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Unlock nanopores: Fundamental Understanding and engineering implications

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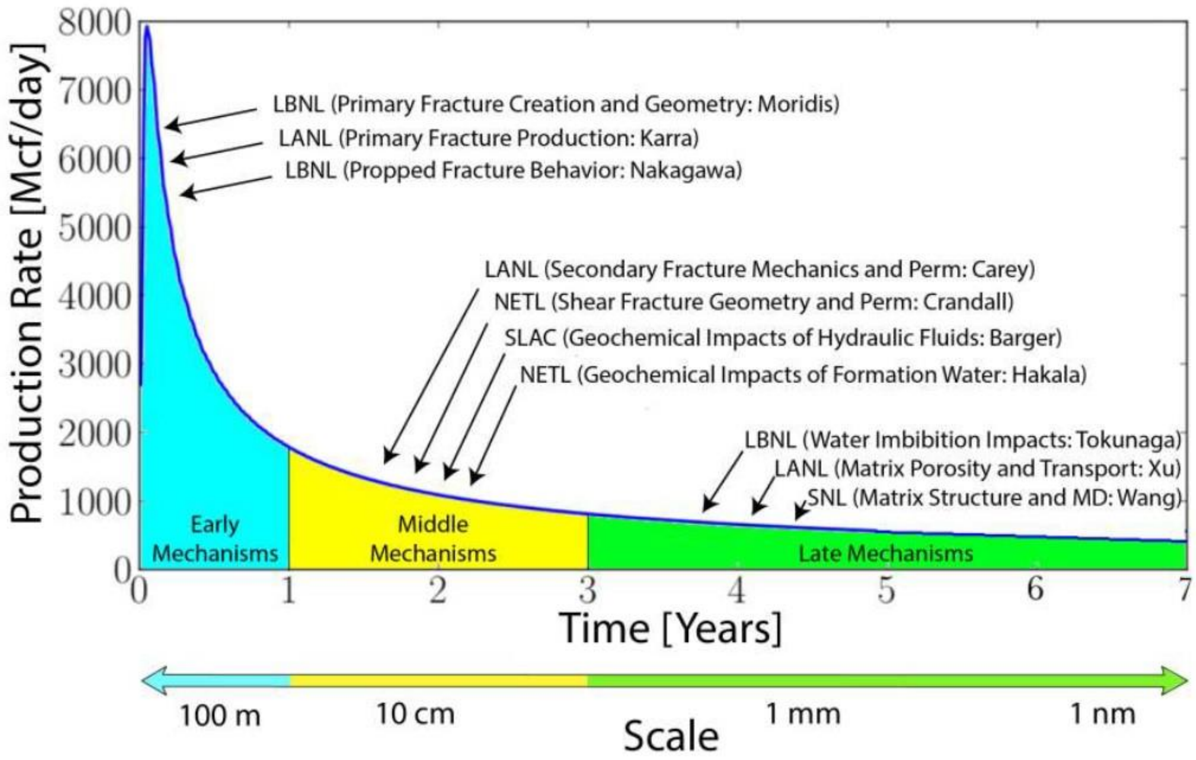

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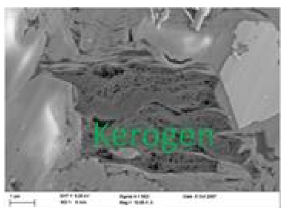
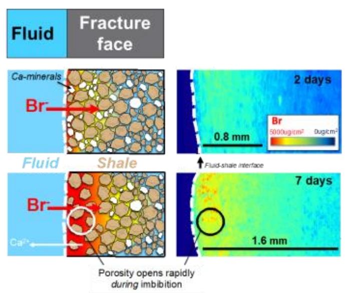
Insights on the Relationship between Matrix Geochemistry and Production: From Pores to Fractures

Insights on geochemical processes influencing production from shales at multiple spatial scales, from nanopores through the matrix and fractures to the reservoir

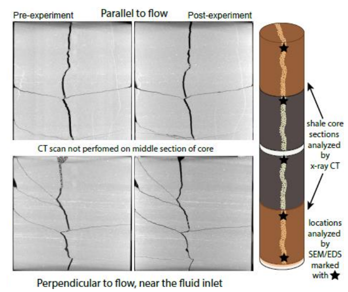
Nanopores



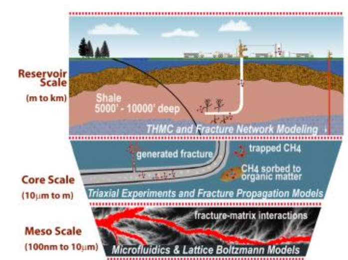
Matrix



Fractures



Reservoir

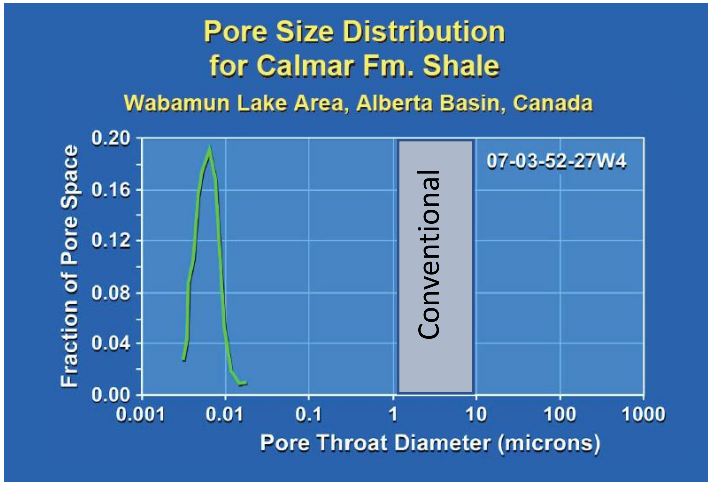


nm — *µm* — *mm* — *m* — *km*

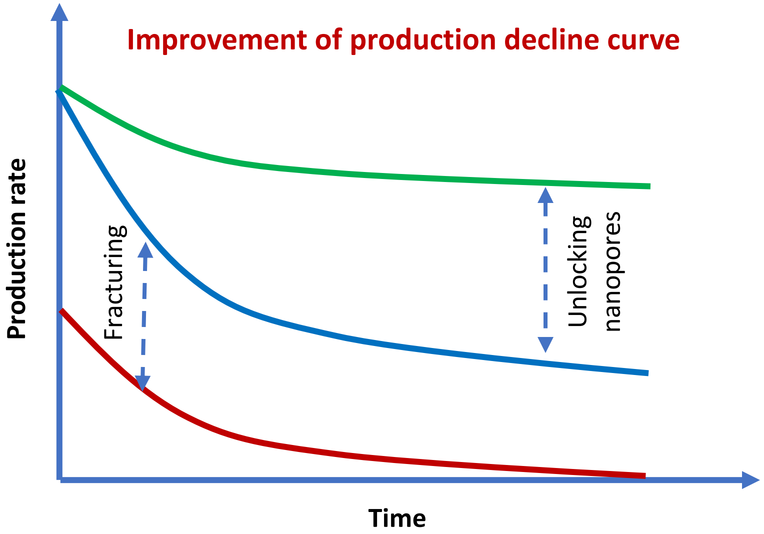
U.S. Department of Energy, Fossil Energy, Office of Oil & Natural Gas · National Energy Technology Laboratory · Berkeley Lab · Los Alamos National Laboratory · Sandia National Laboratories · SLAC National Accelerator Laboratory

Unlock Nanopores In Shale Matrix

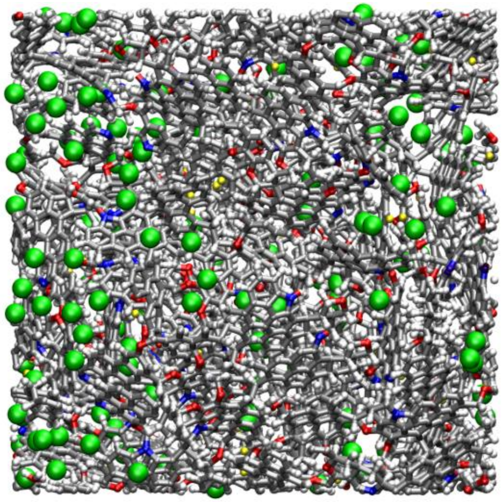
- **Unconventional reservoir: What makes it unconventional?**
  - Nanopores (~1 - 100 nm) accounts for > 90% of total porosity in shale.
  - Fluids confined in nanopores behave drastically differently from their bulk phases (Wang, 2014, Chem. Geol.).
- **Objectives:**
  - Understand fluid (CH_4-CO_2-H_2O) behaviors in shale nanopores;
  - Explore possible engineering approaches to unlocking these nanopores to improve the sustainability of a wellbore production.

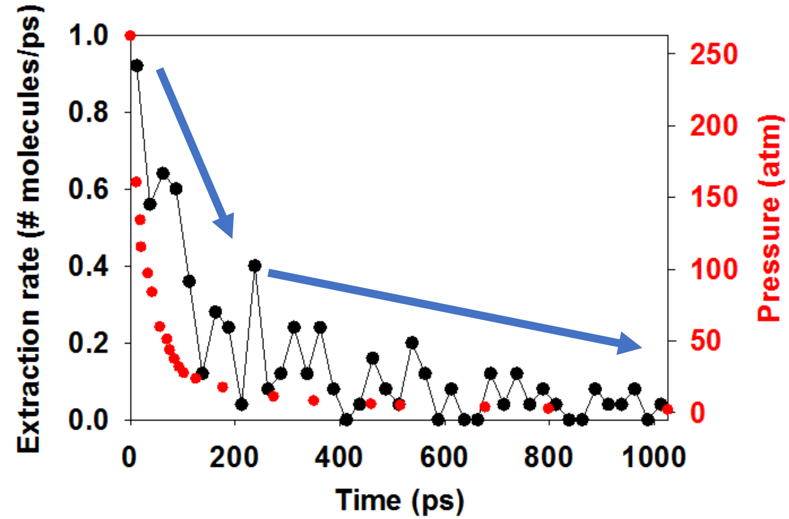


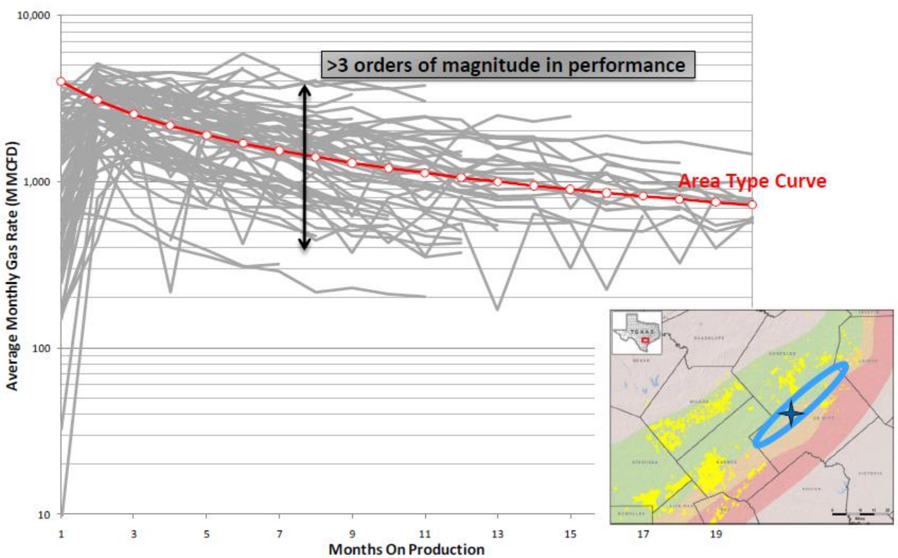
Bachu & Bennion (2006)



Methane sorption and release within kerogen







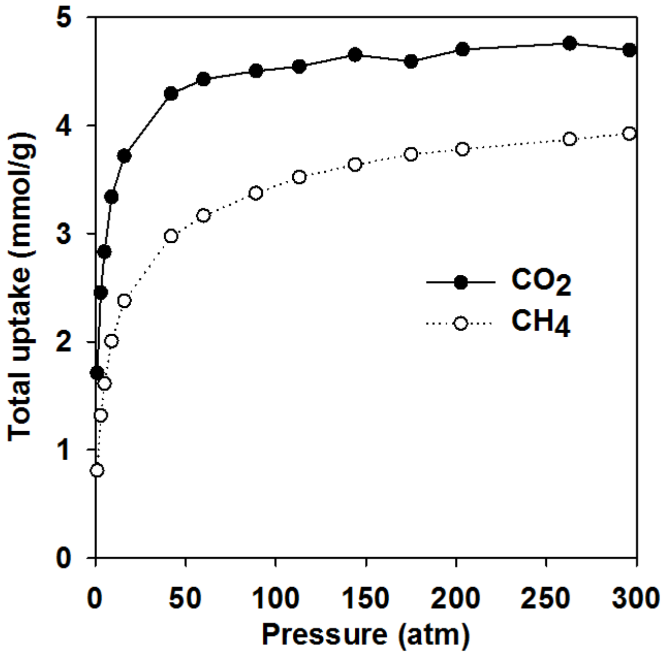
Robertson (2013)

Key messages:

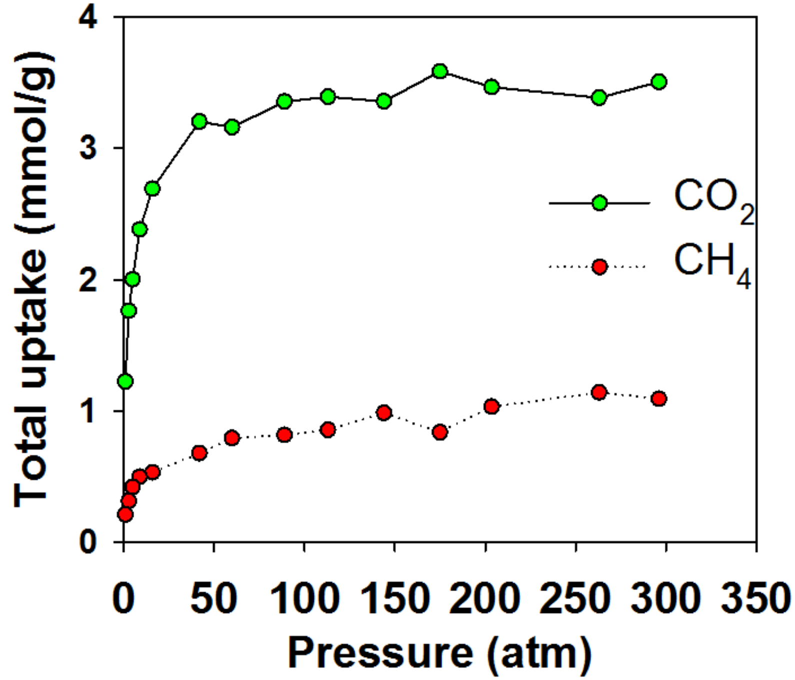
- Two stages of methane release: As the pressure draws down, fast advective release of compressed free gas followed by slow diffusion of adsorbed gas.
- Fracturing controls the total stimulated volume, while the decline rate is an intrinsic property of a shale formation (i.e., independent of fracture patterns).
- Pressure management, periodic shut in, etc.

Displacement of CH_4 by CO_2 in kerogen nanopores

Pure gas adsorption



1:1 binary gas adsorption



Key messages:

- Supercritical CO_2 as a chemical agent for enhanced oil/gas recovery
- Simultaneous shale gas extraction and carbon sequestration

Kerogen reaction with supercritical CO_2

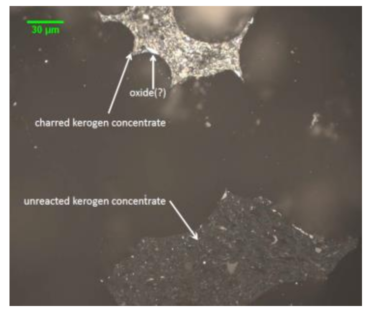
Observations:
- After reaction, C and H decrease and O increases.
- Pyrolysable carbon and residual carbon both decrease, presence of significant amount of inorganic carbon.

Implication: Chemical reaction with supercritical CO_2 as an alternative maturation process?

Original kerogen

Reacted kerogen

Reacted kerogen

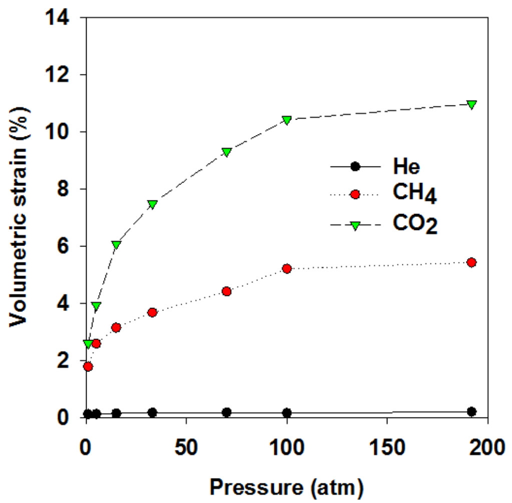


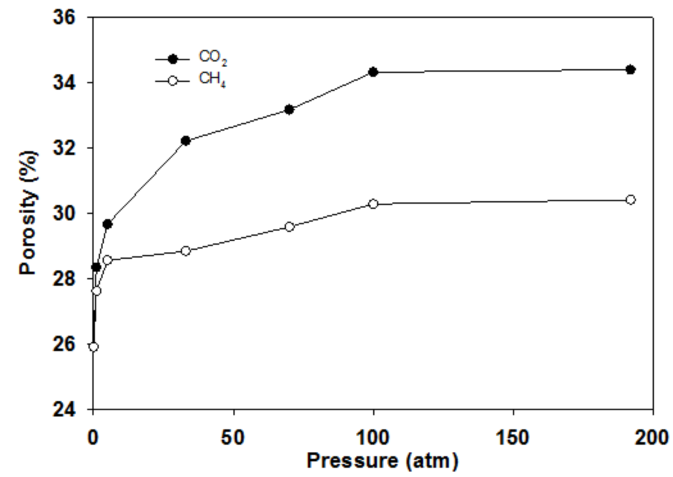
Experiment: Immature kerogen reacted with supercritical CO_2 saturated brine (1M) at 90 °C and 2800 psi for 30 days

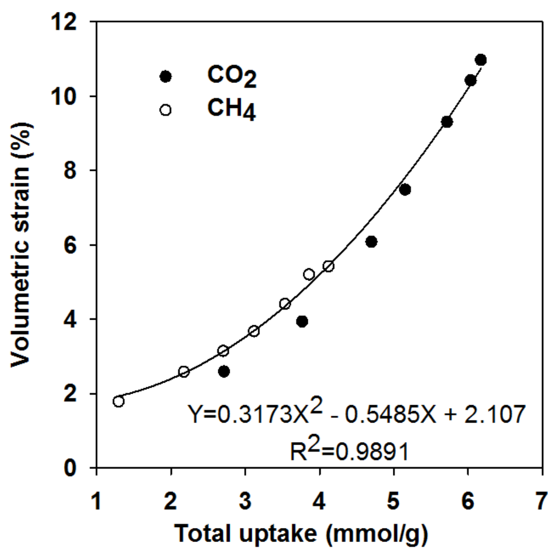
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Ash	C/H	C/O	C/N
	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	atom	atom	atom
original kerogen	73.91	7.59	2.67	8.40	2.73	3.0	0.81	0.73	32.3
reacted residual kerogen	62.68	4.54	1.64	12.36	1.49	24.10	1.15	0.42	44.6

	S1	S2	S3	Tmax	Pyrolysable organic carbon	Residual organic carbon	TOC	Hydrogen index	Oxygen index	Mineral inorganic carbon
	mg HC/g	mg HC/g	mg CO_2/g	°C	% wt	% wt	% wt	mg HC/g TOC	mg CO_2/g TOC	% wt
original kerogen	5.63	412.11	6.47	431	35.24	37.97	73.21	563	9	0.93
reacted residual kerogen	1.91	181.38	13.54	424	16.23	33.90	50.13	362	27	11.89

Open up nanopores in kerogen through chemical-mechanical coupling





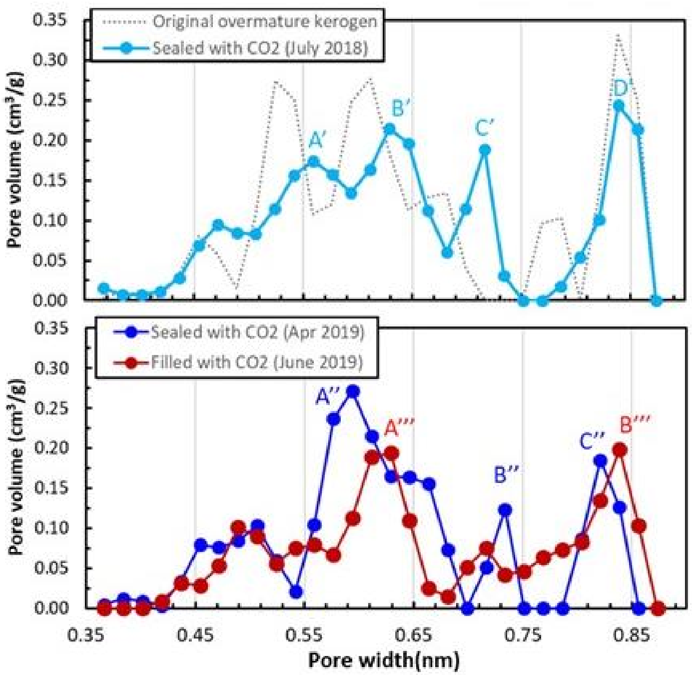


Key messages:

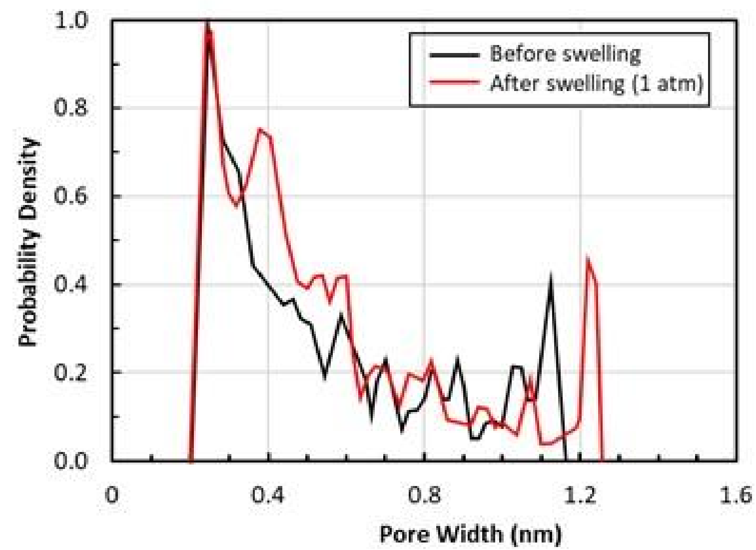
- Gas sorption and desorption is a strongly coupled chemical-mechanical process.
- Supercritical CO_2 may help open up nanopores in kerogen.

Swelling is controlled by the surface layer of gas adsorbed.

Open up nanopores in kerogen (cont.)



Experiments: Expose kerogen to 1 atm CO_2 and then measure pore size changes.



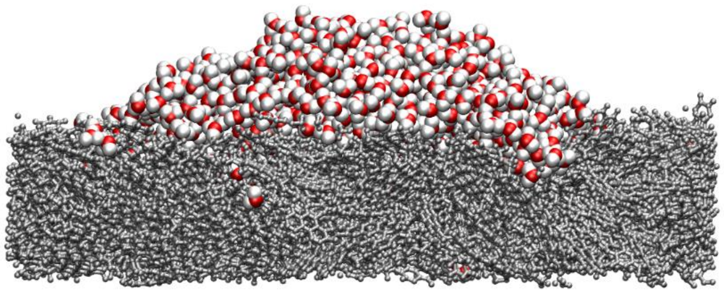
MD simulation

Key messages:

- Kerogen is mechanically compliant! → easy to open up nanopores through chemical-mechanical coupling.
- Implications to reservoir engineering, especially, for organic carbon-rich plays → use of CO_2 to prevent pore collapse?

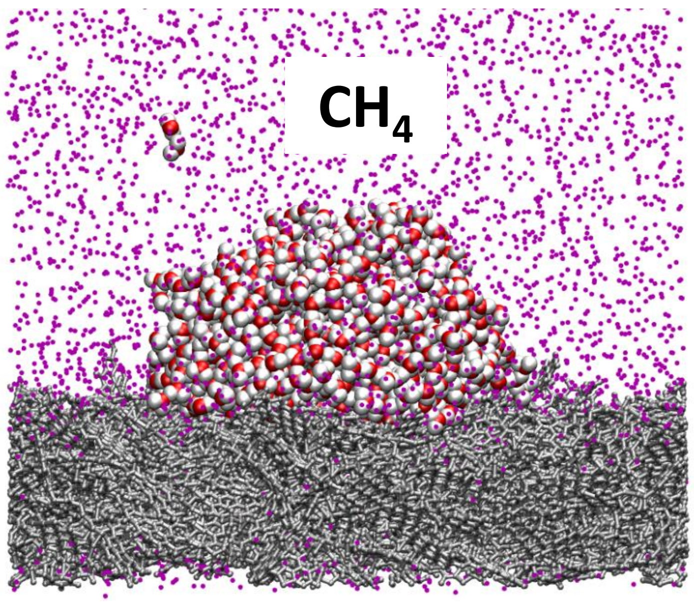
Understanding water blockage: Wettability of kerogen

$42.8^{o} \pm 6.5^{o}$

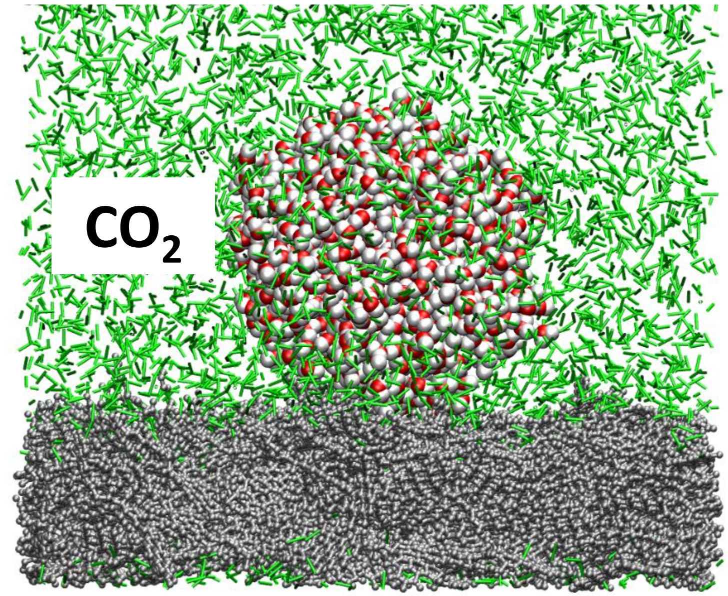


Low pressure

$79.18^{o} \pm 1.97^{o}$



High pressure



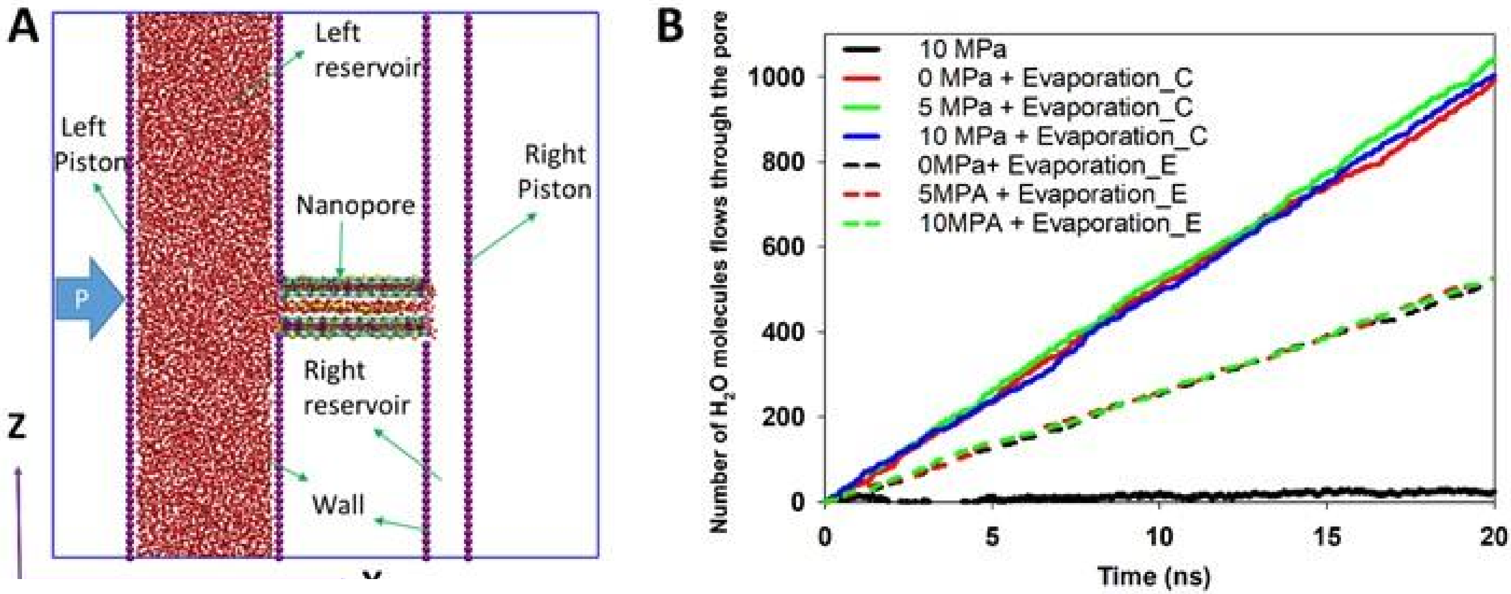
High pressure

Key messages:

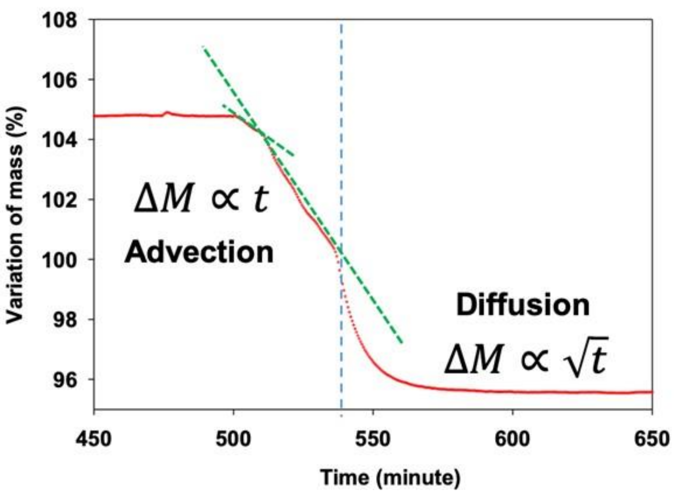
- Supercritical CO_2 may change kerogen pore surfaces from hydrophilic to hydrophobic transition.
- It may reduce water blockage in shale matrix.

Understanding water imbibition/loss/blockage and well cleanup: Advective water flow in clay interlayers

MD simulations



Experiments



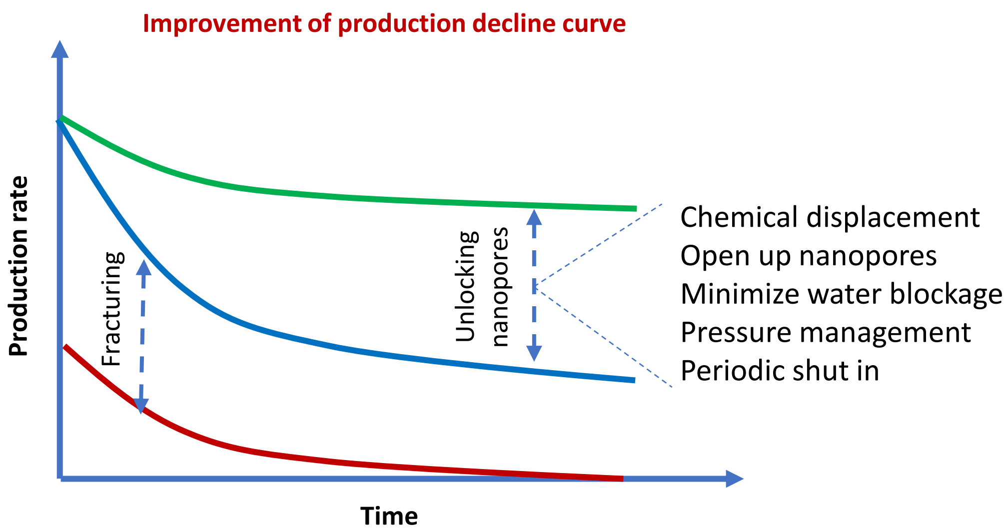
Dehydration of < 2 μm bentonite measured with thermo-gravimetric (TGA) analysis.

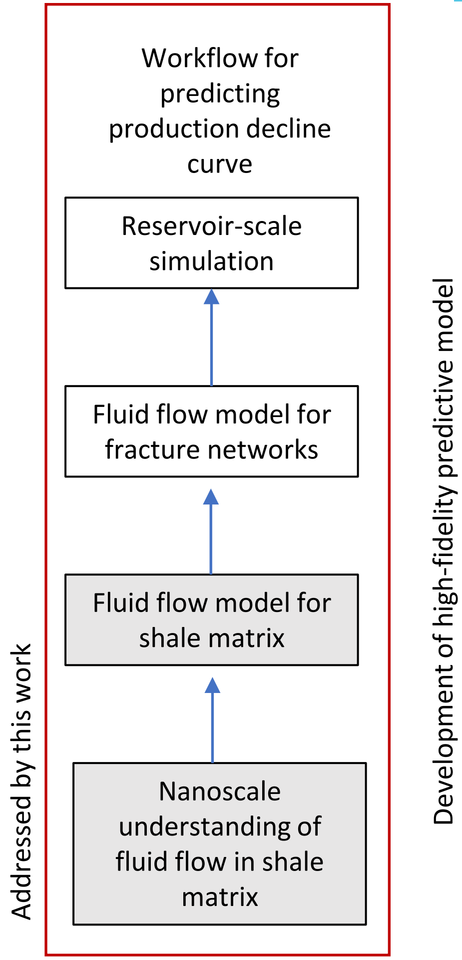
Key messages:

- It is extremely difficult to push water through nanopores by an externally hydraulic pressure.
- Fast advective water flow can be induced by a chemical potential gradient (capillary pressure).
- Water imbibition during hydrofracturing
- Wellbore stability
- Well treatment (removal of water skin, e.g., using dry supercritical CO_2.

Concluding Remarks

- Nanopore confinement plays a critical role in gas disposition and release in unconventional reservoirs.
- Our work reveals complex interactions of CH_4-CO_2-H_2O in shale nanopores.
- Mechanistic understanding of these interactions will help explore possible ways to unlock shale nanopores.
- Such understanding is critical to design an effective stimulation, EOR and carbon management strategy for shale oil/gas extraction.





Acknowledgment

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