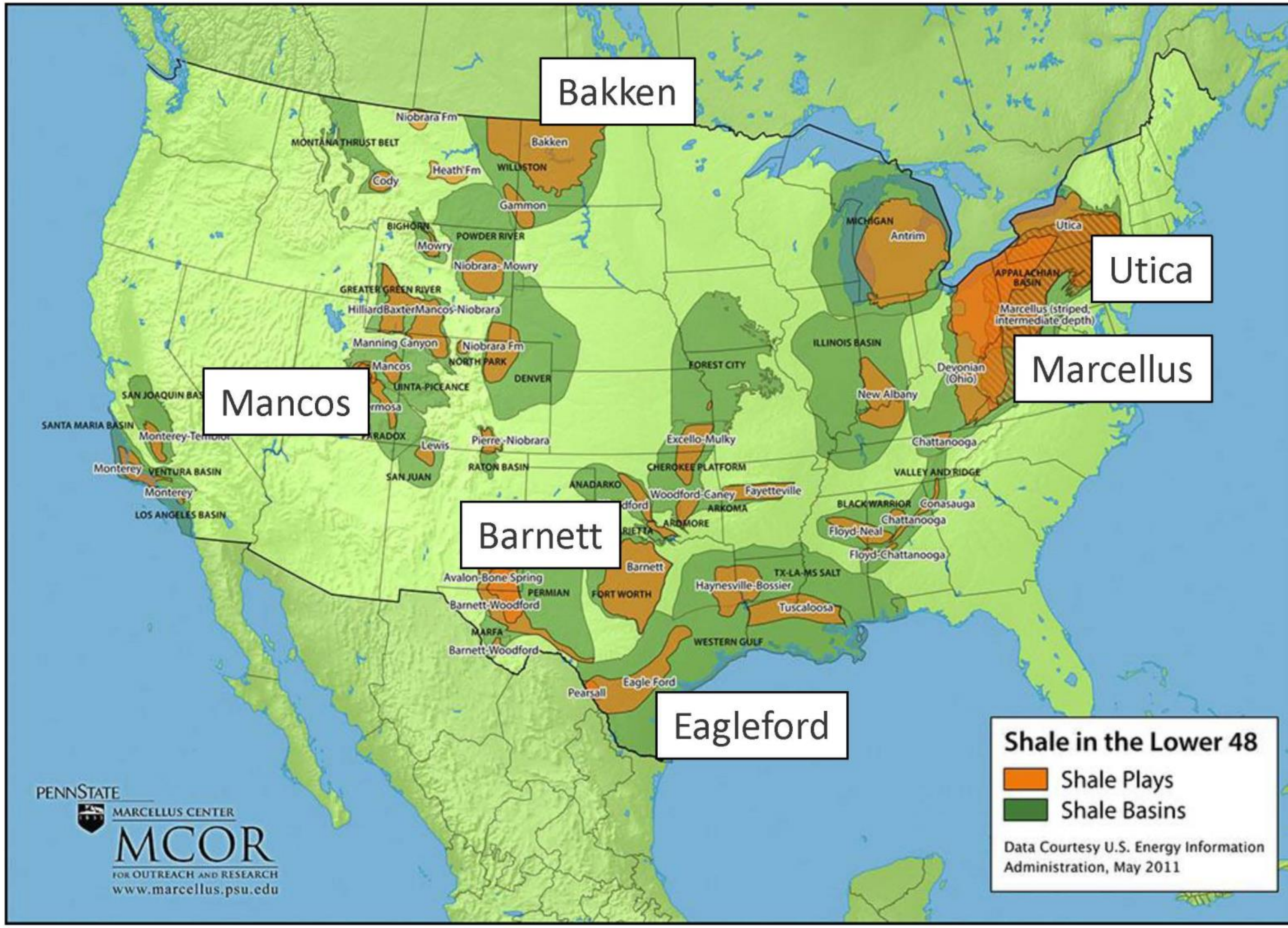


Bakken Shale Core

**Potential for hydrocarbon extraction and $CO_2$ storage**

# Future Work

- **Predict how different shales interact with $CO_2$ and fluid at a national scale**
- **Understand if geochemical reactions influence storage mechanisms or hydrocarbon extraction flow paths**
- **Quantify the role of shale formations in CCS activities**



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# Disclaimer

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