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Fundamental Understanding of Methane-Carbon Dioxide-Water (CH_4-CO_2-H_2O) Interactions in Shale Nanopores under Reservoir Conditions

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Objectives:

Understand two important processes that control gas-in-place(GIP) & well production:

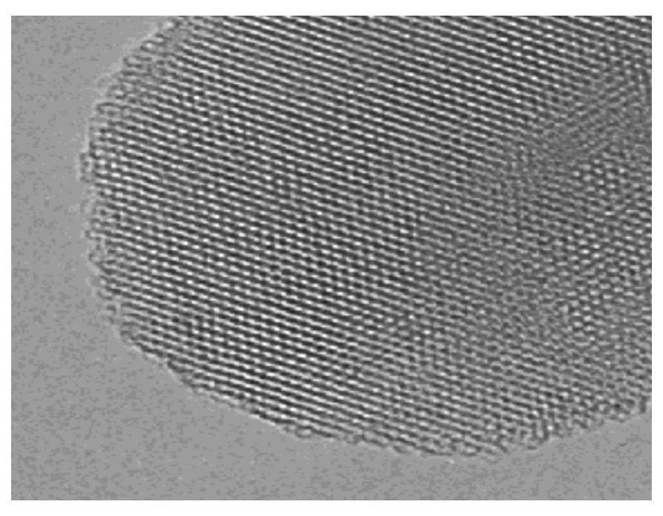
- Methane partitioning in the nanopores of mudstone matrices.
- Methane transport from low-permeability matrices to fracking-induced fracture networks.

Field observations
- Core/outcrop sample collection
- Quantification of heterogeneities

Material characterization
- Pore structures: SANS, BET, TEM, SEM, etc
- Chemistry & mineralogy: XRD, XRF, etc

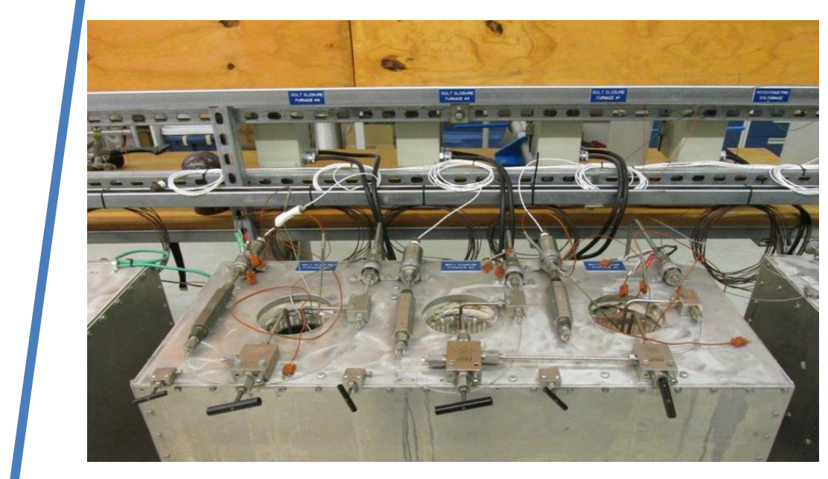
Sorption/desorption measurements
- Methane sorption/desorption on model materials
- Methane sorption/desorption under high P & high T
- Chemical/physical stimulations

Column experiments
- Diffusive fluxes
- Advective fluxes



Synthesis of nanoporous materials

Gas disposition & release
- Gas in place (GIP)
- Gas migration from matrix into fractures
- Stimulated volume
- Gas for secondary recovery



High pressure/high temperature sorption/desorption measurements

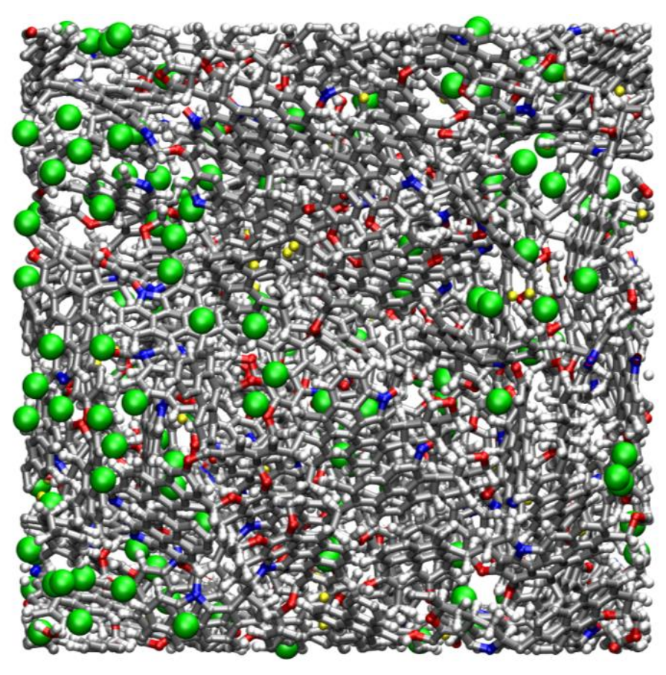
Molecular dynamic (MD) modeling
- Binding energies of methane sorption
- Diffusion rates

Nanoscience
- Effects of nanopore confinement on fluid thermodynamic properties
- Effects of nanopore confinement on methane transport (microfluidics in shale)

Upscaling
- Percolation theory
- Fractal representation
- Lattice Boltzmann modeling

Predictive models
- Constitutive relationships
- Continuum models
- Reactive transport modeling

Adsorption isotherm of CH_4 in kerogen:

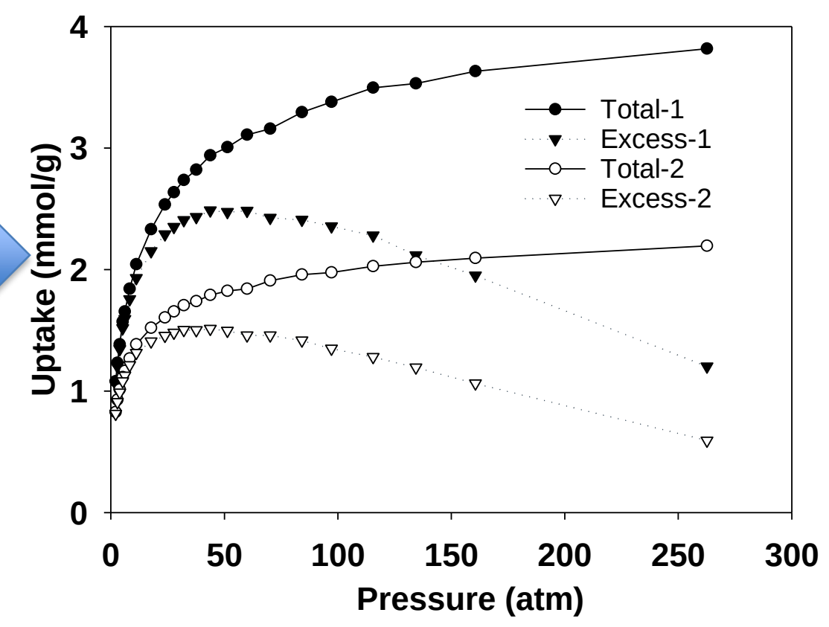


Grand Canonical or Gibbs-NPT Monte Carlo Simulations

$$n_{excess} = n_{total} - \rho_{P,T} V_{free}$$

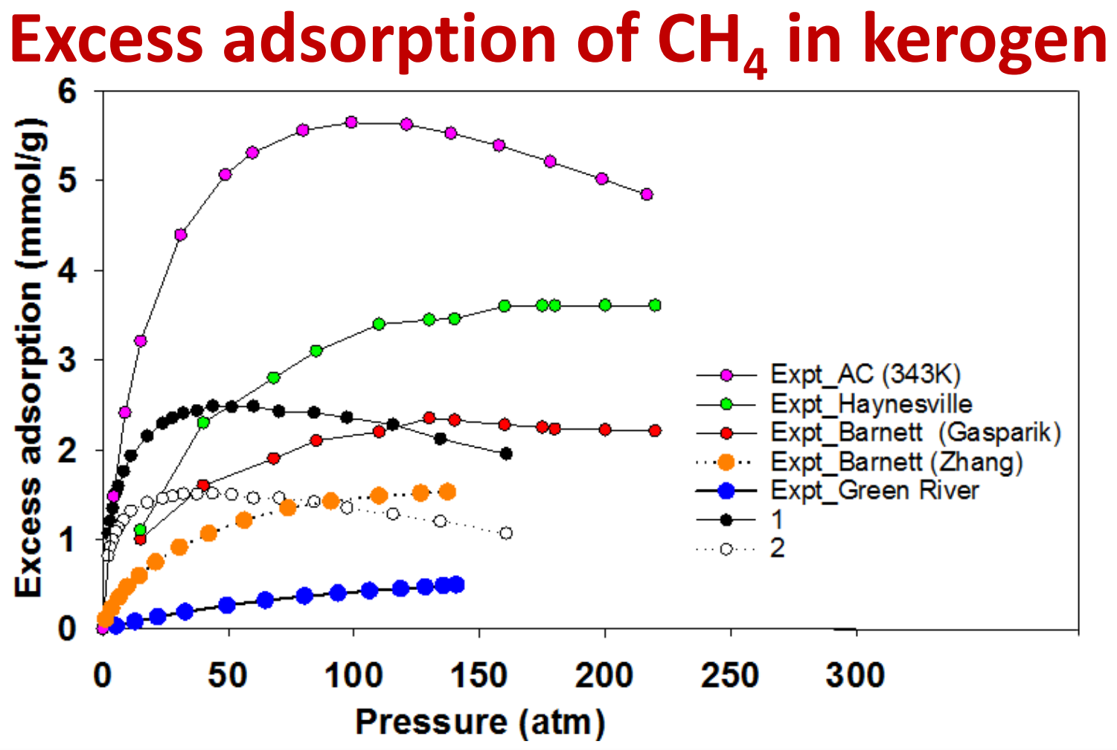
- At low pressure gas present in kerogen is mainly adsorbed gas
- At high pressure more gas fills into the free volume inside kerogen matrix.

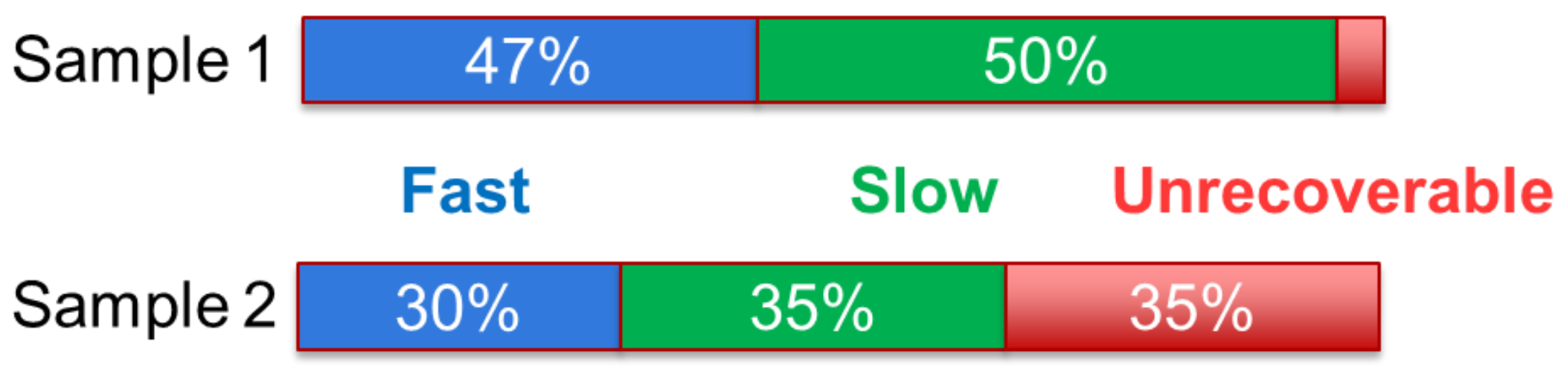
Total uptake of CH_4 in kerogen



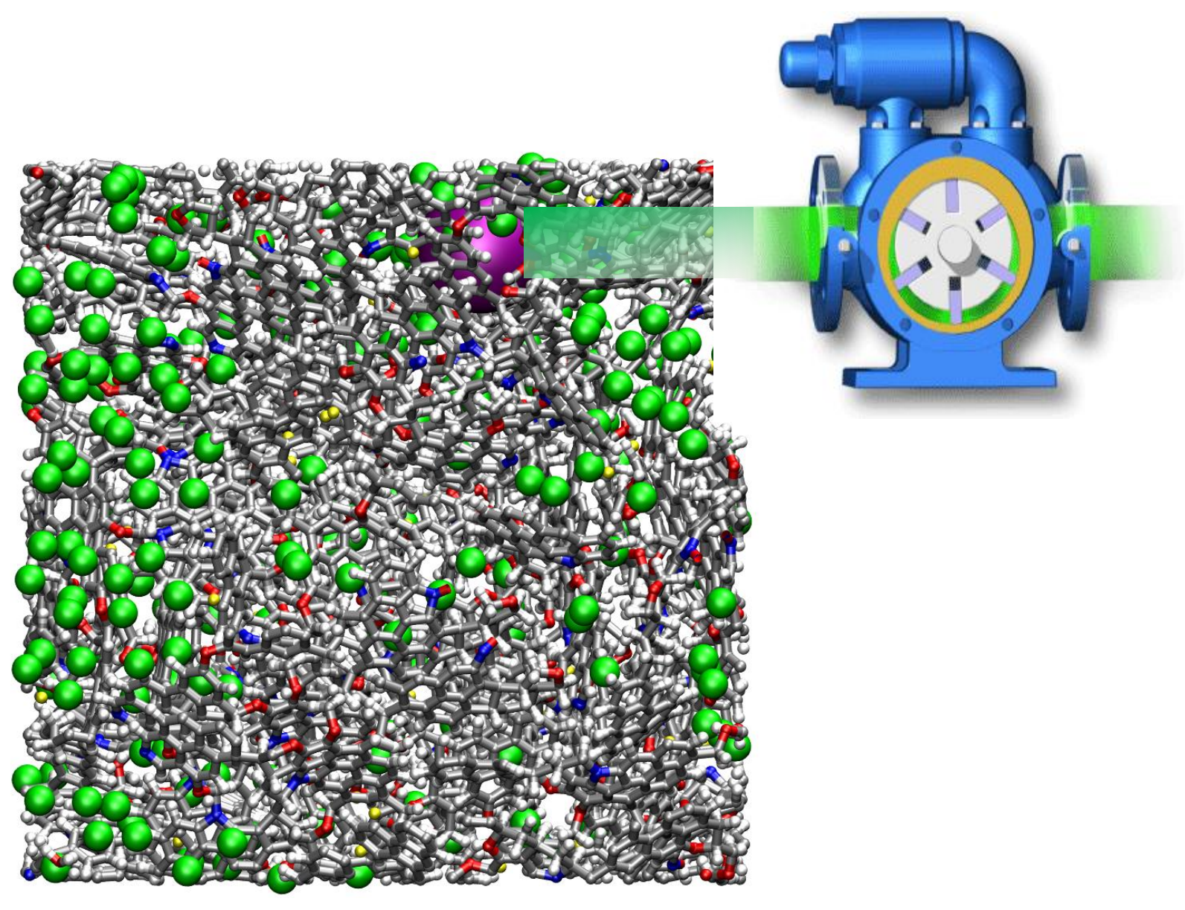
Our excess adsorption is of the same order of magnitude with actual measurements on Barnett and Haynesville shales.

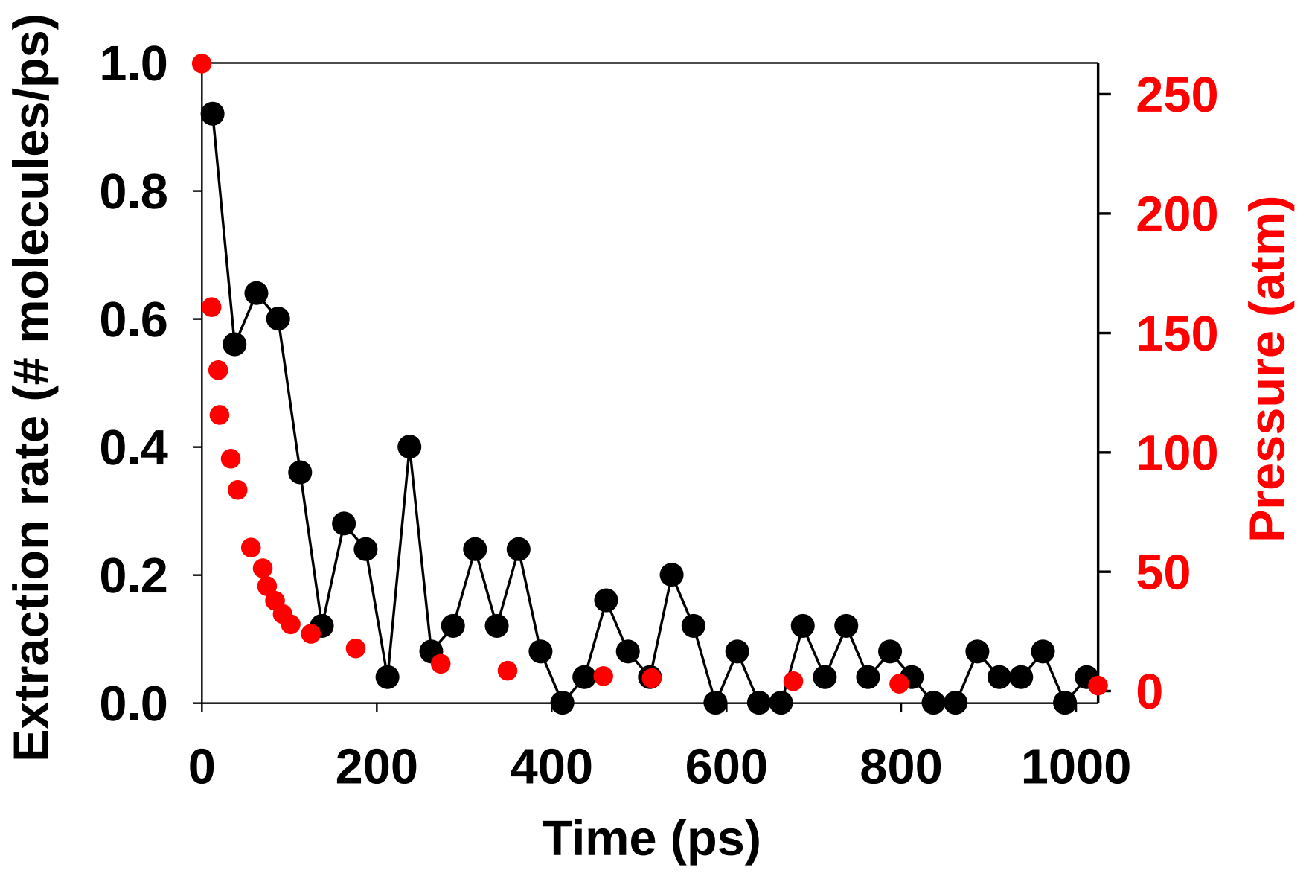
Excess adsorption of CH_4 in kerogen





Extraction of CH_4 from nanopores in kerogen

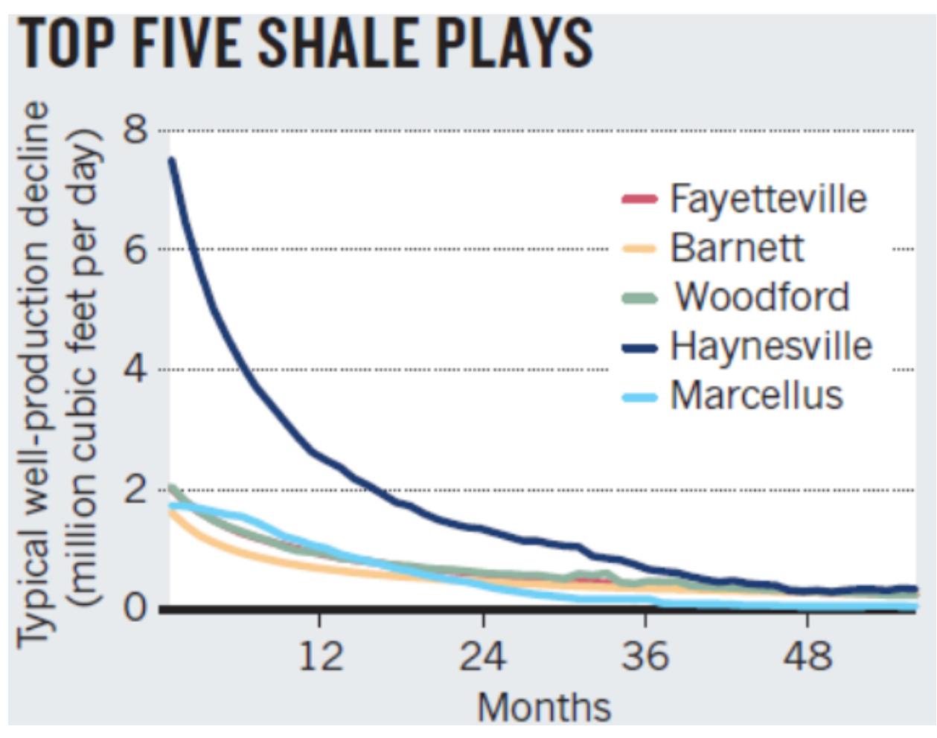


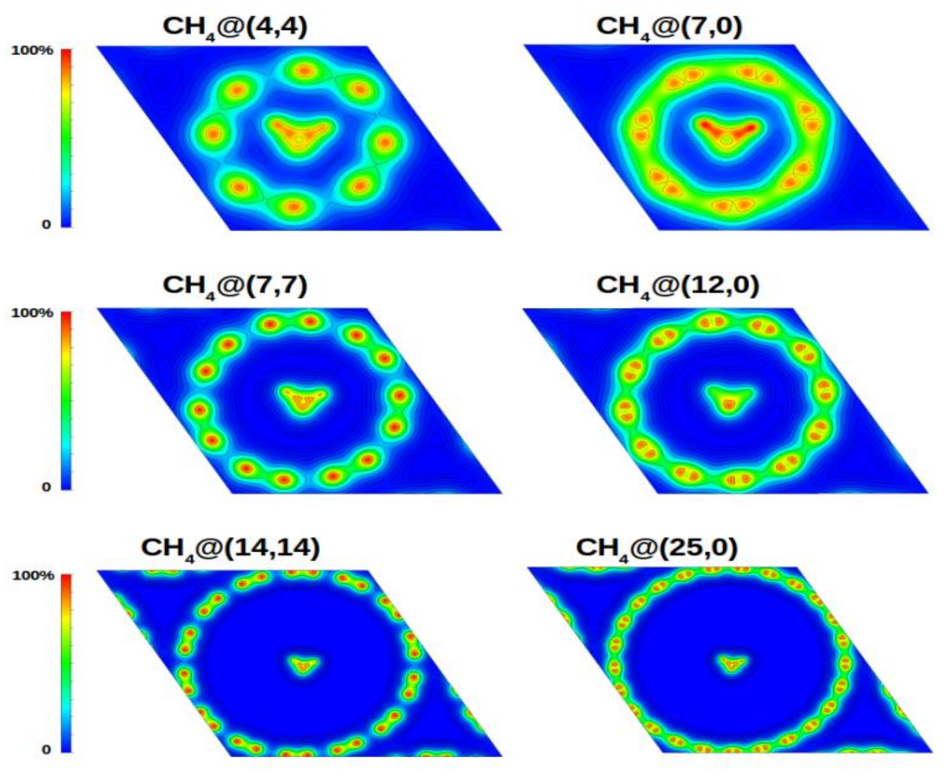


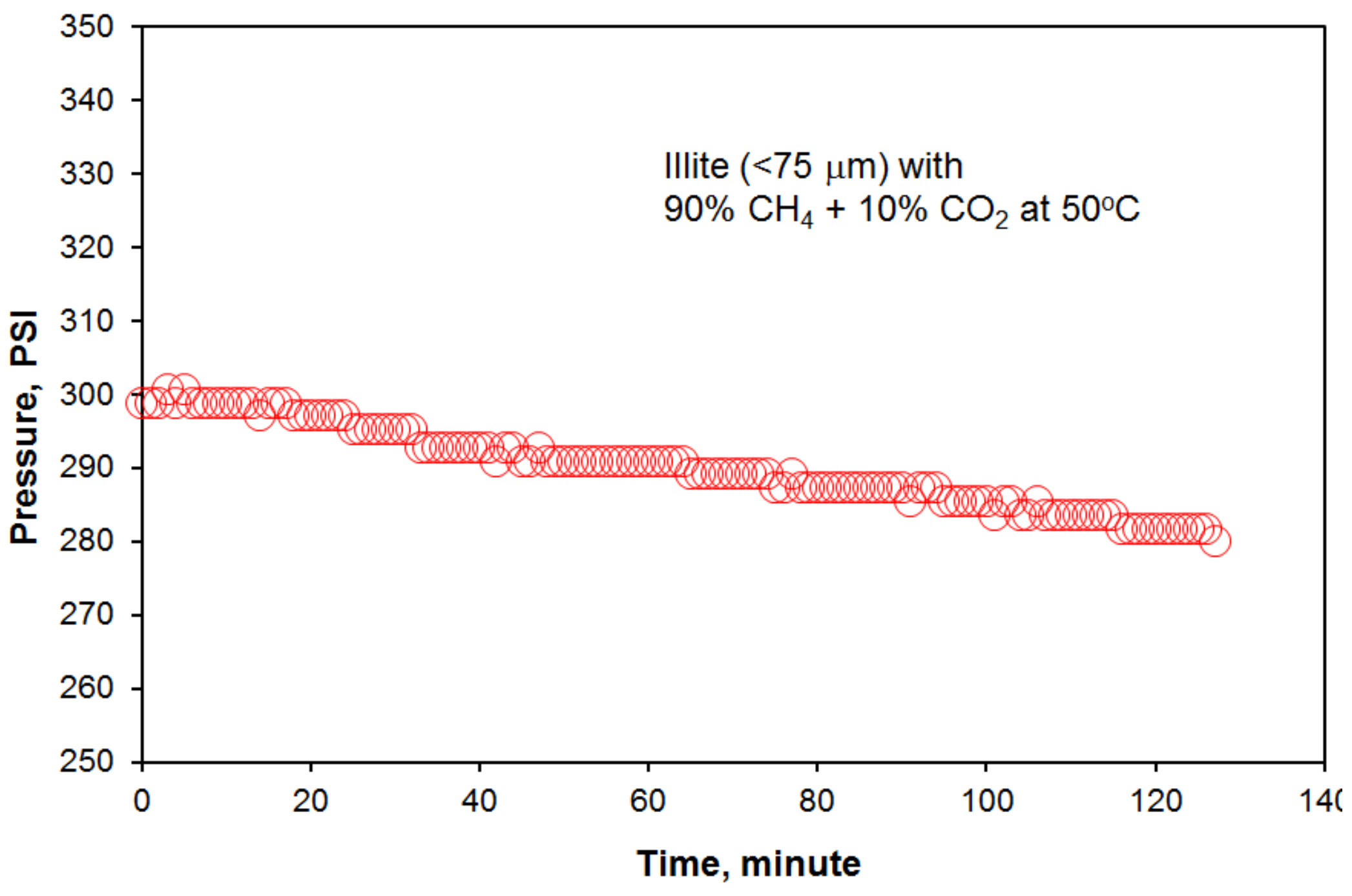
Methane release from kerogen matrix is characterized by a fast release of pressurized free gas followed by a slow release of adsorbed gas.

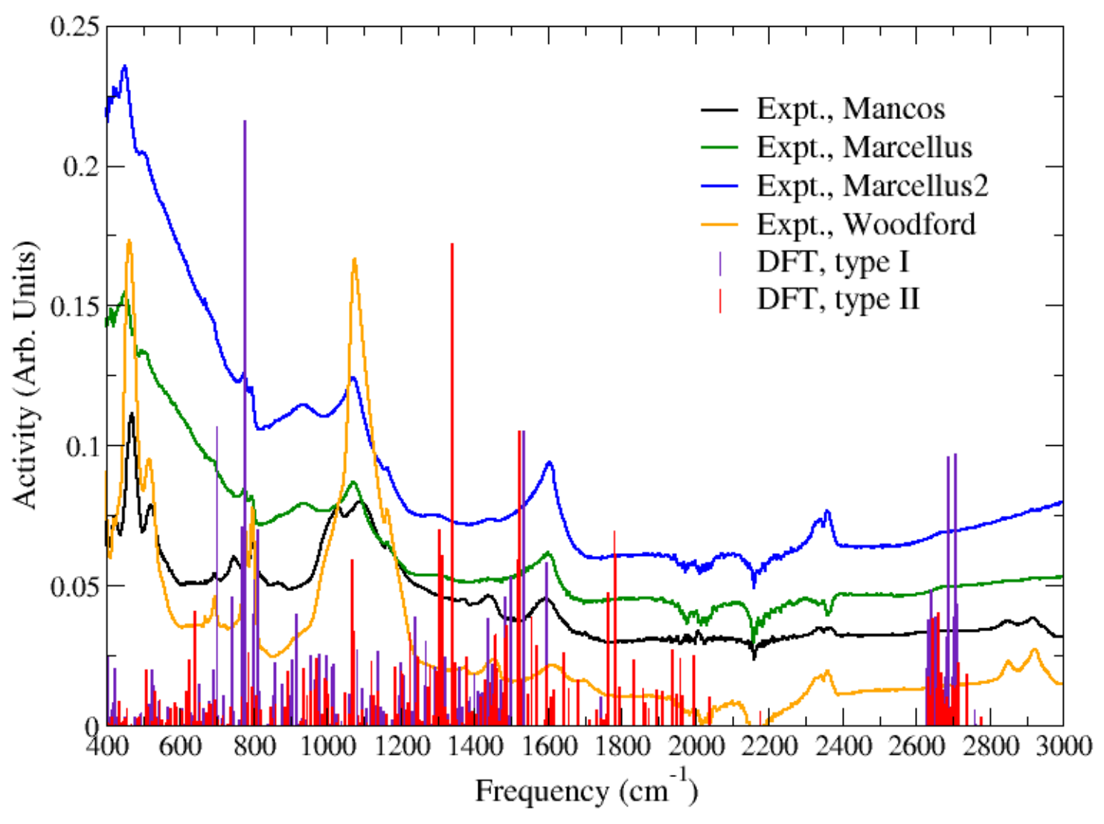
Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at 1 bar total pressure

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min^{-1}
DARCO activated carbon	25	85% CH_4 + 15% CO_2	1	28	0.68
	50	85% CH_4 + 15% CO_2	1	11	0.59
	75	85% CH_4 + 15% CO_2	1	9.0	0.31
	100	85% CH_4 + 15% CO_2	1	2.1	0.14
	125	85% CH_4 + 15% CO_2	1	1.8	0.10
Montmorillonite, <75 μm	25	85% CH_4 + 15% CO_2	1	2.8	4.7×10^{-2}
	50	85% CH_4 + 15% CO_2	1	0.30	9.6×10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.19	6.7×10^{-3}
	100	85% CH_4 + 15% CO_2	1	0.18	5.1×10^{-3}
	125	85% CH_4 + 15% CO_2	1	0.12	3.3×10^{-3}
Crushed Shale	25	85% CH_4 + 15% CO_2	1	0.29	3.3×10^{-3}
	50	85% CH_4 + 15% CO_2	1	0.21	2.7×10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.16	1.7×10^{-3}









Conclusions:

- Our kerogen model can reproduce the experimental results such as the kerogen density, pore size distribution, and methane adsorption isotherm in organic shales.
- Methane diffusion in kerogen nanopores behaves significantly different from the bulk phase.
- We found that methane release from kerogen matrix is characterized by a fast release of pressurized free gas followed by a slow release of adsorbed gas.
- Significant amount of gas deposited in kerogen can be trapped in isolated pores and thus not recoverable.
- Significant fraction methane can sorb onto clay minerals.
- A new kerogen model is needed to reproduce FTIR data.

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