

# Characterizing the Geochemistry of the CO<sub>2</sub>-Fluid-Shale Interface

Research & Innovation Center



Sean Sanguinito<sup>1,2</sup>, Angela L. Goodman<sup>1</sup>, Mary Tkach<sup>1</sup>, Barbara Kutchko<sup>1</sup>, Sittichai Natesakhawat<sup>1,3</sup>, Dustin Crandall<sup>1</sup>, Jim Fazio<sup>1,2</sup>, Isis Fukai<sup>1,4</sup>

<sup>1</sup>US Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA /Morgantown, WV; <sup>2</sup>AECOM Corporation, Pittsburgh, PA; <sup>3</sup>University of Pittsburgh, Pittsburgh, PA; <sup>4</sup>Presently at Battelle Memorial Institute, Columbus, OH

## Abstract Key Points

- Traditionally, shale formations studied as seals
- Recent research focused on:
  - Storage of CO<sub>2</sub> in shale
  - Use of CO<sub>2</sub> as a fracturing fluid in shale
- Injected CO<sub>2</sub> will interact with shale components (i.e. clays, organic matter) and affect rock properties through chemical alteration, matrix swelling/shrinkage, and related geomechanical effects
- Rock property changes will impact effectiveness of CO<sub>2</sub> storage and hydraulic fracturing using CO<sub>2</sub>
- In-situ Fourier Transform infrared (FT-IR) spectroscopy
  - Examine the interaction for CO<sub>2</sub> at molecular scale
  - Characterize vibrational changes of sorption bands sensitive to gas-fluid-solid environment
- Surface Feature Relocation via Scanning Electron Microscopy (FE-SEM)
  - Analyze chemical and physical changes before and after dry CO<sub>2</sub> and wet CO<sub>2</sub> exposure

## Samples

Utica Shale: Stream Outcrop

Marcellus Shale: Stream Outcrop

Marcellus Shale: Quarry Exposure

**Clays**

- Kaolinite
- Illite
- Illite-Smectite
- Chlorite

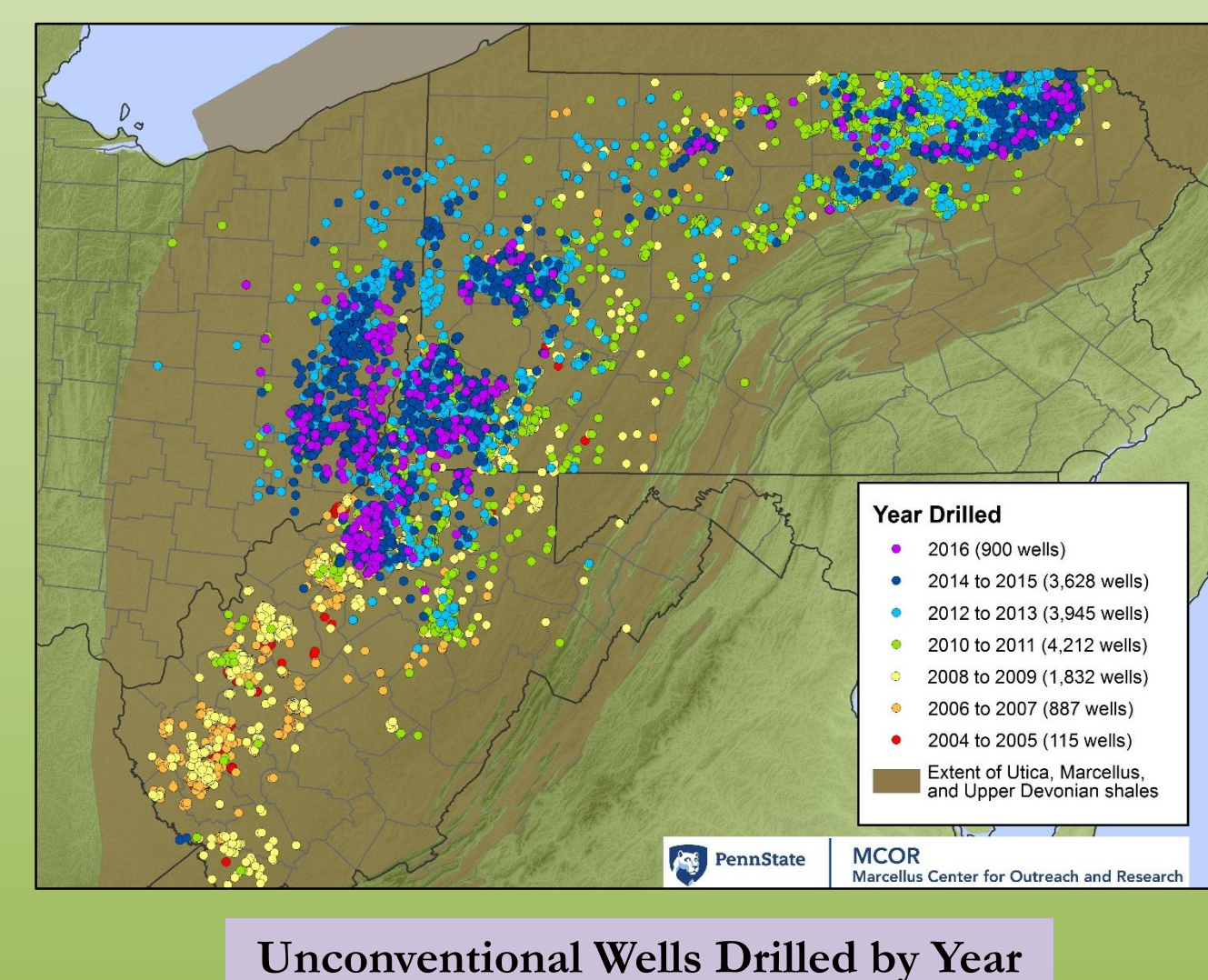
**Kerogen**

- Extracted from the New Albany Shale

## Research Approach

### CO<sub>2</sub>-(Fluid)-Shale Interface

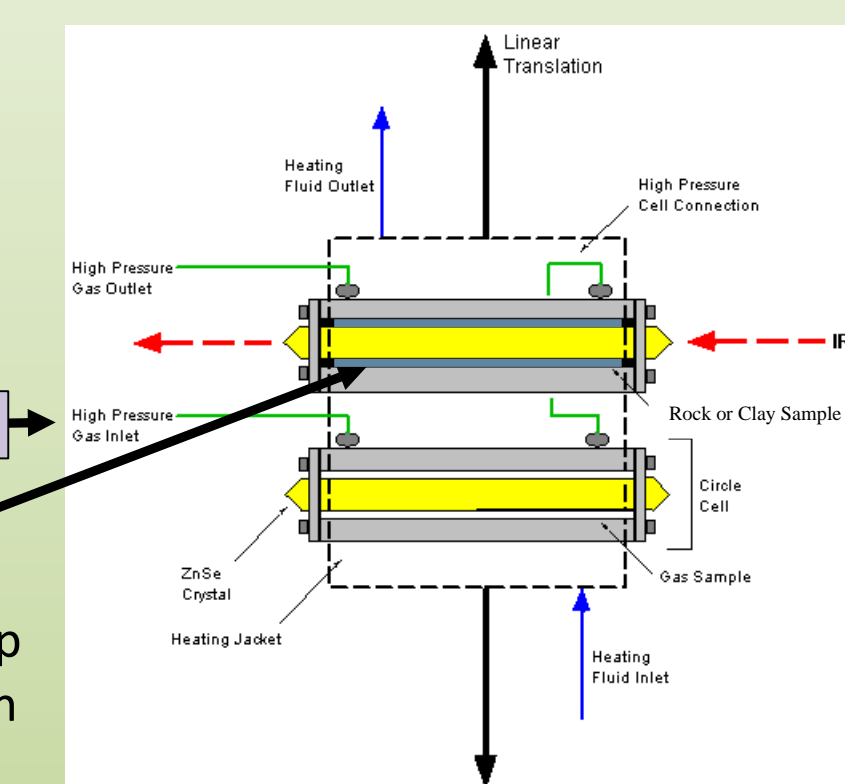
- Fourier Transform Infrared Spectroscopy
- Feature Relocation-Scanning Electron Microscopy
- Surface Area and Pore Size Analysis
- Sorption Analysis



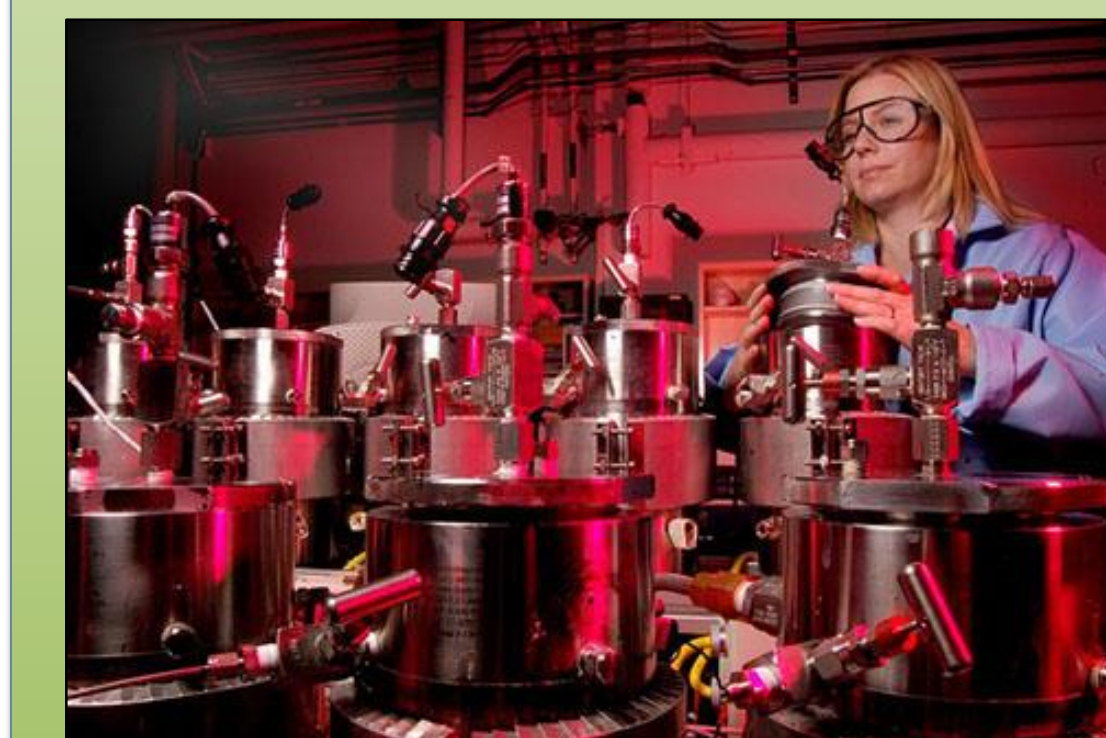
## Analytical Instruments



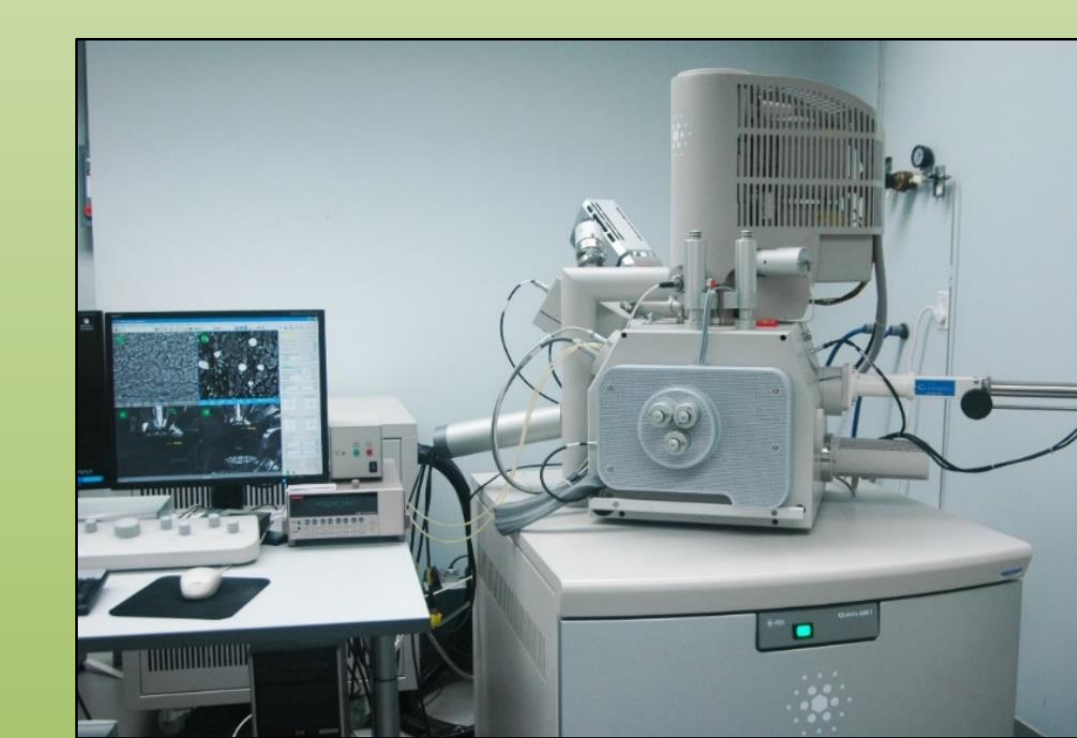
Left. FT-IR Spectrometer used to conduct In-situ high temperature and pressure experiments.



Right. Sample holder set up for FT-IR. Note the addition of a water film.

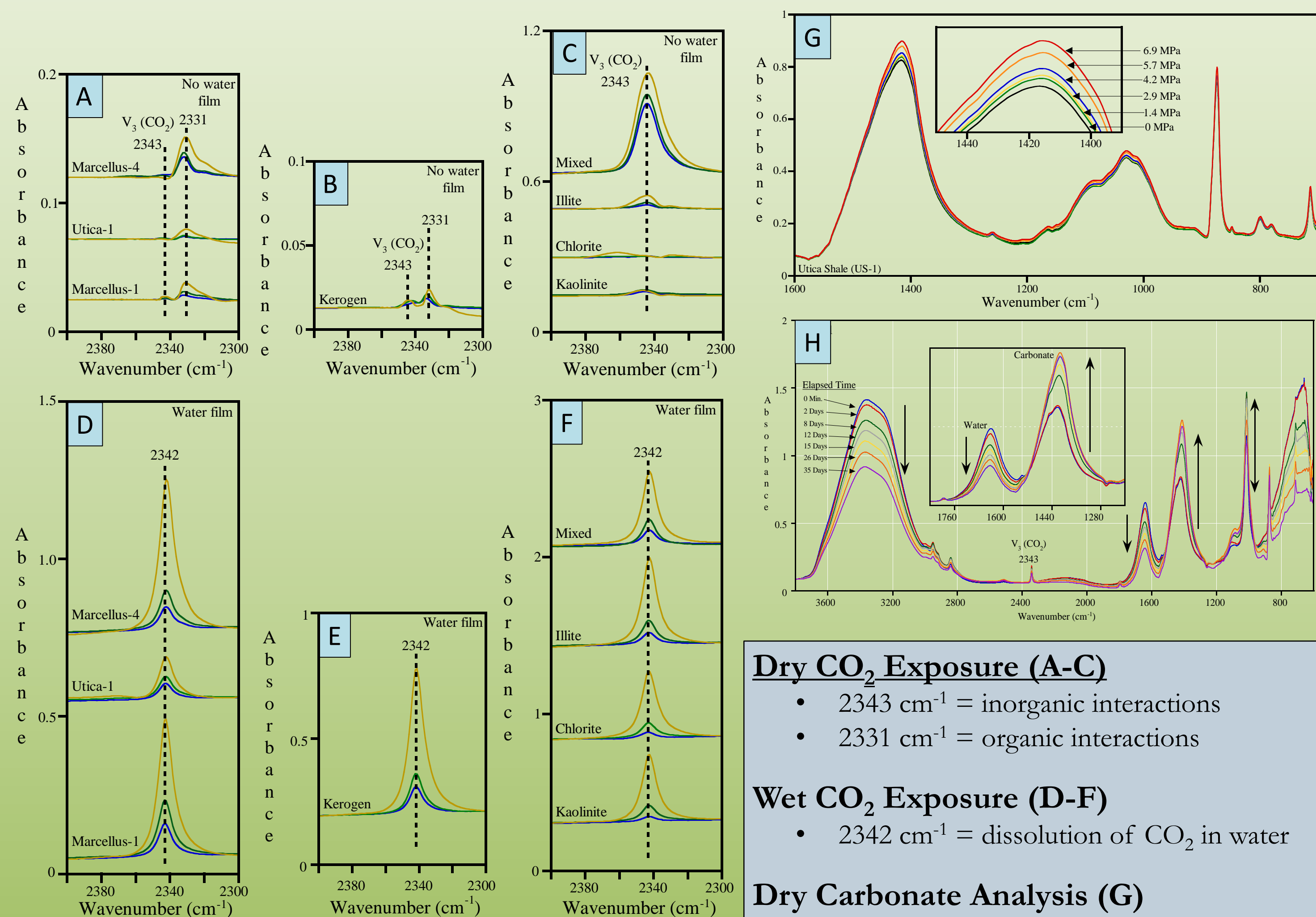


Reaction vessels used to expose samples to dry and wet CO<sub>2</sub> at 40°C and 1500 PSI.



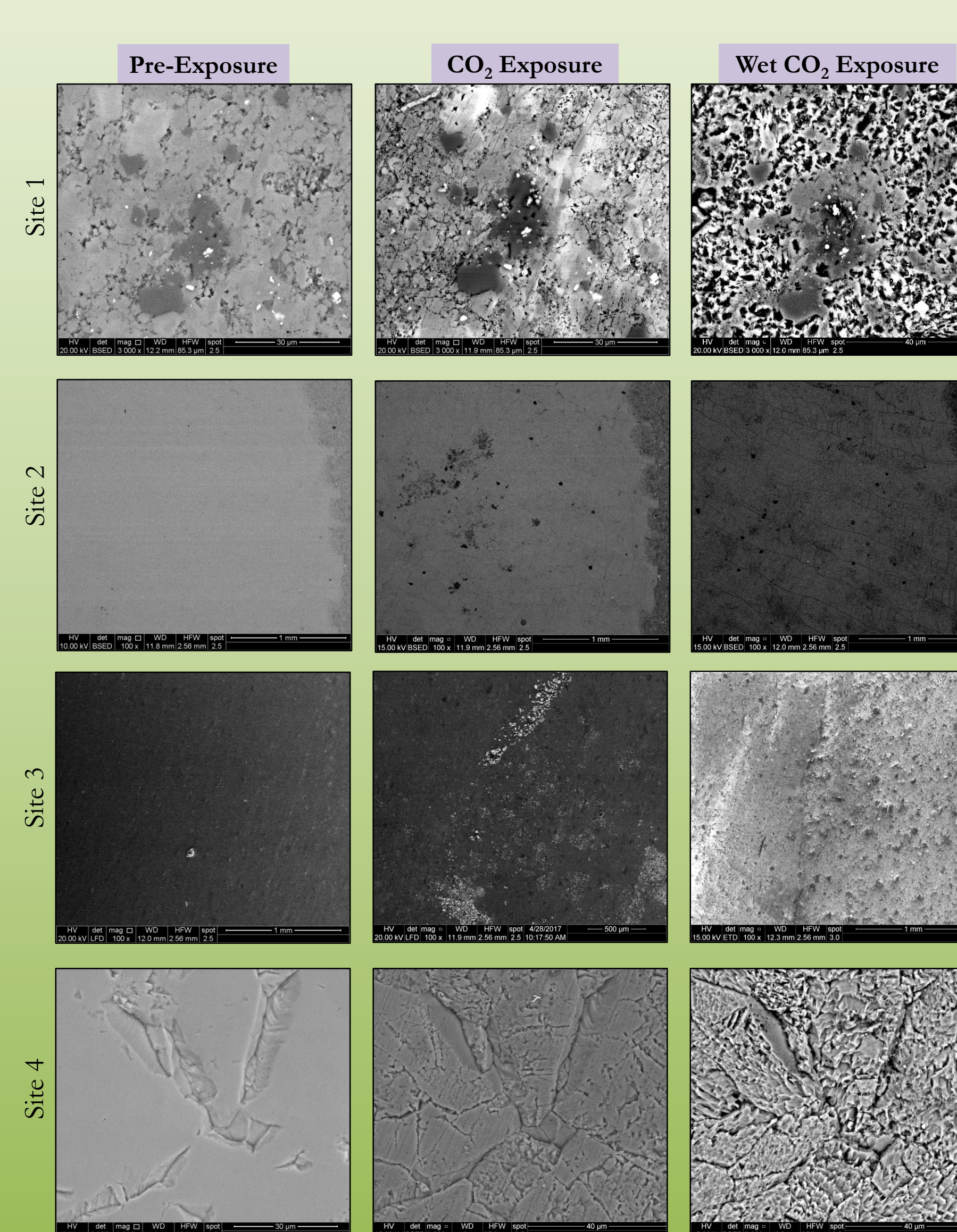
Scanning Electron Microscope used for feature relocation before and after dry/wet CO<sub>2</sub> exposure.

## Infrared Spectroscopy: Results



- Dry CO<sub>2</sub> Exposure (A-C)**
- 2343 cm<sup>-1</sup> = inorganic interactions
  - 2331 cm<sup>-1</sup> = organic interactions
- Wet CO<sub>2</sub> Exposure (D-F)**
- 2342 cm<sup>-1</sup> = dissolution of CO<sub>2</sub> in water
- Dry Carbonate Analysis (G)**
- Carbonate fluctuated but increased overall
- Wet Carbonate Analysis (H)**
- Water decreased and carbonate increased

## Scanning Electron Microscopy: Results



**Dry CO<sub>2</sub> Exposure**

- Minor etching, dissolution, and precipitation

**Wet CO<sub>2</sub> Exposure**

- Major etching, dissolution, and precipitation

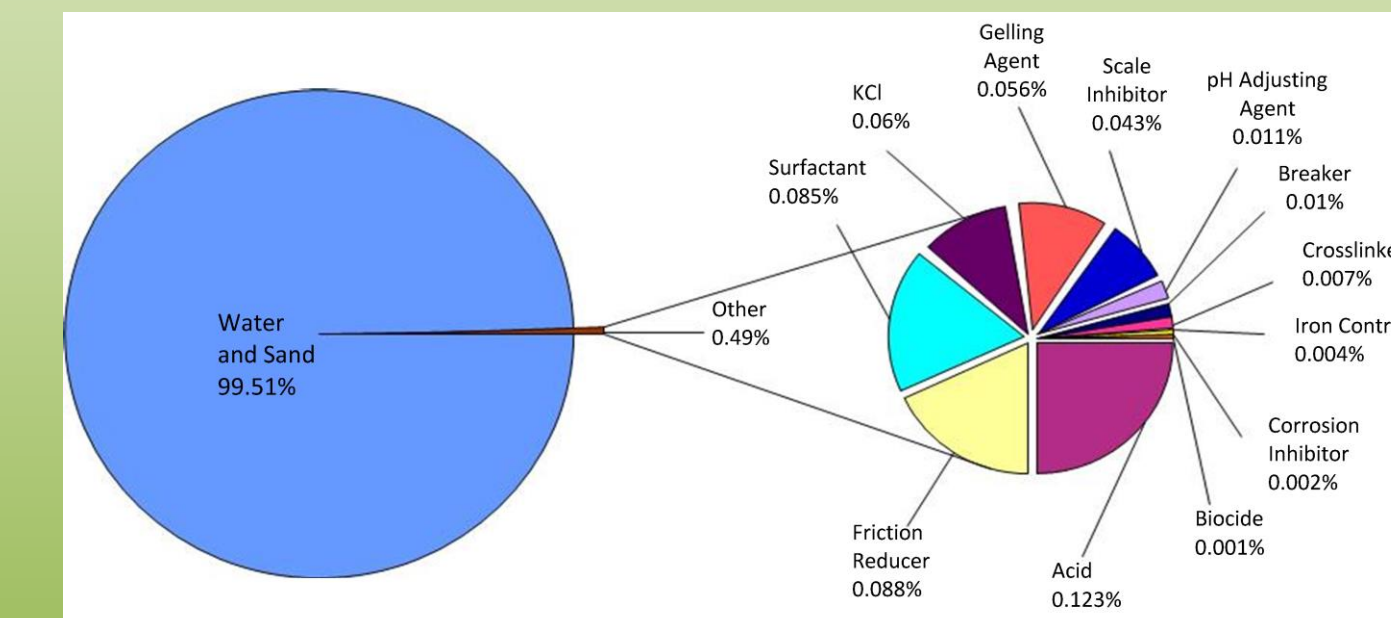
**Conclusions:**

- Water contained in the interstitial pore space may interact with supercritical CO<sub>2</sub> in dry reactions
- Dissolution and precipitation occur as the carbonate reactions reach equilibrium upon exposure to CO<sub>2</sub>

## Future Work

### Increase complexity of the fluid

- Various brine compositions
- Fracturing fluid



## References

• Dieterich, M., Kutchko, B., Goodman, A., 2016. Characterization of Marcellus Shale and Huntersville Chert before and after exposure to hydraulic fracturing fluid via feature relocation using field-emission scanning electron microscopy. Fuel, p. 227-235.

• Goodman, A.L., Campus, L.M., Schroeder, K.L., 2005. Direct Evidence of Carbon Dioxide Sorption on Argonne Premium Coals Using ATR-FTIR Spectroscopy. Energy & Fuels, v. 19, p. 472-476.

• <http://www.marcellus.psu.edu/resources-maps-graphics.html>

• <http://naturalgas.org/shale/shaleshock/>

• Kutchko, B.G., Goodman, A.L., Rosenbaum, E., Natesakhawat, S., Wagner, K., 2013. Characterization of coal before and after supercritical CO<sub>2</sub> exposure via feature relocation using field-emission scanning electron microscopy. Fuel, v. 107, p. 777-785.

• Levine, J.S., Fukai, I., Soeder, D.J., Bromhal, G., Dilmore, R.M., Guthrie, G.D., Rodosta, T., Sanguinito, S., Fralley, S., Gorecki, D., Peck, W., Goodman, A.L., 2016. U.S. DOE NETL Methodology for Estimating the Prospective CO<sub>2</sub> Storage Resource of Shales at the National and Regional Scale. International Journal of Greenhouse Gas Control, v. 51, p. 81-94.

• Sanguinito, S., Goodman, A., Tkach, M., Barbara, K., Culp, J., Natesakhawat, S., Crandall, D., Fazio, J., Fukai, I., In Prep.

• Steefel, C.I., Molins, S., Trebotich, D., 2013. Pore scale processes associated with subsurface CO<sub>2</sub> injection and sequestration. Reviews in Mineralogy and Geochemistry, v. 77, p. 259-303.

• US DOE-NETL. 2015. Carbon Storage Atlas, fifth edition. U.S. Department of Energy—National Energy Technology Laboratory—Office of Fossil Energy.

## Acknowledgments

We would like to graciously thank Maria Mastalerz at Indiana University and Indiana Geologic Survey in Bloomington, IN for providing a kerogen sample extracted from the New Albany Shale.