

# Fundamental Study of Disposition and Release of Methane in a Shale Gas Reservoir: Experimental Studies

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## Purpose and Approach

Our goal is to conduct an integrated experimental and modeling study to fundamentally understand methane partitioning in the nanopores of mudstone matrices. We examine two important processes that control gas-in-place and well production:

- Methane partitioning in the nanopores of mudstone matrices.
- Methane transport from low-permeability matrices to fracture networks induced by hydraulic fracturing.

## Pore Morphology Characterization of Mancos Shale

SANS Characterization Provides

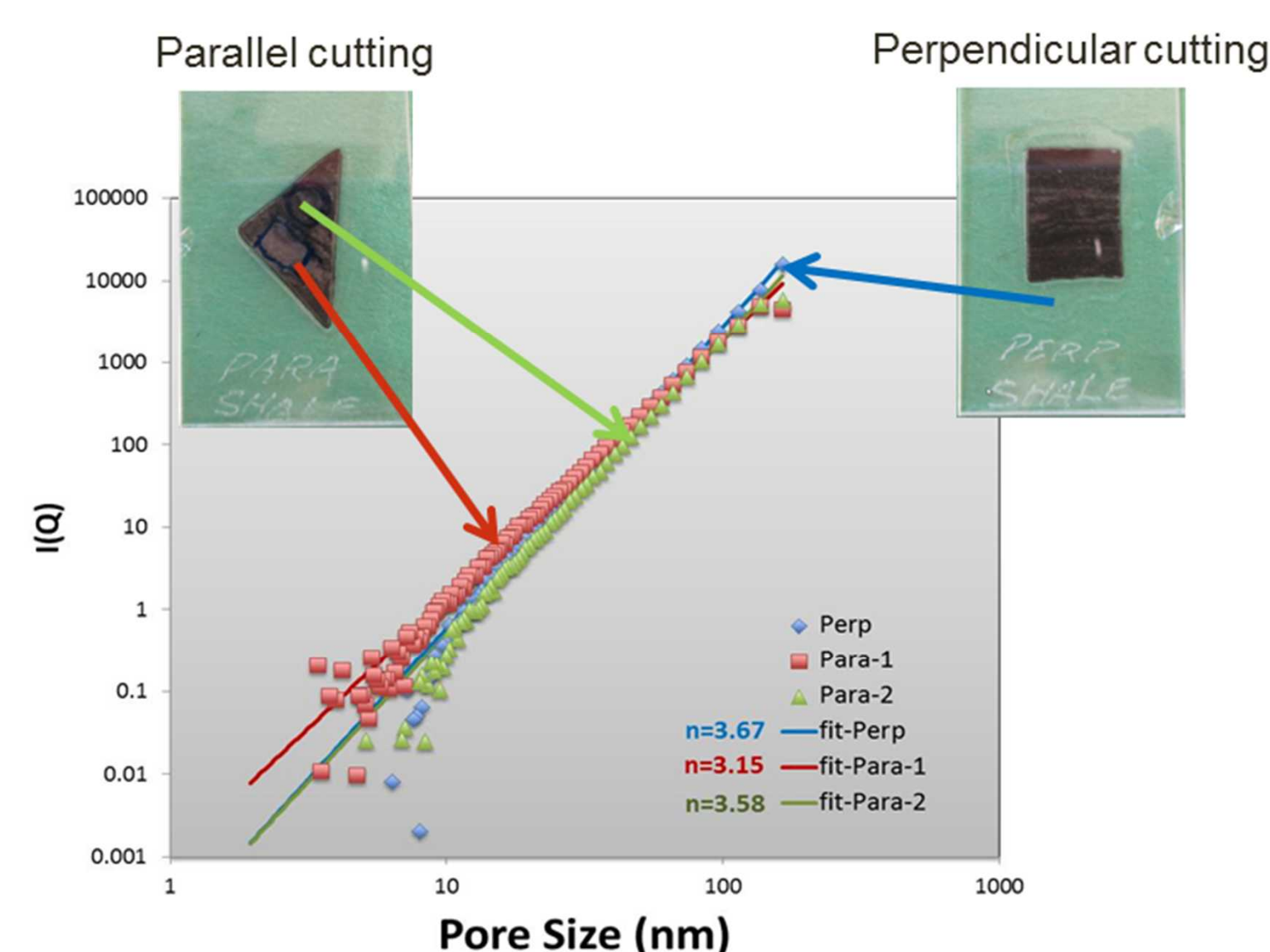
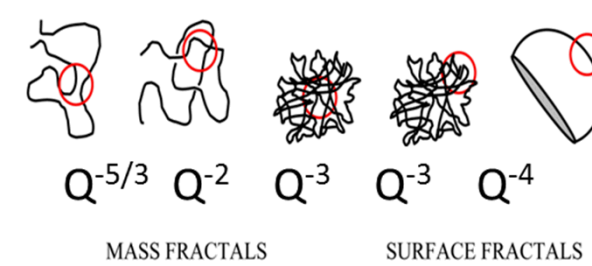
$$I(Q) = \phi P(Q) S(Q)$$

$P(Q)$ : Particle factor,  
Particle shape  
 $S(Q)$ : Structure factor, Interactions  
between particles  
 $R_g$ : Radius of Gyration,  
Size of particles and voids

Preliminary Data Interpretation

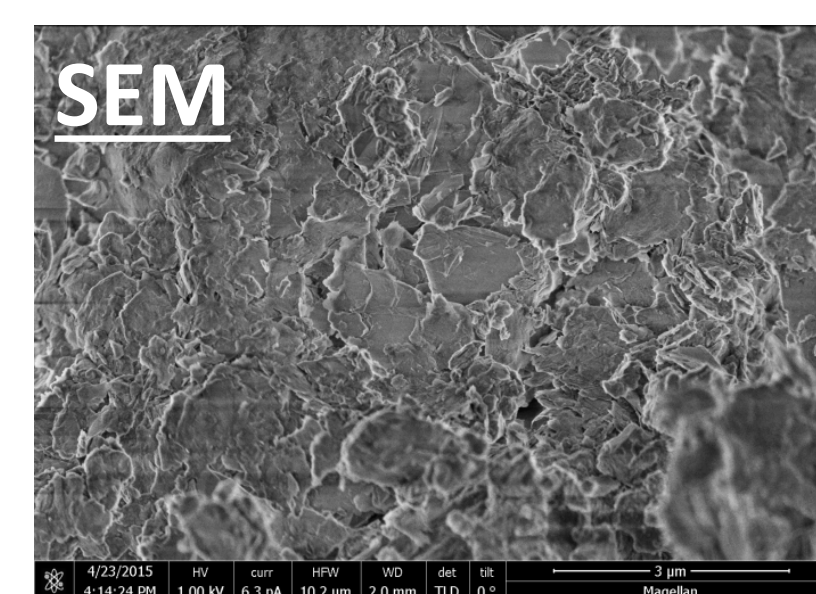
Porod Fitting

$$I(Q) = A/Q^n + B \quad \text{or} \quad \text{Log}[I(Q) - B] = \text{Log}(A) - n \text{Log}(Q)$$



**Method:** Small angle neutron scattering (SANS) for characterizing porosity.

**Results:** The preliminary data show that the predominant pores in shale are nanopores (1-100 nm).

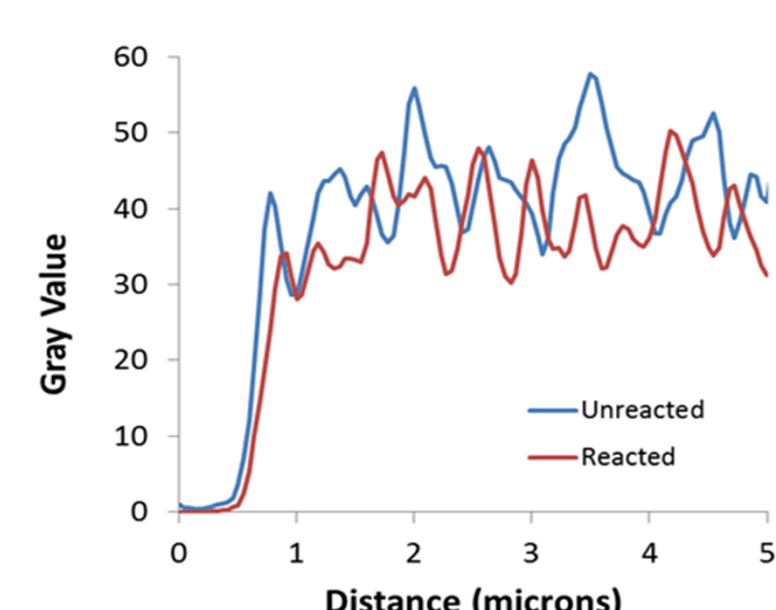
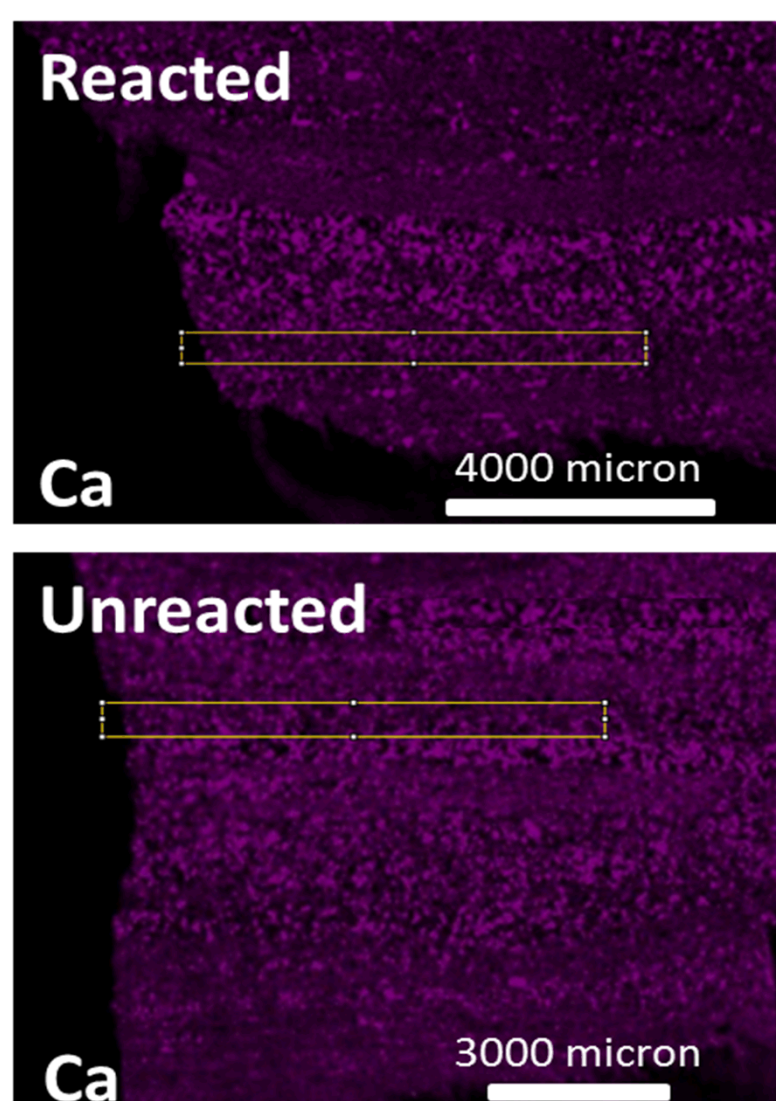


## Alteration of Mancos Shale by hydrofracturing fluid

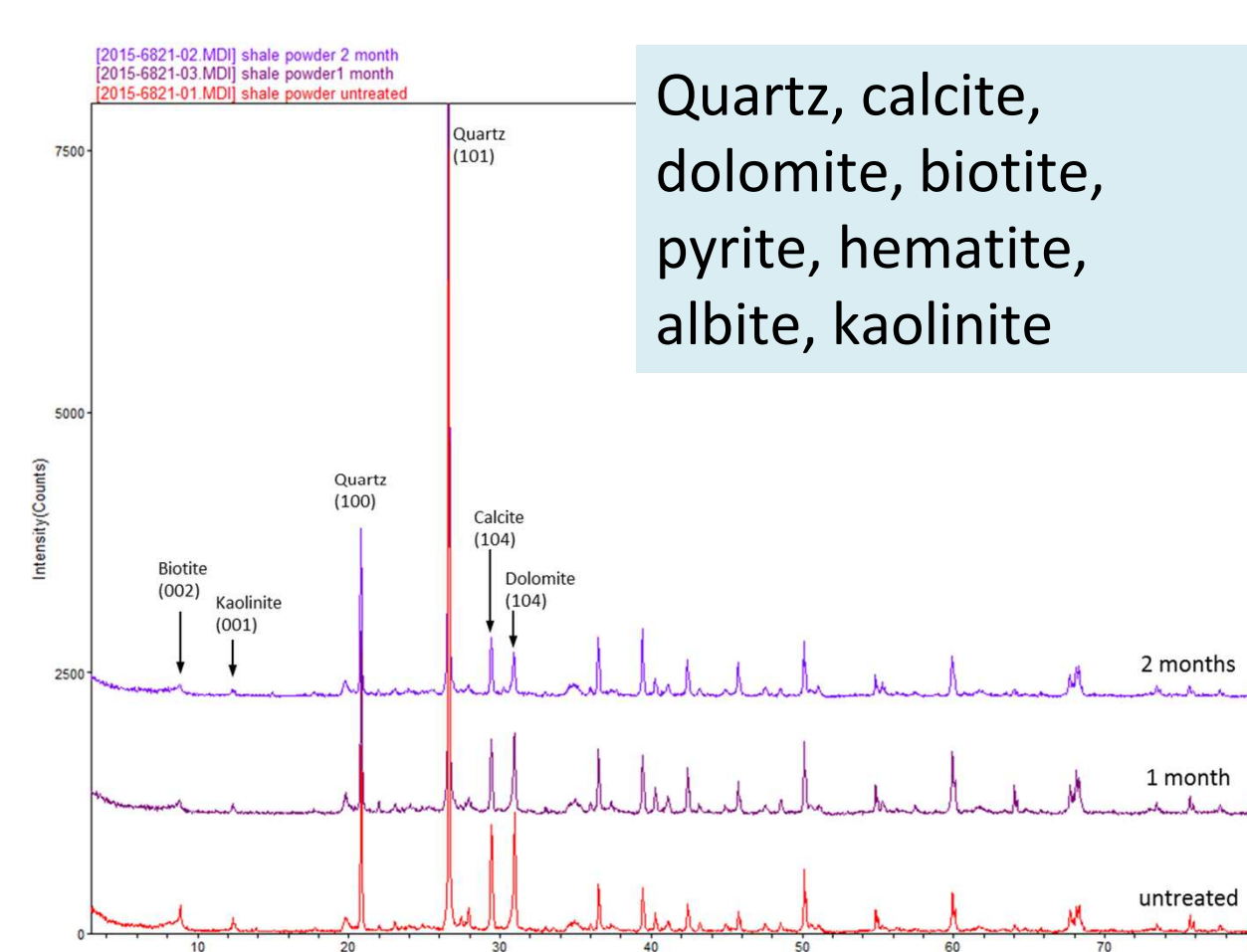
**Method:** The alteration of Mancos shale in hydrofracturing fluid at 90 °C, in Parr digestion vessels for 1-2 months. Control experiment-pure clay minerals (illite and illite/smectite) were reacted under the same conditions. Characterization – X-ray diffraction (XRD) – powder and micro-XRD, and micro-X-ray fluorescence mapping (micro-XRF). Analysis of liquids for major anions and cations – ion chromatography (IC), and for trace metals by inductively coupled plasma mass spectrometry (ICP-MS).

**Synthetic hydrofracturing fluid:** 0.01% Polyacrylamide; 0.05% Sodium polyacrylate; 0.1% Sodium chloride; 0.02% Methanol; 0.01% Hydrochloric acid; 0.007% Tetrakis(hydroxymethyl)phosphonium sulfate.

### Micro-XRF maps

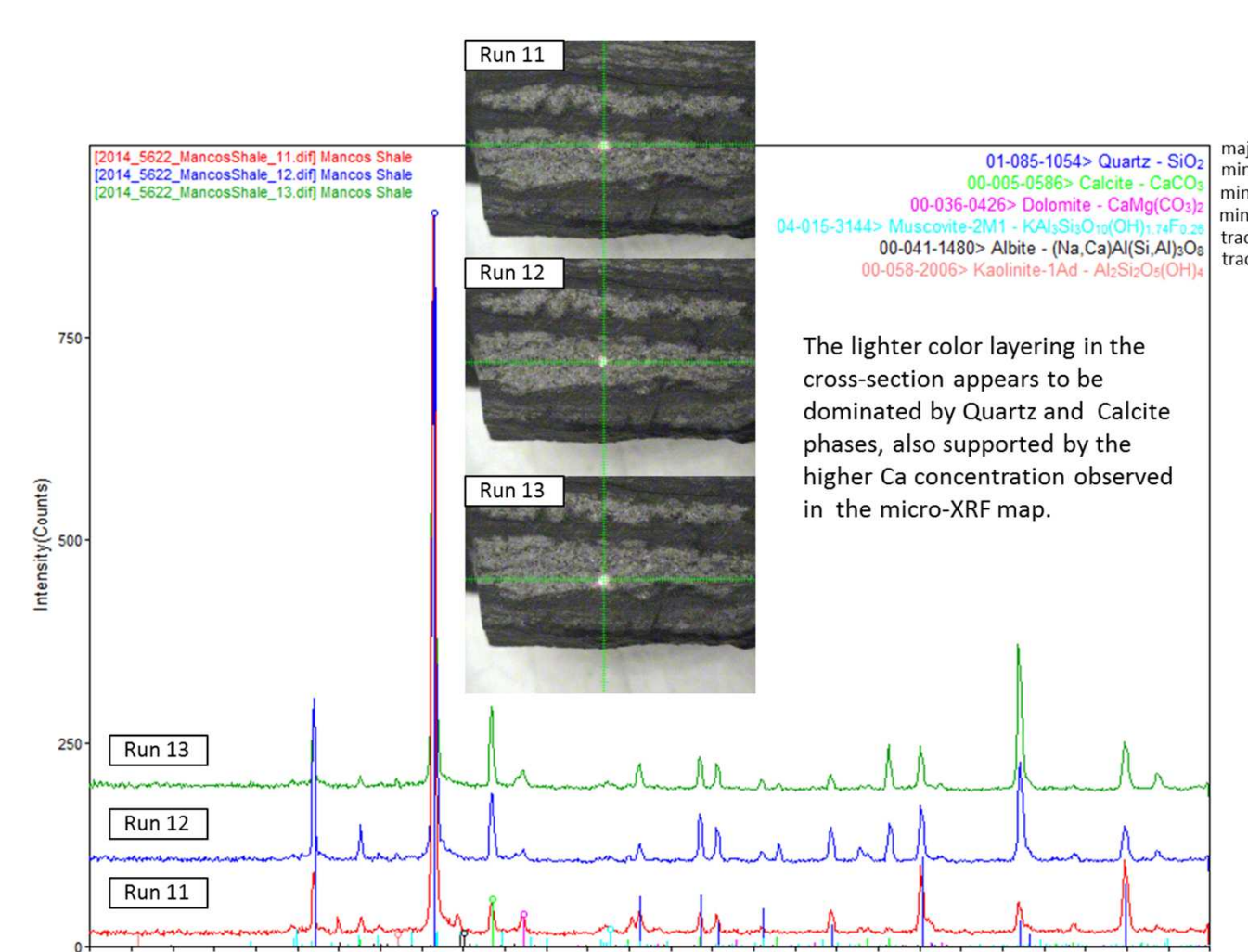


### Bulk XRD



**Results:** Calcium, barium, strontium, magnesium, manganese, silica, sodium, chloride and sulfate were released from Mancos shale after reaction with hydrofracturing fluid. Altered zones on shale surface after 2 months of reaction are thin – likely, within a few microns. The XRD patterns normalized to the 100% peak for quartz indicate that the dolomite, calcite, biotite, and kaolinite peaks decrease in intensity relative to the quartz peaks with increased treatment time. Similarly to crushed shale, increased silica, calcium and strontium were observed in the control reactors with illite and illite/smectite clay mineral mixtures. Understanding mineralogical composition of the altered layer will provide insight whether methane transport through these zones will be affected compared to the unaltered material.

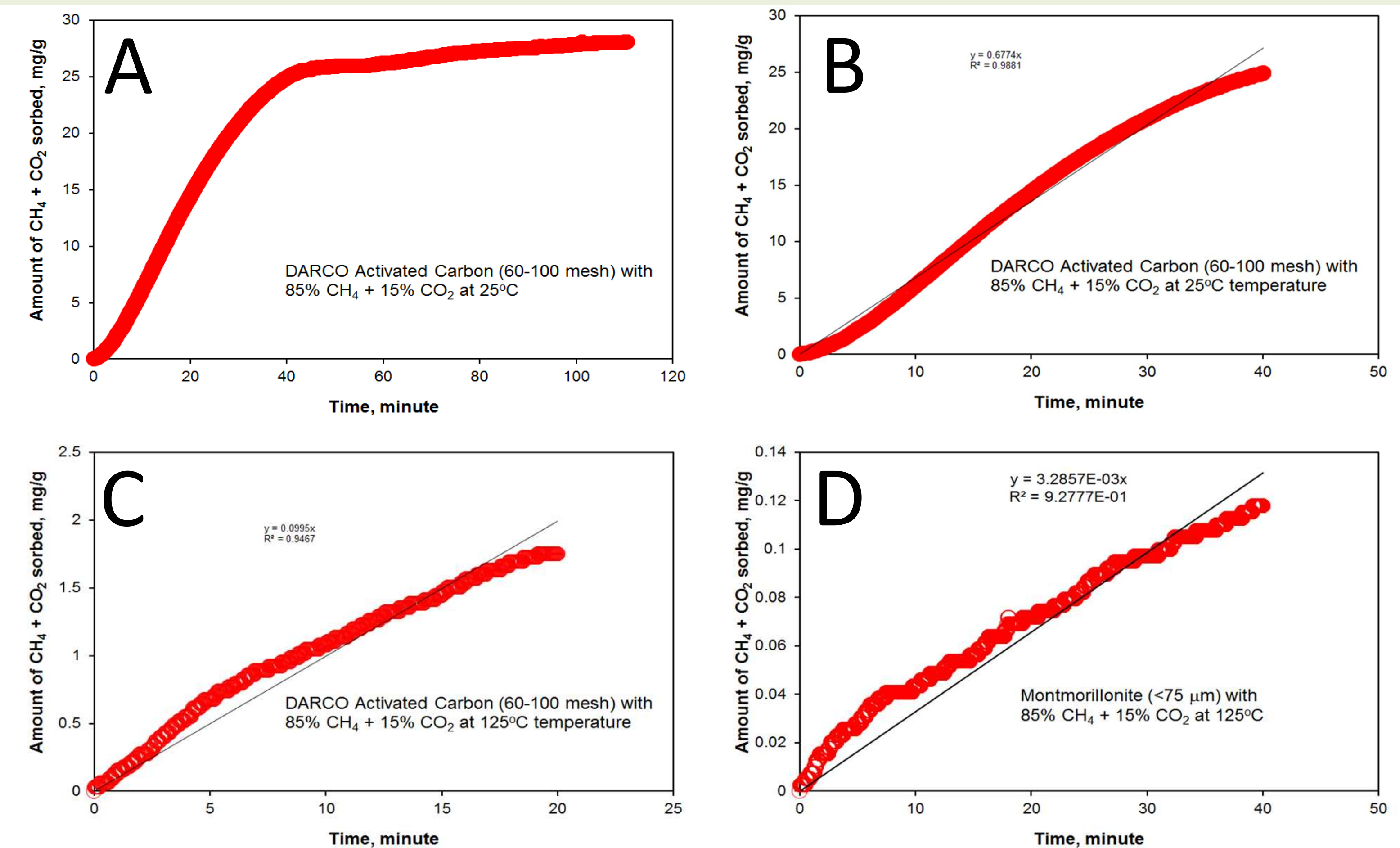
### Micro-XRD



## Experimental Determination of P-V-T-X Properties and Sorption Kinetics in the CO<sub>2</sub>-CH<sub>4</sub>-H<sub>2</sub>O System under Reservoir Conditions

### Model Materials for CO<sub>2</sub>-CH<sub>4</sub> Mixtures to 125°C

**Method:** The application of the gravimetric method using a Netzsch STA 409 thermal gravimetric analyzer (TGA) with differential scanning calorimeter (DSC) and differential temperature analyzer (DTA) adapted for measurement of adsorption capacities and kinetics of the three types of materials at temperatures up to 125 °C and constant pressures up to 1 bar. We monitored the evolution of the weight change as a function of time from the instant a dose of CO<sub>2</sub> and CH<sub>4</sub> gas mixture is adsorbed onto the sample, and until the moment saturation equilibrium is reached.



**Results:** In Figure A, a typical sorption curve is presented. The linear portion of the curve is used for determination of sorption kinetics. The portion that indicates the sorption saturation is used for determination of sorption capacities. As an example, the sorption rates for activated carbon and montmorillonite are determined from the linear portion of the sorption curve as shown in Figures B through D. We have used this methodology to measure the sorption capacities and kinetics for a series of model substances including activated carbon, crushed shale, illite and montmorillonite, up to 125 °C.

Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at 1 bar total pressure

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min <sup>-1</sup>
DARCO activated carbon	25	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	28	0.68
	50	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	11	0.59
	75	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	9.0	0.31
	100	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	2.1	0.14
	125	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	1.8	0.10
Montmorillonite, <75 μm	25	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	2.8	4.7 × 10 <sup>-2</sup>
	50	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	0.30	9.6 × 10 <sup>-3</sup>
	75	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	0.19	6.7 × 10 <sup>-3</sup>
	100	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	0.18	5.1 × 10 <sup>-3</sup>
	125	85% CH <sub>4</sub> + 15% CO <sub>2</sub>	1	0.12	3.3 × 10 <sup>-3</sup>

In Table 1, the sorption capacities and sorption kinetics of activated carbon and montmorillonite (< 75 mm) for the mixture of 85% CH<sub>4</sub> and 15% CO<sub>2</sub> from 25 °C to 125 °C and the total pressure of 1 bar are summarized.

### Acknowledgements

Mark Rodriguez and James Griego, Sandia National Labs, performed micro-XRD, and micro-XRF mapping.