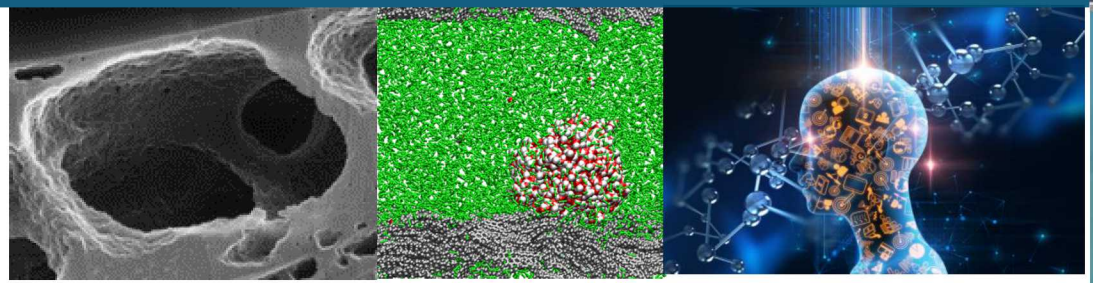
Sandia National Laboratories

SAND2018-12628PE

Fundamental Understanding of CH_4-CO_2-H_2O Interactions in Shale Nanopores under Reservoir Conditions



PRESENTED BY

Yifeng Wang, Tuan Anh Ho, Guangping Xu, Philippe Weck, Yongliang Xiong, Edward Matteo, Louise Criscenti, Jessica Kruichak

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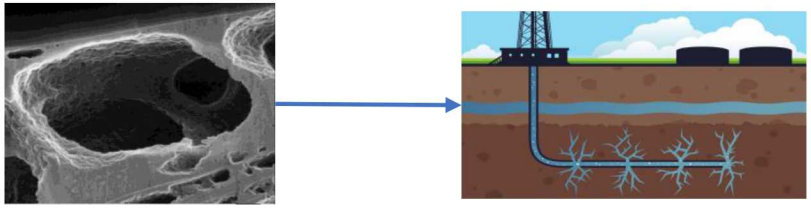
Fundamental Understanding of CH_4-CO_2-H_2O Interactions in Shale Nanopores under Reservoir Conditions (P.I.: Yifeng Wang, NETL POC: Bruce Brown)

Project Goal

- Obtain a fundamental understanding of CH_4-CO_2-H_2O interactions in shale nanopores under high-pressure and high temperature reservoir conditions and integrate this understanding into reservoir engineering for efficient shale gas recovery and subsurface carbon sequestration.

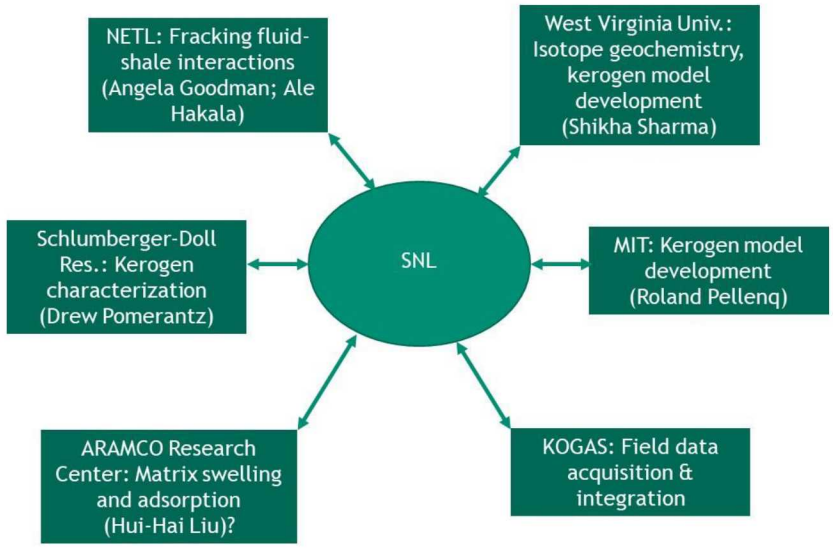
Potential Impacts

- Significantly advance fundamental understanding of hydrocarbon storage, release, and flow in shale.
- Provide more accurate predictions of gas-in-place and gas mobility in reservoirs.
- Help to develop new stimulation strategies to enable efficient resource recovery from fewer and less environmentally impactful wells.
- Provide the basic data set to test the concept of using supercritical CO_2 as an alternative fracturing fluid for simultaneous methane extraction and CO_2 sequestration.
- Leverage unique SNL capabilities: nanogeochemistry, high pressure and high temperature geochemistry, numerical modeling, and nanoscience.



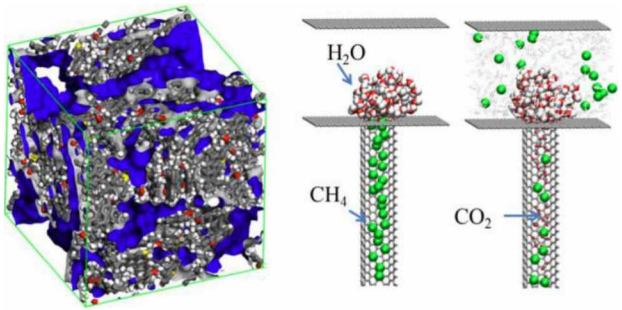
Major Accomplishments and/or Deliverables (11 journal publications; 6 invited conference presentations)

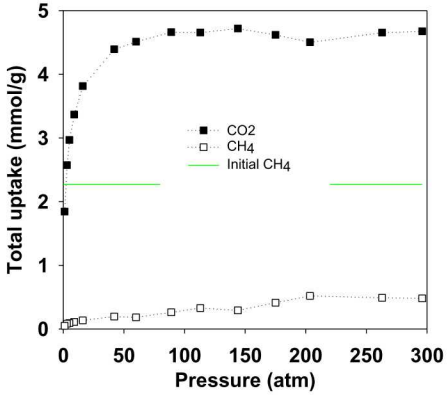
- Significant portion of CH_4 can adsorb to clay minerals.
- Wellbore production decline could be attributed to nanoscale gas disposition and migration in kerogen nanopores.
- Significant progress has been made in understanding complex interactions CH_4-CO_2-H_2O components in kerogen nanopores.
- Existing kerogen models were found inadequate in representing actual kerogen structures.
- Close collaborative relationships have been established with universities and industries.

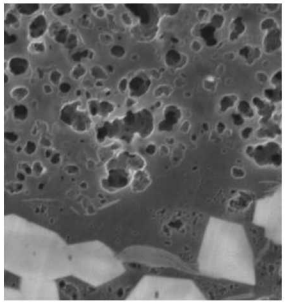


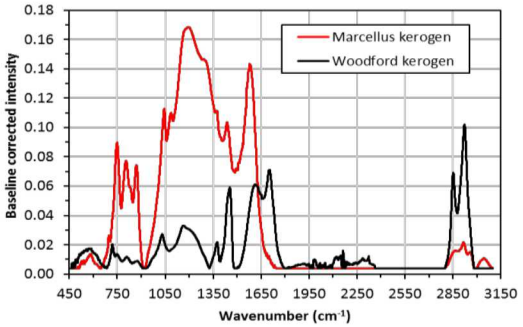
Publications

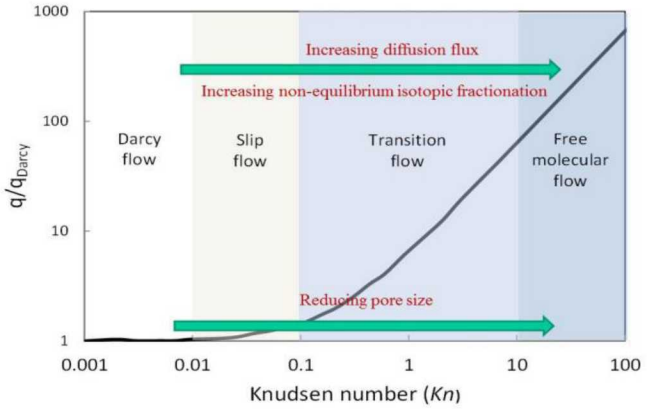
- Xiong, Y., Wang, Y. & Olivas, T. (2015) Experimental Determination of P-V-T-X Properties and Sorption Kinetics in the CO_2-CH_4-H_2O System under Shale Gas Reservoir Conditions: Part One, P-V-T-X Properties, Sorption Capacities and Kinetics of Model Materials for CO_2-CH_4 Mixtures to 125°C , **High Temperature Aqueous Chemistry**, HiTAC-II Workshop, Heidelberg, April 16, 2015.
- Ho, T. A., Criscenti, L. J. & Wang, Y. (2016) Nanostructural control of methane release in kerogen and its implications to wellbore production decline. **Scientific Reports** 6, 28053; doi: 10.1038/srep28053.
- Weck, P. F., Kim, E. & Wang, Y. (2016) van der Waals forces and confinement in carbon nanopores: Interaction between CH_4, COOH, NH_3, OH, SH and single-walled carbon nanotubes. **Chem. Phys. Lett.** 62, 22-26.
- Cristancho, D., Akkutlu, I.Y., Criscenti, L.J., Wang, Y. (2016) Gas storage in model kerogen pores with surface heterogeneities, **SPE**-180142-MS, DOI: 10.2118/180142-MS.
- Wang, Y. (2017) On subsurface fracture opening and closure. **J. Petrol. Eng.** 155, 46-53.
- Wang, Y. (2018) From nanofluidics to basin-scale flow in shale: Tracer investigations, In: **Shale Subsurface Science and Engineering** (in press, book chapter)
- Weck, P. F. Kim, E., Wang, Y. et al. (2017) Model representation of kerogen structures: An insight from the density functional theory. **Scientific Reports,** 7, DOI:10.1038/s41598-017-07310-9.
- Ho, T. A., Greathouse, J. A., Wang, Y, and Criscenti, L. J. (2017) Atomistic structure of mineral nano-aggregates from simulated compaction and dewatering. **Scientific Reports**, 7, 15286.
- Ho, T. A., Wang, Y., Criscenti, L. J. & Xiong, Y. (2017) Differential retention and release of CO_2 and CH_4 in kerogen nanopores: Implications to gas extraction and carbon sequestration. **Fuel**, 220, 1-7.
- Ho, T. A. Wang, Y. and Criscenti, L. J. (2018) Chemo-mechanical coupling in kerogen gas adsorption/desorption. **Phys. Chem. Chem. Phys.**, 20, 1239.
- Ho, T. A, Wang, Y. et al. (2018) Supercritical CO2-induced atomistic lubrication for water in a rough hydrophilic nanochannel. **Nanoscale** (online now)
- Wang, Y. et al. (2019) Nanogeochemistry of unconventional oil/gas reservoirs (invited paper by **Chemical Geology**).
- **Book:** Wang, Y., **Nanogeochemistry: Emergent Properties of Nano-Scale Mineral Phases and Confined Fluids**, Elsevier (in preparation).











Why do we care?

Sustainability of shale oil/gas production:

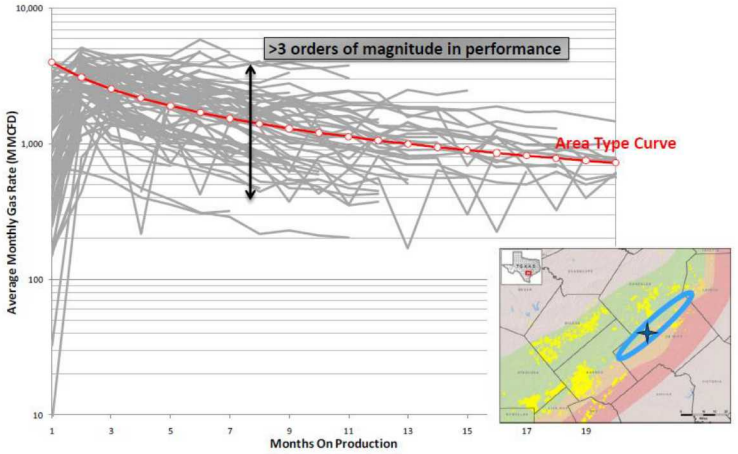
- Large variability and unexpected rapid decline in well production (up 95% reduction over first 3 years)
- New wells to be drill to maintain the supply, with increasing cost/well
- Low recovery rates (<10%), with little known about secondary gas recovery in "brown fields" (>90% of total gas reserve!!!).
- Long-term production projection largely empirical

Locating sweet spots, maximizing individual wellbore production while minimizing environmental impacts.

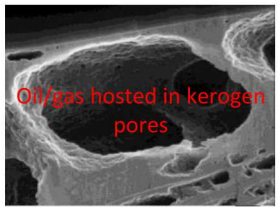
- Existing practice largely empirical.

Limiting step of oil/gas production:

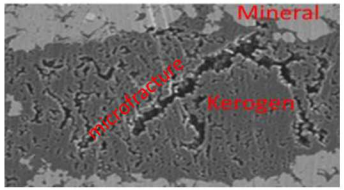
- Fluid interaction and transport in nanoporous shale matrix
- Knowledge drawn from conventional reservoirs is not applicable.
- Mechanistic understanding of oil/gas disposition and release in shale matrix is crucial for developing engineering approach to maximizing wellbore production and extending the production cycle.



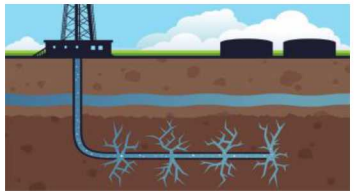
Robertson (2013)



Oil/gas release from kerogen pores (Pore size: nanometer scale)



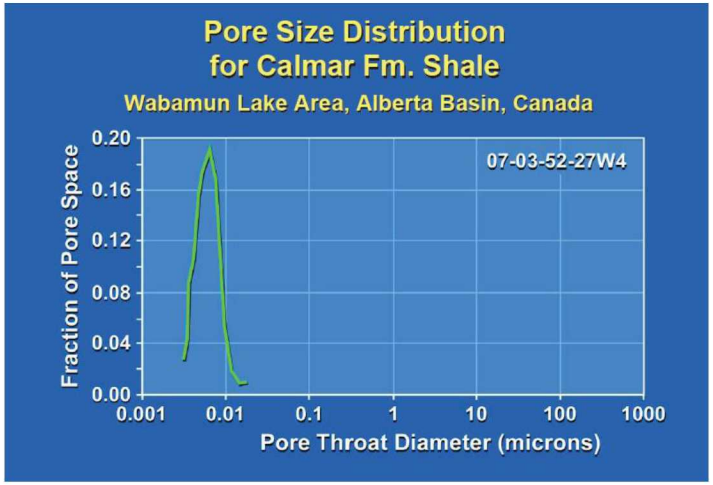
Fluids "flow" from kerogen via nano- or micro-fractures (Channel size: nanometer to micrometer scale)



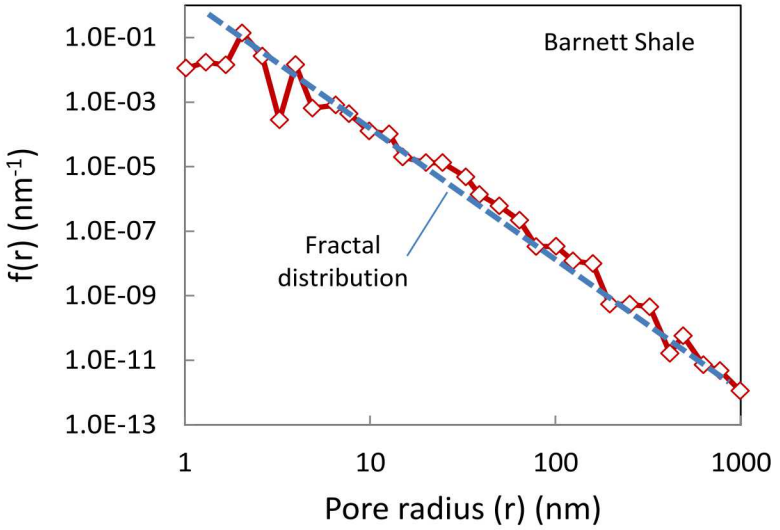
Fluids flow into hydraulic fractures then to production well
(Channel size: millimeters to decimeters)

Limiting step(s)

Why nanoscale?

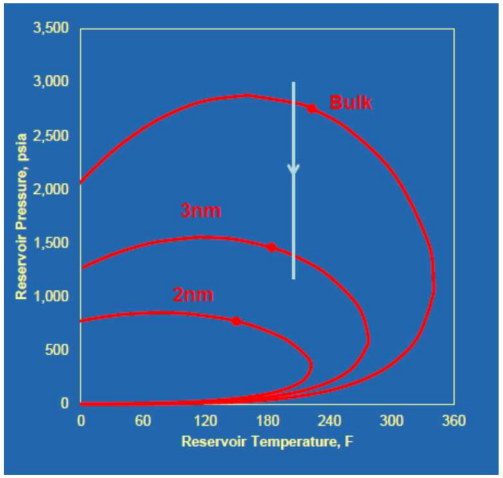


Bachu & Bennion (2006)

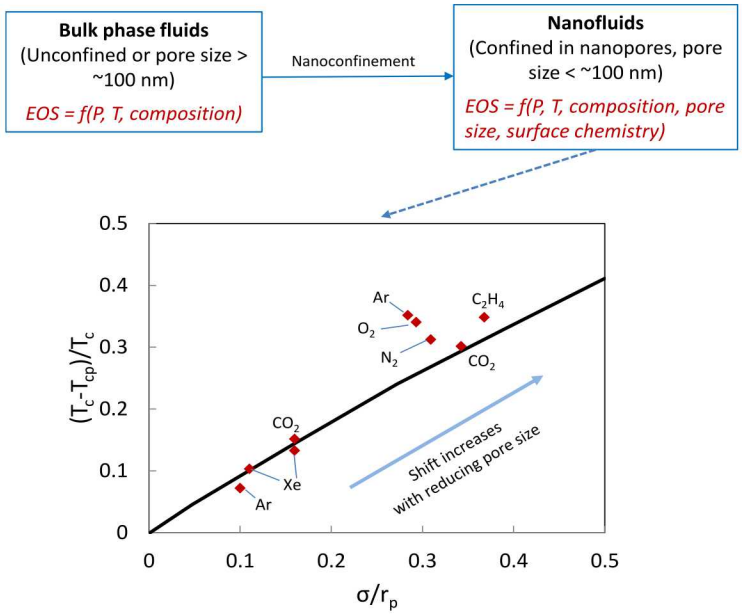


Clarkson et al. (2012)

Effects of nanopore confinement



Akkutlu, 2013



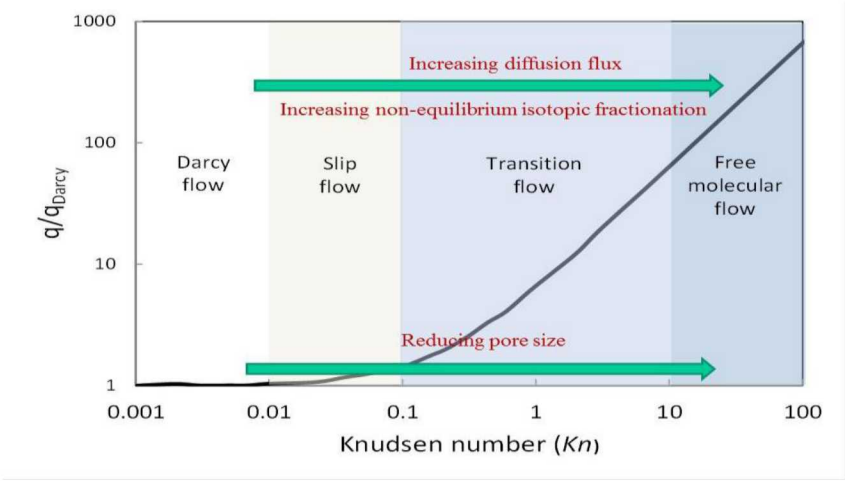
Wang (2014); Zarragoicoechea and Kuz (2004)

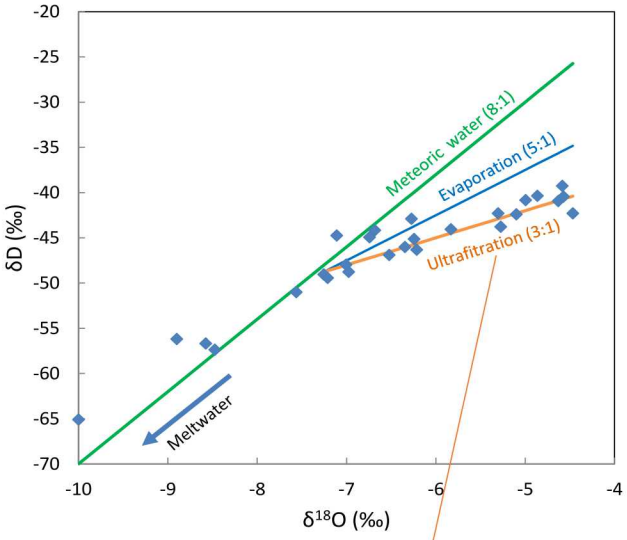
Rule of thumb: Chemical species under nanoconfinement behave drastically differently from those unconfined (i.e., those in bulk phase). Nanoconfinement modifies:

- Thermodynamic properties
- Kinetic properties
- Transport properties
- Others

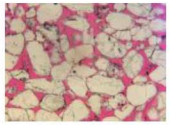
Most of the knowledge obtained from conventional reservoirs is not applicable to shale oil/gas.

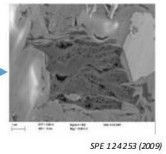
Emergent transport properties in nanopores: Isotopic fractionation as unique signature for real time monitoring for gas production





Conventional reservoir





SPE 124253 (2009)

Shale formation

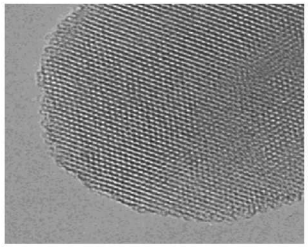
$$k_{app} = \frac{2r}{3RT}\left(\frac{8RT}{\pi M}\right)^{1/2} + \left[1 + \left(\frac{8\pi RT}{M}\right)^{1/2}\frac{\mu}{pr}\left(\frac{2}{\alpha} - 1\right)\right]\frac{cr^2}{8\mu}$$

M - Molecular weight

Mass dependent transport

Wang (2018)

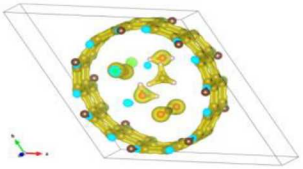
Technical Approach



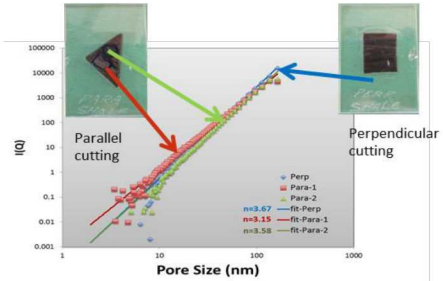
Synthesis of nanoporous materials

Isolation of kerogen from Mancos shale

Pioneering work in nanogeochemistry. Access to DOE Center of Integrated Nanotechnology



Density functional theory (DFT) modeling



Pore structure characterization

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

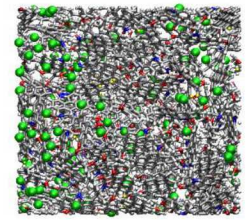
Gas disposition & release
- Gas in place (GIP)
- Gas migration from matrix into fractures
- Stimulated volume
- Gas for secondary recovery

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

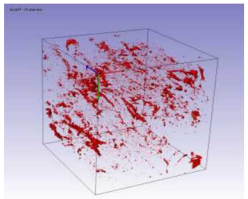
Nanoscience
- Effects of nanopore confinement on fluid thermodynamic properties
- Effects of nanopore confinement on methane transport (microfluidics in shale)

Upscaling
- Percolation theory
- Fractal representation
- Lattice Boltzmann modeling

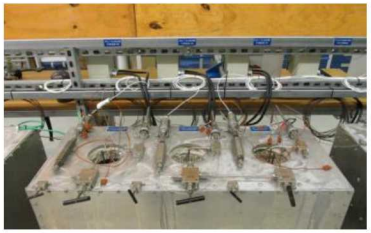
Predictive models
- Constitutive relationships
- Continuum models
- Reactive transport modeling



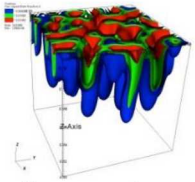
Molecular dynamics (MD) simulation



Pore structure characterization (FIB)

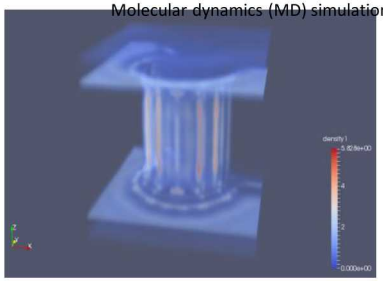


High pressure/high temperature sorption/desorption measurements



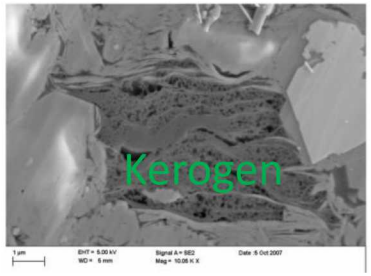
http://www.pflotran.org/applications.html

PFLOTRAN: Reactive transport modeling



TRAMANTO: Classical Density Functional Theory

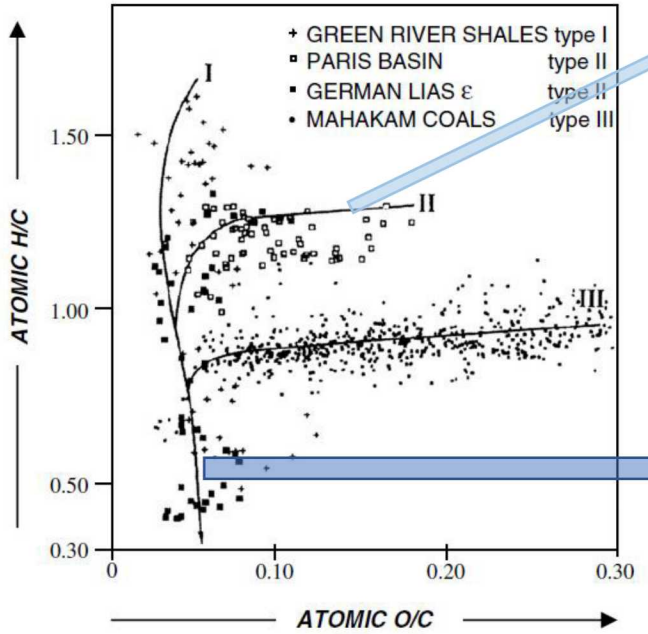
Kerogen 101

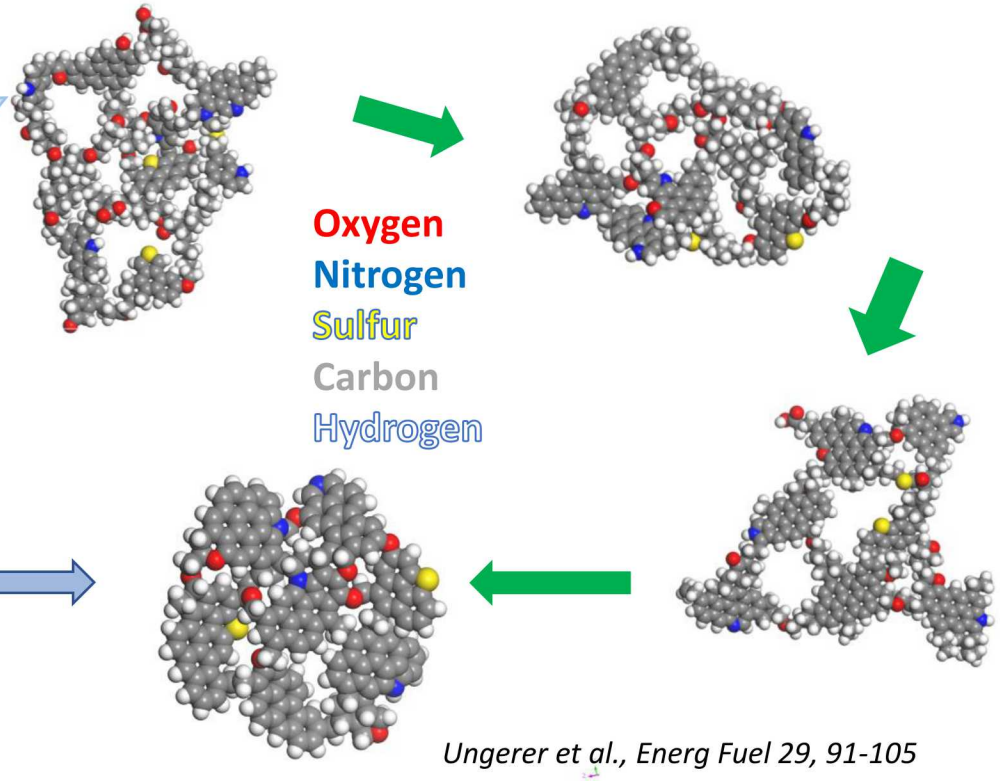


- Insoluble organic matter found in sedimentary rocks (geochemistry)
- Cracks into petroleum products (kerogen maturation, petroleum generation)

Van Krevelen diagram

Organic Geochemistry 38, 719-833 (2007)

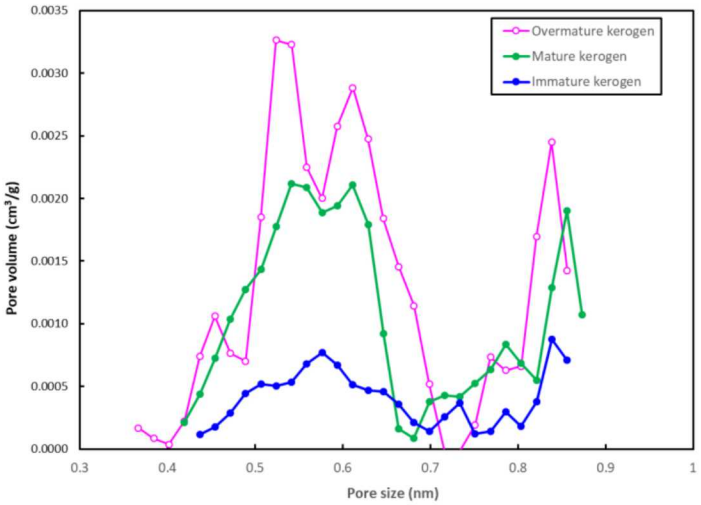




Ungerer et al., Energ Fuel 29, 91-105

- **Hosts pore space responsible for petroleum storage and transport**

Kerogen characterization



BET measurements

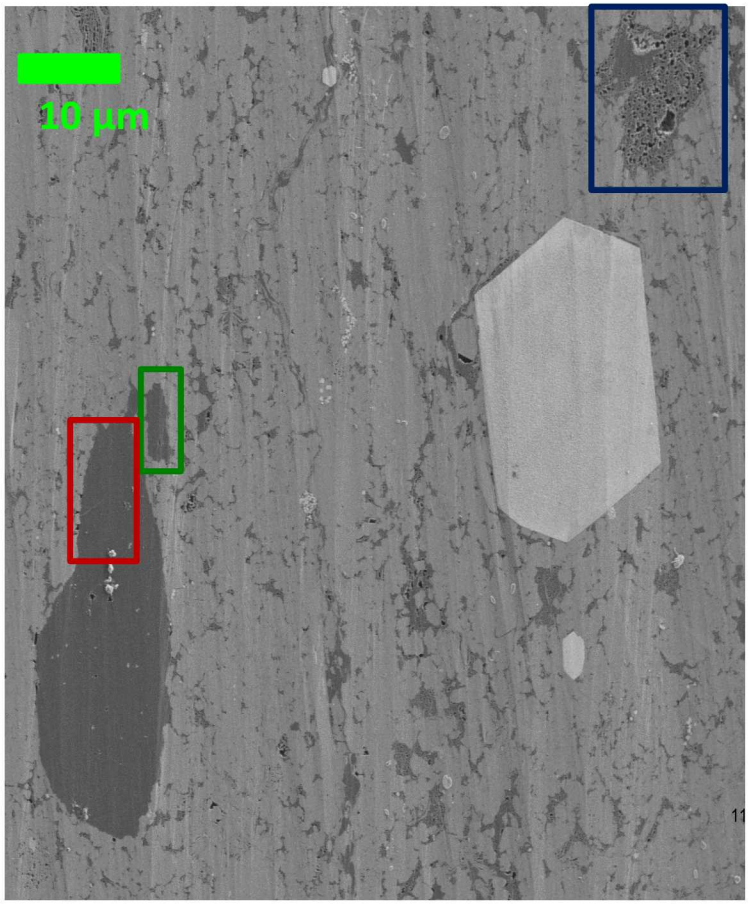
	Ro%	BET (m2/g)	*Pore volume (< 0.9 nm) cm3/g*	Micropore volume (< 2 nm) cm3/g	Mesopore volume (2-50 nm) cm3/g
Immature	0.7	54	*0.011*	0.020	0.150
Mature	1.4	205	*0.029*	0.080	0.393
Overmature	2.5	301.5	*0.038*	0.131	0.395
CO2 swelled overmature		281.7	*0.035*	0.105	0.348

NMR ^{13}C analyses of kerogen

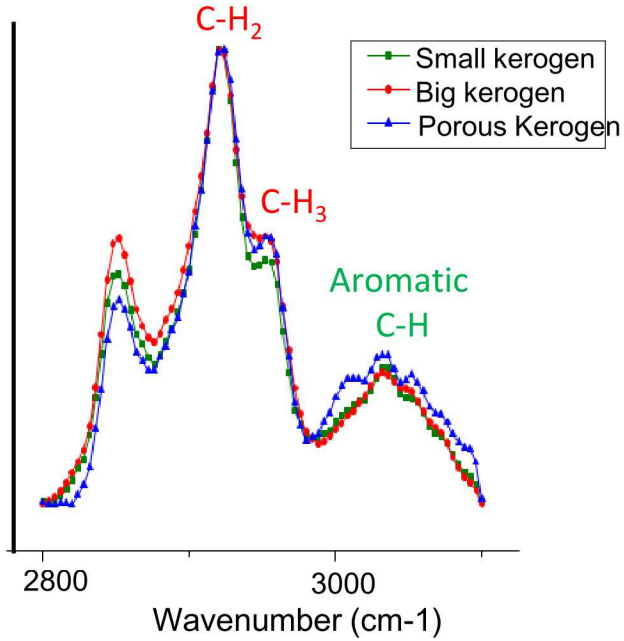
	Aromatic			Aliphatic		
	alkene ring and benzyl ring			-CH2 -	alkane (-CH3)	
	124 ppm	110 ppm	total	30 ppm	19 ppm	total
Mature kerogen	89.81%	4.81%	94.6%	2.03%	3.35%	5.4%
Overmature kerogen	86.27%	11.18%	97.5%	0.36%	2.19%	2.6%
Activated carbon	66.27%	33.73%	100%			

Compositional and structural heterogeneity of kerogen

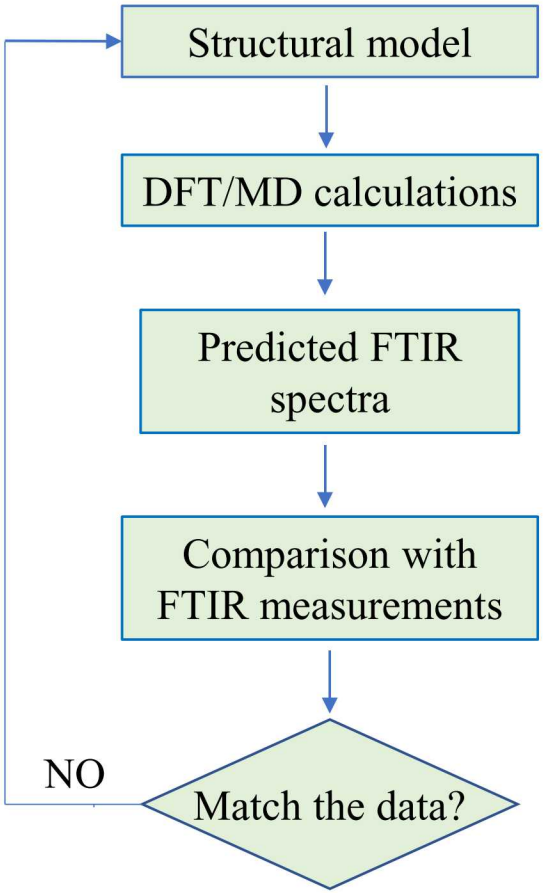
NanoIR spectra of different kerogen grains



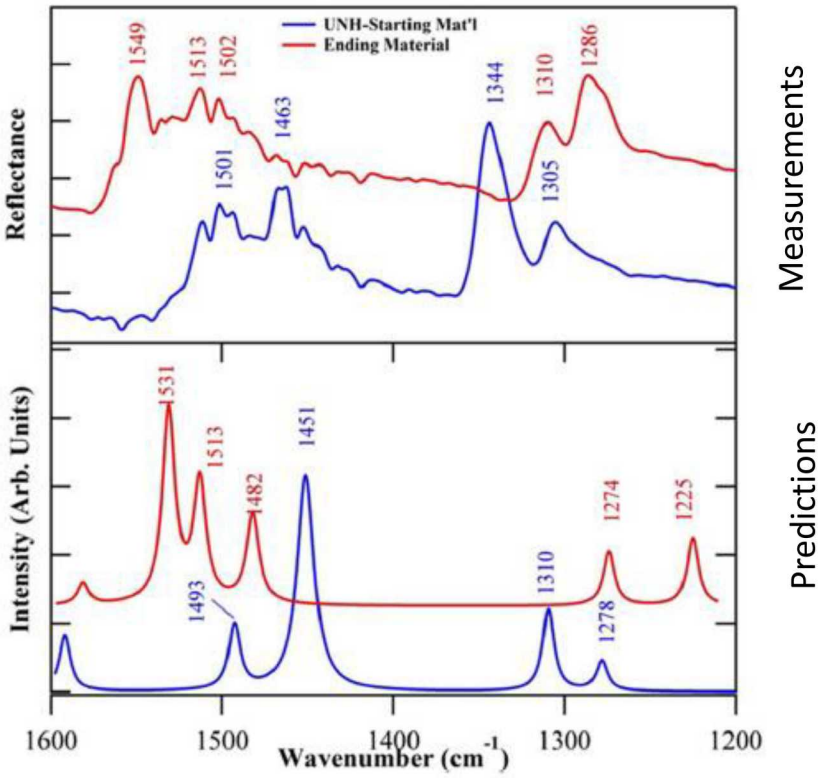
- Strong aromatic absorption – mature kerogen
- Subtle differences in composition between porous and non-porous kerogen grains



Testing adequacy of existing kerogen structural models: Approach

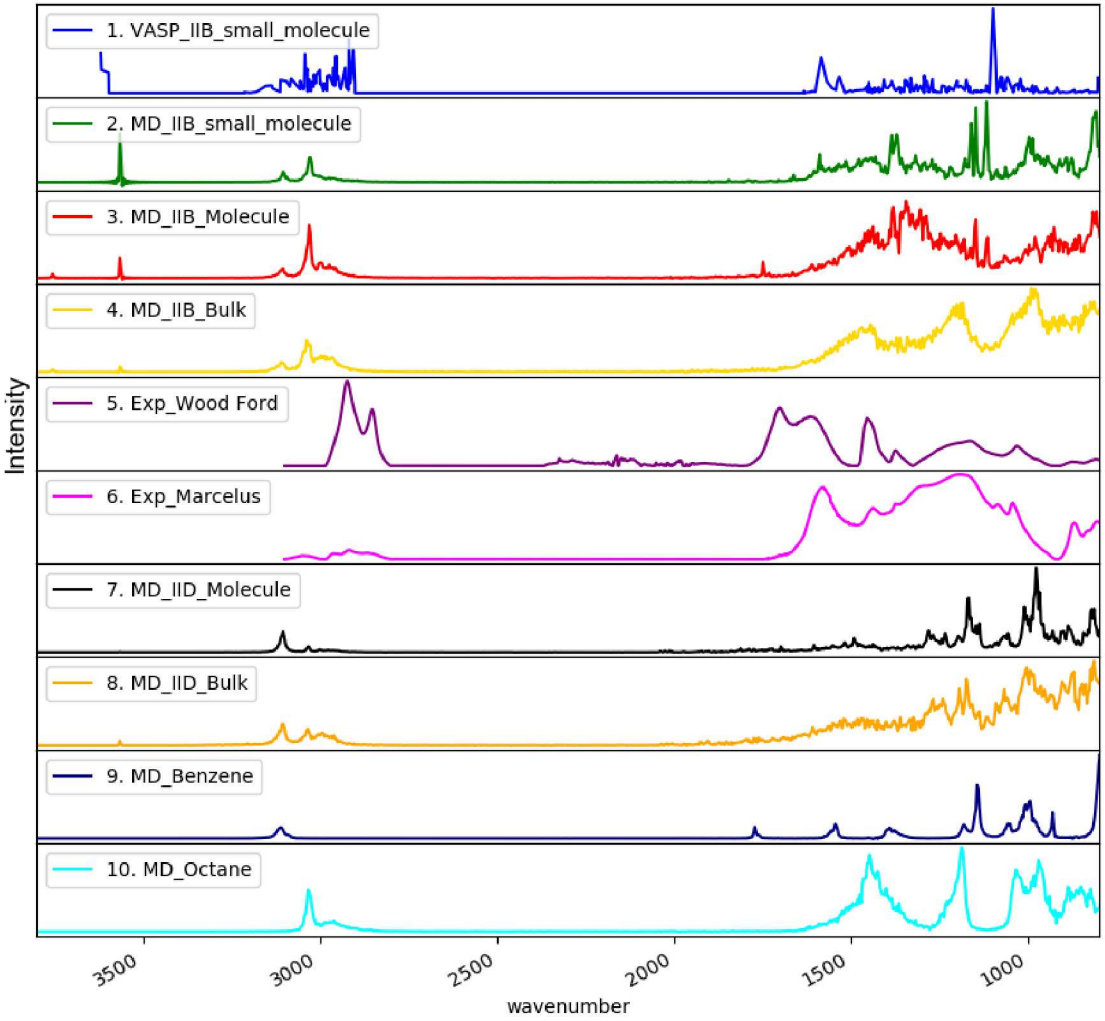


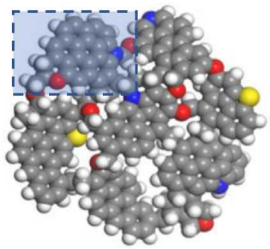
Uranium nitrate hydrate

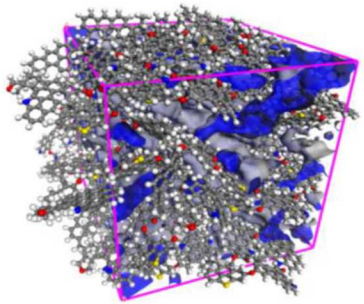


Johnson et al. (2015)

Adequacy of existing kerogen structural models







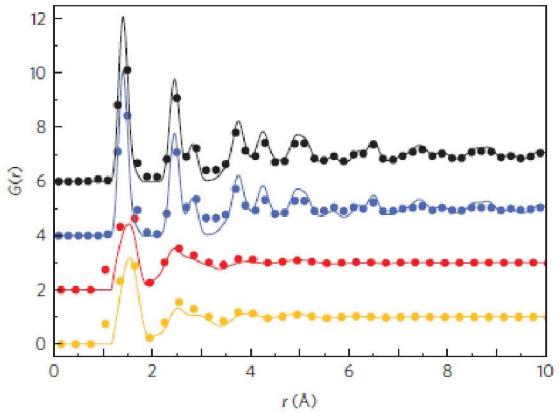
- A significant gap exists in the representation of functional groups.
- Existing force field for MD simulations needs to be refined.

Development of new kerogen models

Table 1
Composition and structural parameters of the type II kerogen.[a]

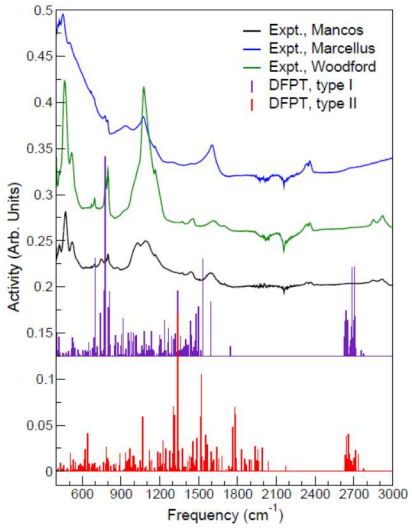
Property	Quantity	Immature		Oil window		Postmature	
		Analytical data	Model unit	Analytical data	Model unit	Analytical data	Model unit
Composition	H/C	1.17	1.17	0.89	0.905	0.56	0.58
	O/C	0.097	0.095	0.05	0.054	0.047	0.051
	N/C	0.029	0.024	0.021	0.021	0.021	0.023
	S/C	0.014	0.012	0.006	0.008	0.01	0.011
C group	Aromatic C from XPS(a) or NMR(b) (%)	40(a), 40(b)	41	54(a), 54(b)	58.7	72(a), 80(b)	79
	C atoms per aromatic cluster	12	11.4	19	20.3	20	19.9
	Fraction of attached aromatic C	0.43	0.46	0.30	0.28	0.24	0.28
	Protonated aromatic C (per 100 C)	13	14	17	14	28	25
O group	O in C—O per 100 C	5.0(a), 7 (b)	5.2	3.5(a), 5 (b)	3.7	4.7(a), 2 (b)	5.1
	O in carboxylic groups (—COOH) per 100 C	1.3	1.6	0.7	0.83	0	0
	O in carbonyl groups (>C=O) per 100 C	3.4	2.8	0.8	0.83	0	0
N groups	Pyrrolic (mol% of N)	52	66	65	60	62	75
	Pyridinic (mol% of N)	27	17	18	40	15	25
	Quaternary (mol% of N)	18	17	17	0	23	0
S Groups	Aromatic S (mol% of S)	46	67	54	50	80	100
	Aliphatic S (mol% of S)	54	33	46	50	20	0

[a] The analytical data corresponds to the experimental work of Kelemen et al. [24]. The model data corresponds to the molecular models of kerogen (type IIA, IIC and IID) detailed in the paper by Ungerer et al. [41].

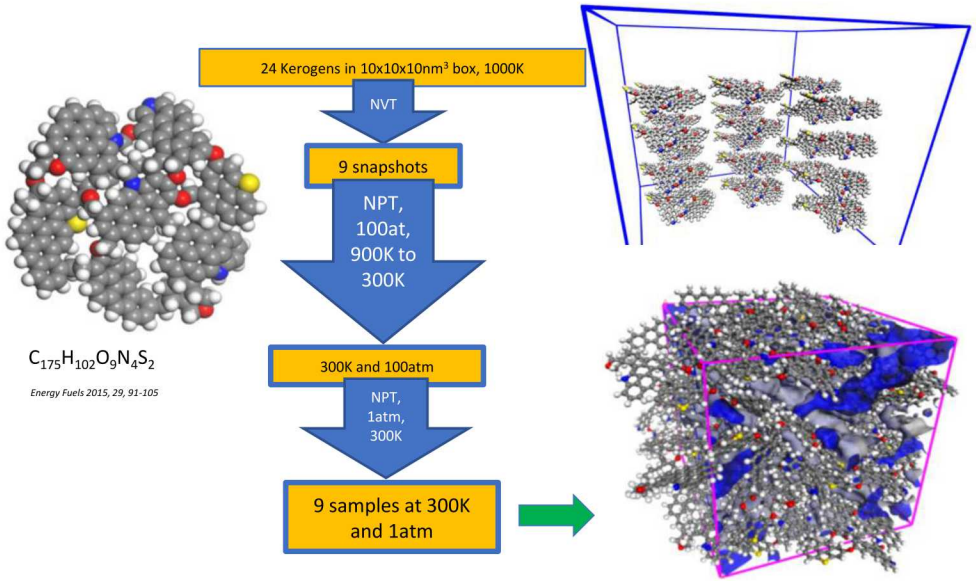


Bousige et al. (2016)

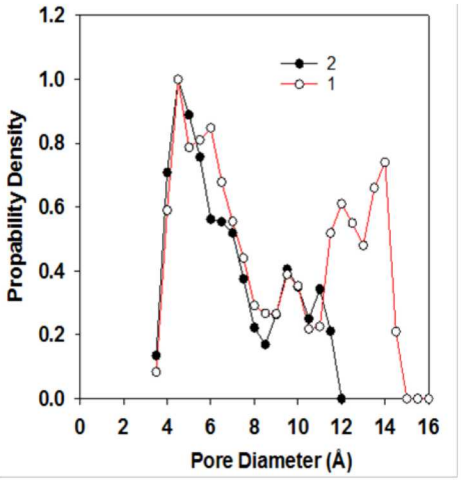
New structural models

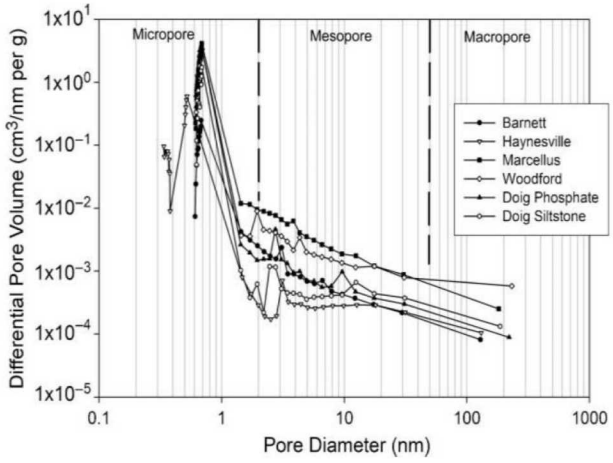


Construction of condensed kerogen structures



Pore size distribution





AAPG 96 (2012), 1099-1119

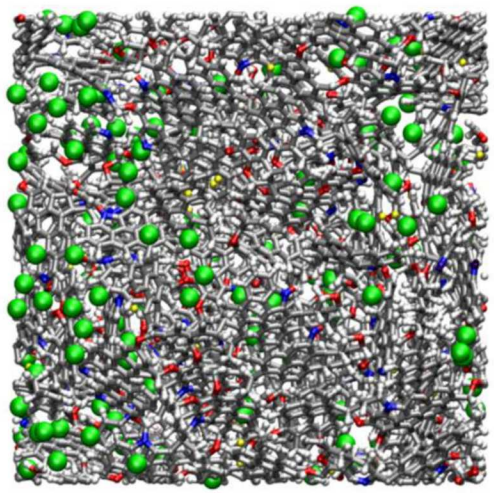
Density

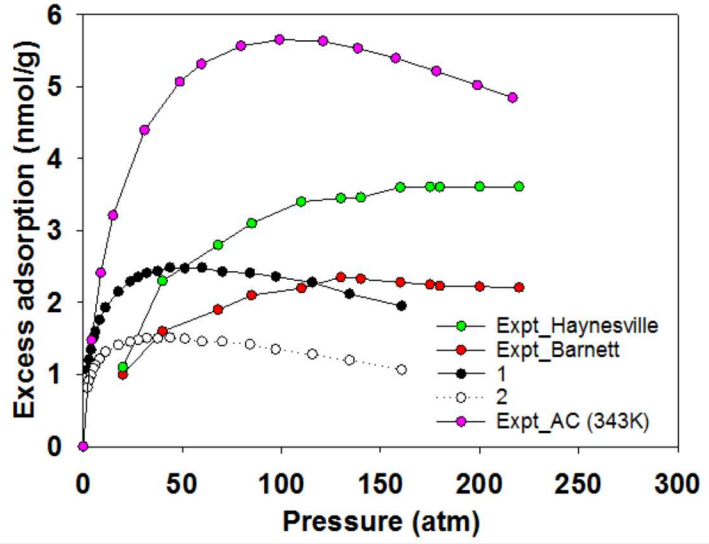
Average :1.22±0.04 g/cm³

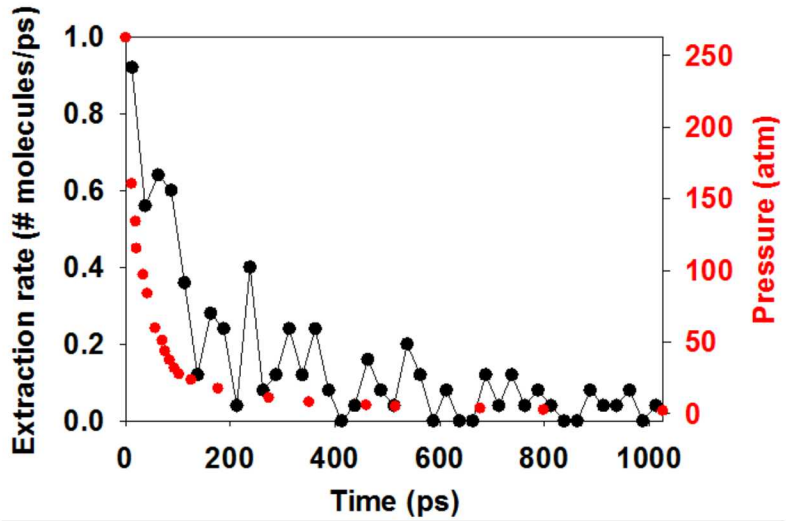
Experiment: 1.28±0.3g/cm³

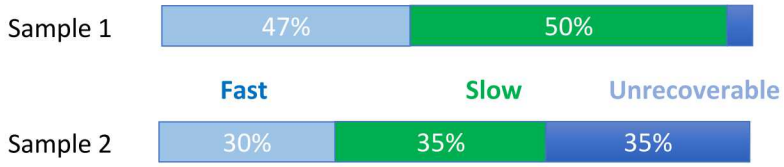
Stankiewicz A, *et al.* (2015) Kerogen density revisited – lessons from the Duvernay Shale. *In: Paper URTeC 2157904 at the Unconventional Resources Technology Conference, San Antonio, Texas, July 2015*

Methane sorption and release within kerogen



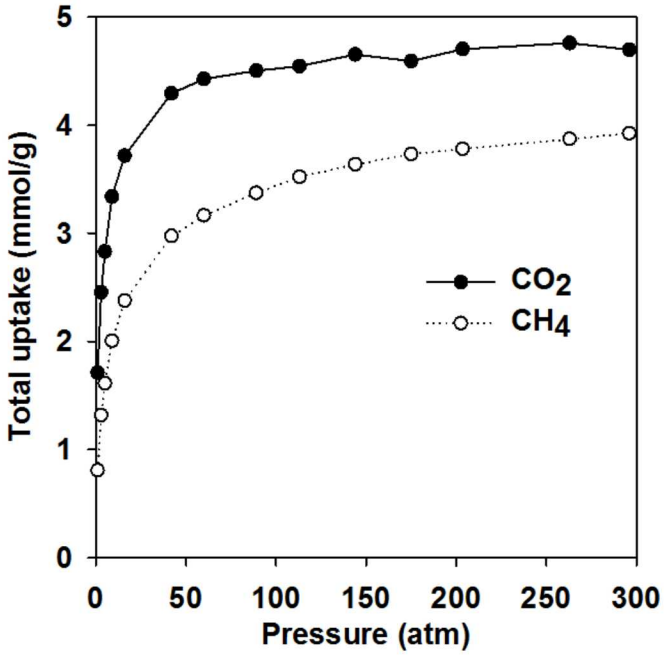




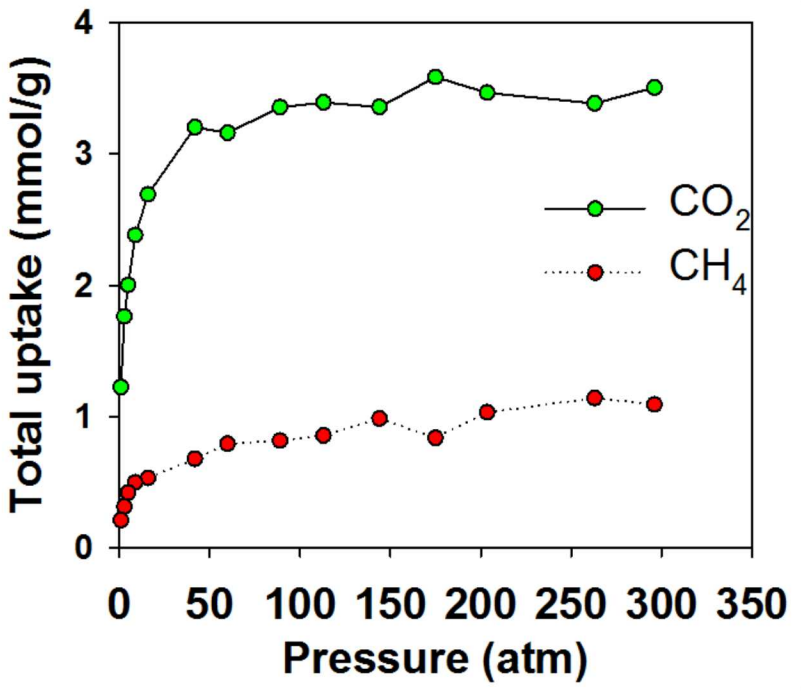


Differential retention and release of CO_2 and CH_4 in kerogen nanopores (Fuel 220, 1-7, 2018)

Pure gas adsorption



1:1 binary gas adsorption



Kerogen preferentially retains CO_2 over CH_4.

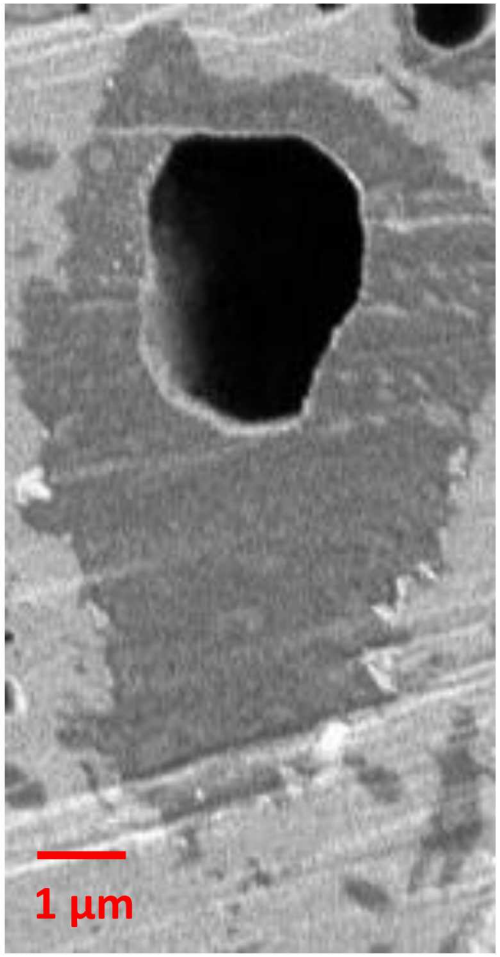
Simultaneous shale gas extraction and carbon sequestration.

Kerogen swelling: Chemo-mechanical coupling (PCCP, 2018)

Rubber swelling in oil

From: Drew Pomerantz, Schlumberger

Will kerogen swell upon gas adsorption?



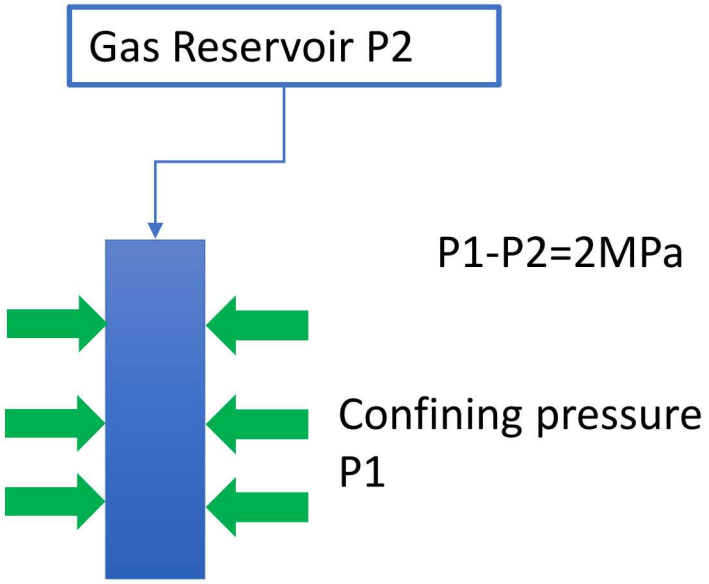
Intact shale with swelled kerogen

Bitumen-extracted shale with collapsed kerogen

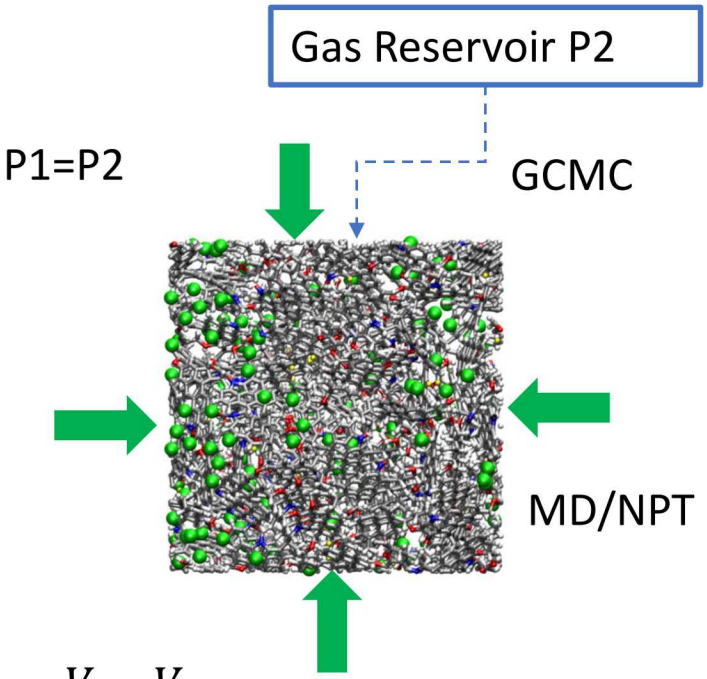
Kerogen swelling: Model setup

Experimental setup

(J. Unconv. Oil Gas Resour., 2014)



Simulation: Hybrid MD/MC

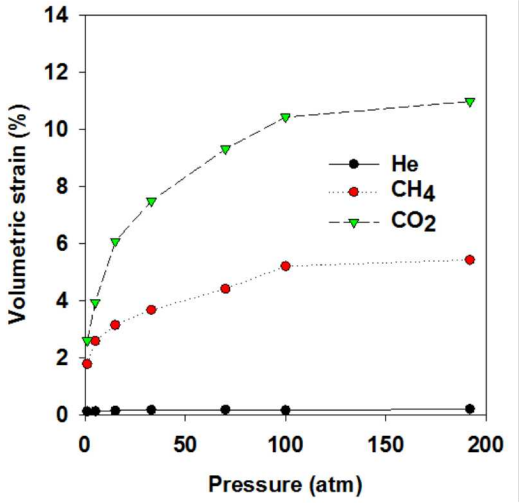


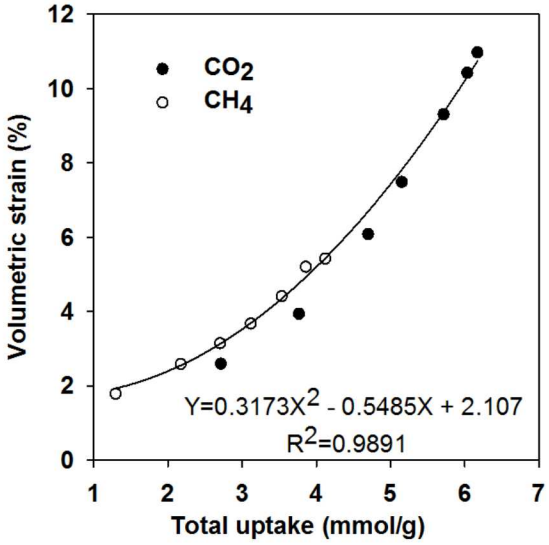
$$Volumetric\ strain = \frac{V - V_o}{V_o}$$

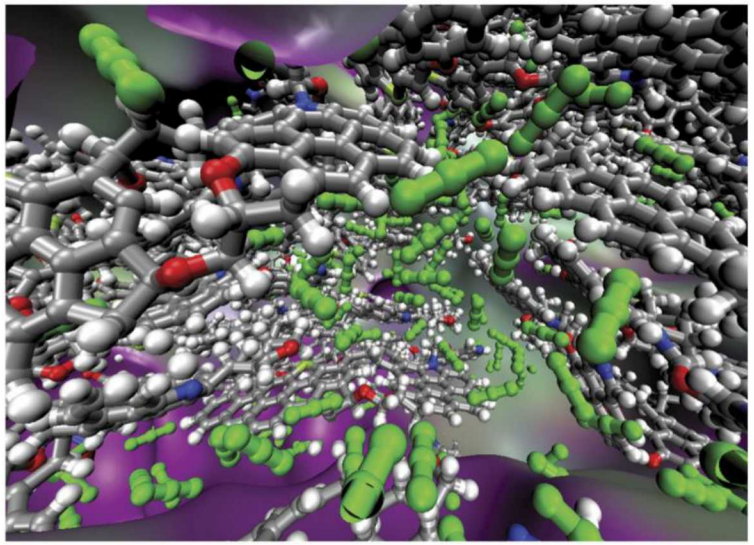
V: kerogen volume after gas adsorption

V_o: kerogen volume before gas adsorption

Kerogen swelling: Simulation results







Highlighting shale gas research from the Geoscience Group, Sandia National Laboratories, NM, USA. This work was conducted by Dr Tuan Ho, thanks to funding granted to Dr Yifeng Wang by the DOE National Energy Technology Laboratory.

Chemo-mechanical coupling in kerogen gas adsorption/desorption

We use an integrated experimental and modeling approach to fundamentally understand the interaction of gas and fluid with kerogen and clay under reservoir conditions. Specifically, nanostructural properties of subsurface porous media, gas adsorption and release from the kerogen network, deformation of shale associated with adsorption and lithostatic stress, and wettability of inorganic and organic matter.

As featured in:

See Tuan Anh Ho *et al.*, *Phys. Chem. Chem. Phys.*, 2018, **20**, 12390.

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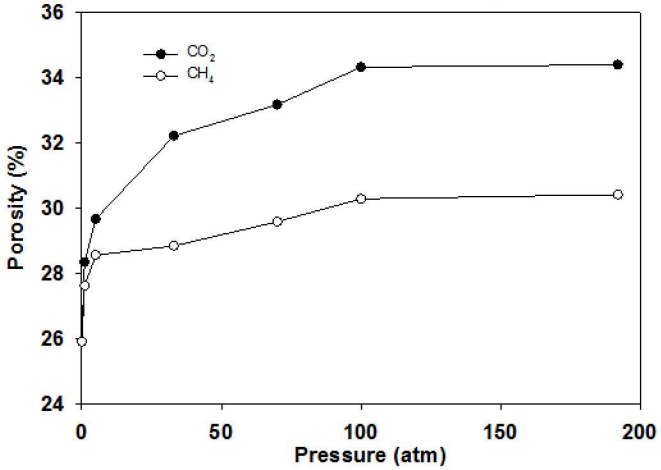
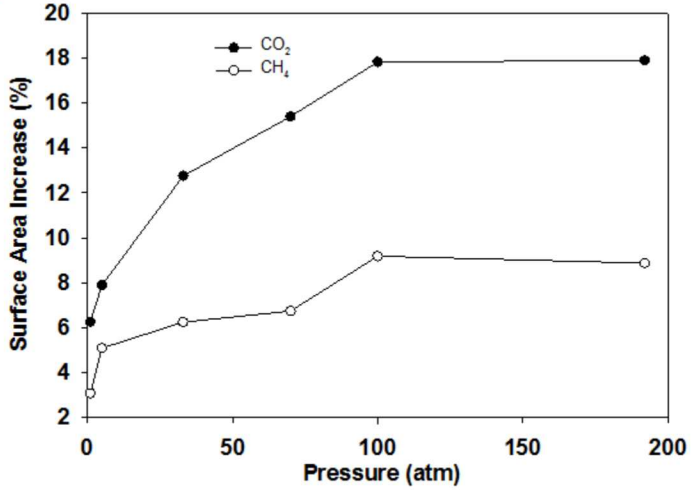
Swelling seems controlled by the surface layer of gas adsorbed.

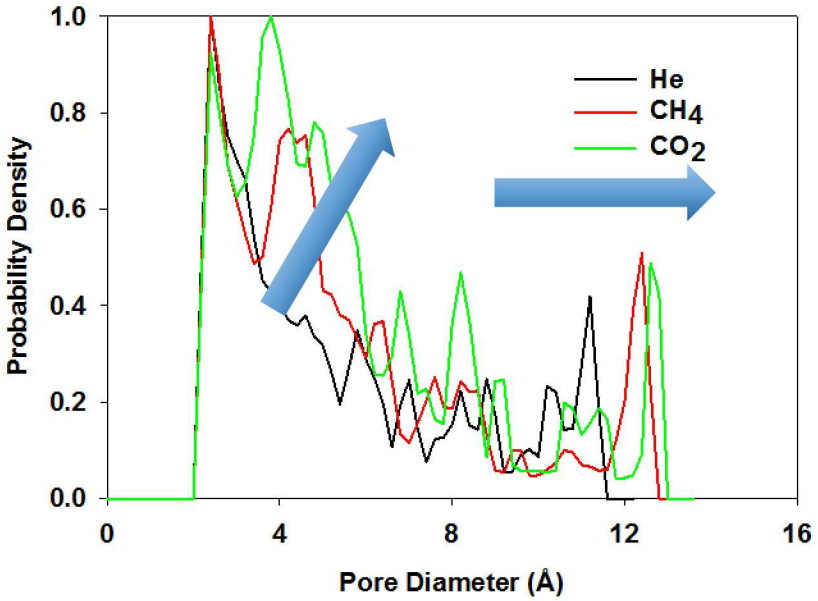
Kerogen swelling: Effects of gas type and pressure

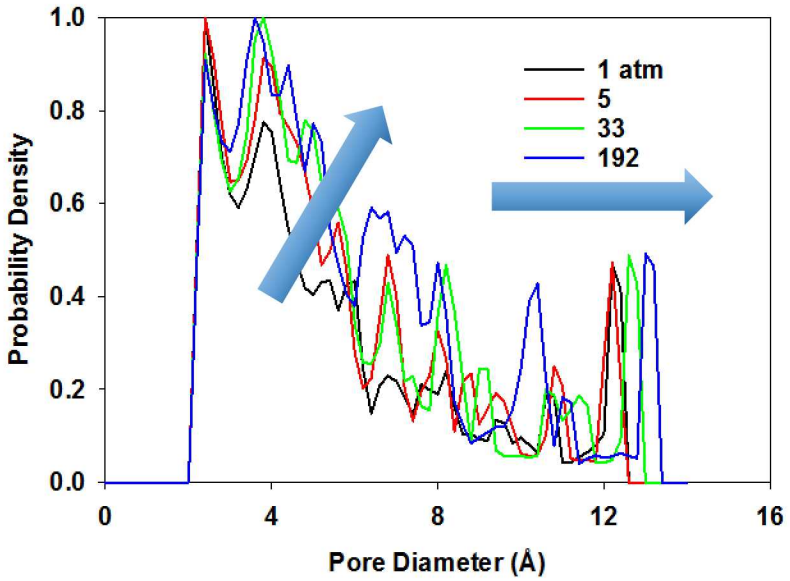
Effects of kerogen swelling on porosity and surface area



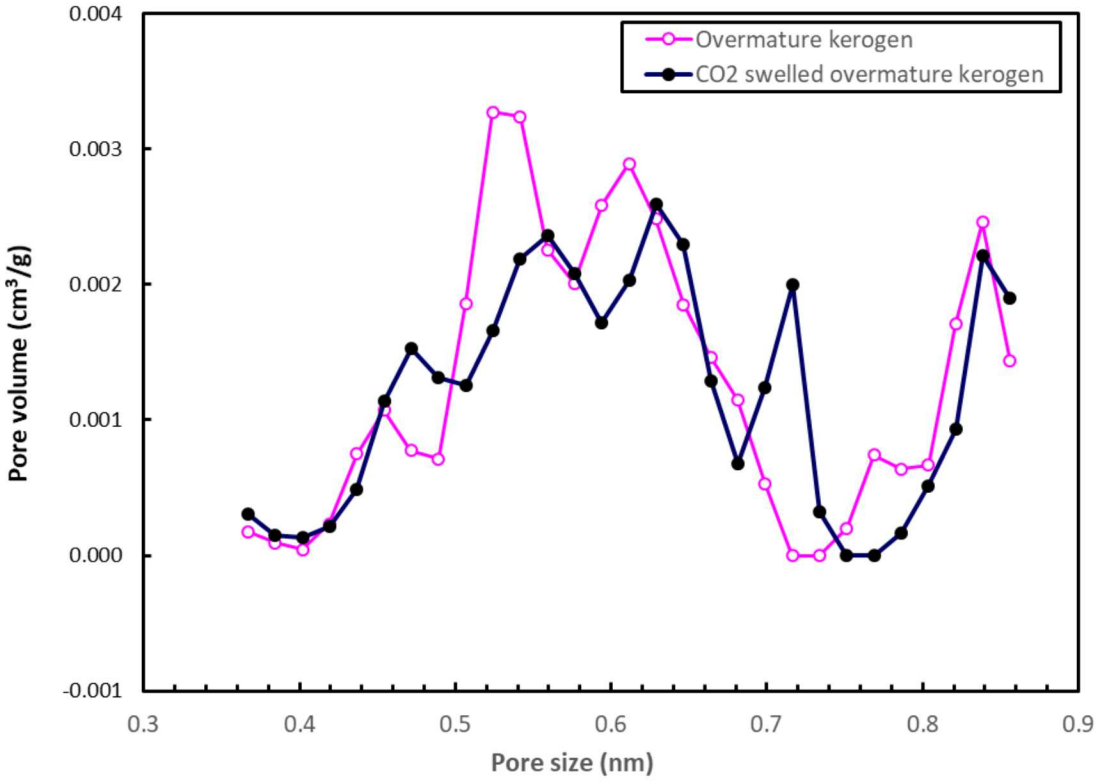


Effects of kerogen swelling on pore size distribution





Kerogen swelling: Experimental observations

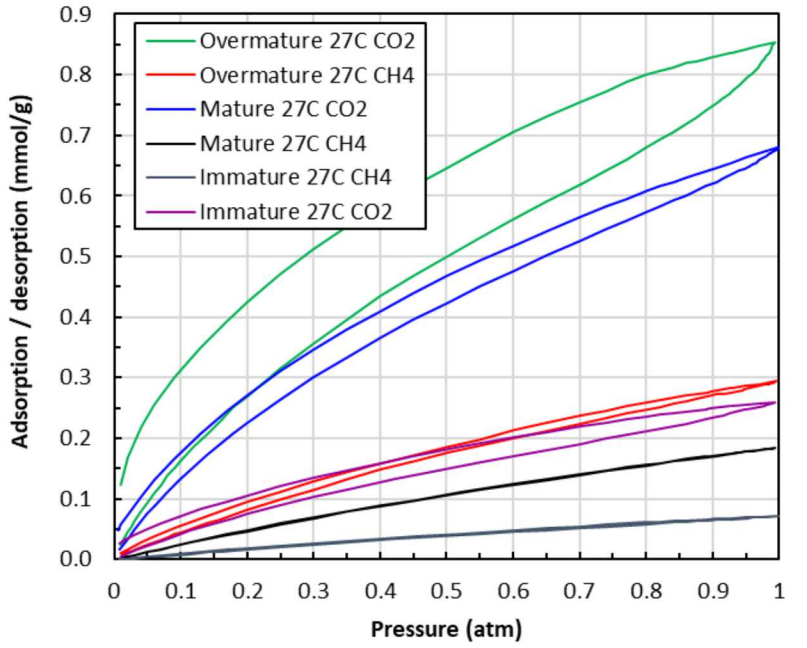


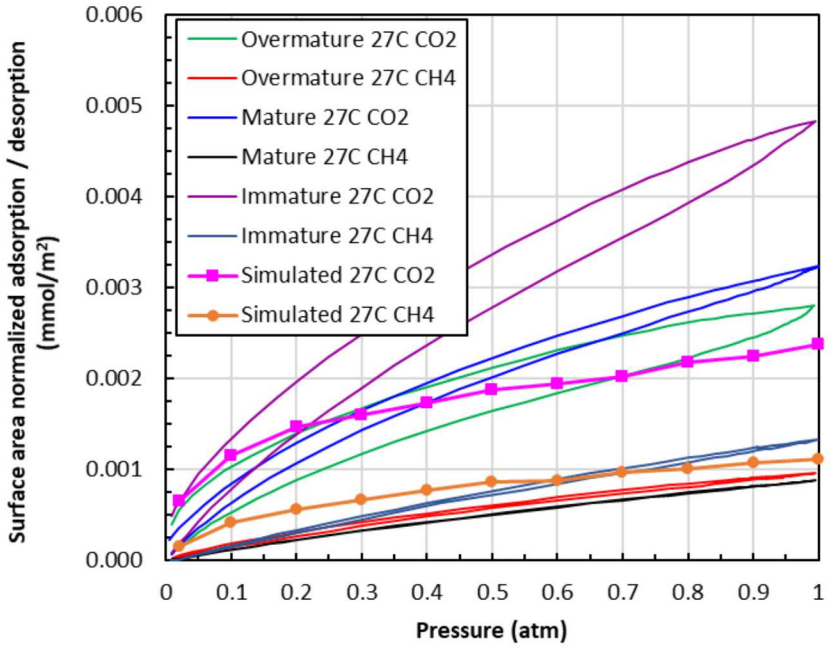
Kerogen is filled with 1 atm CO_2 and sealed for 4 months before being remeasured

- Kerogen is mechanically compliant?!
- Implications to reservoir engineering, especially, for organic carbon-rich plays.

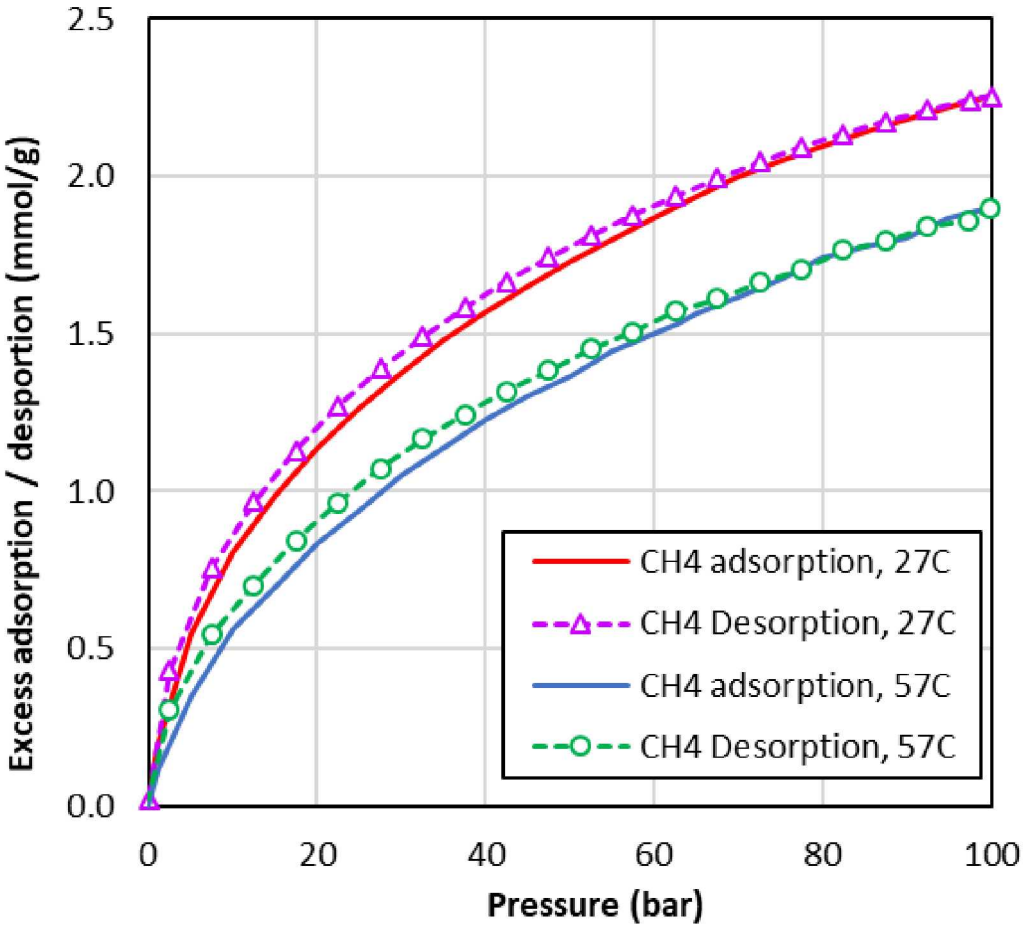
Gas adsorption and desorption on kerogen: Hysteresis loop

- From immature to mature to overmature, adsorption ability increases with maturity; however, after the normalization of surface area, the trend is reversed, suggesting a possible control by functional groups.
- The simulated CO_2 and CH_4 adsorption curves for overmature kerogen are in agreement with with the measured values.



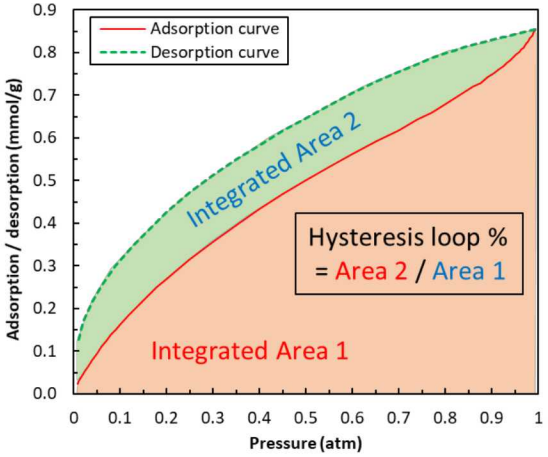


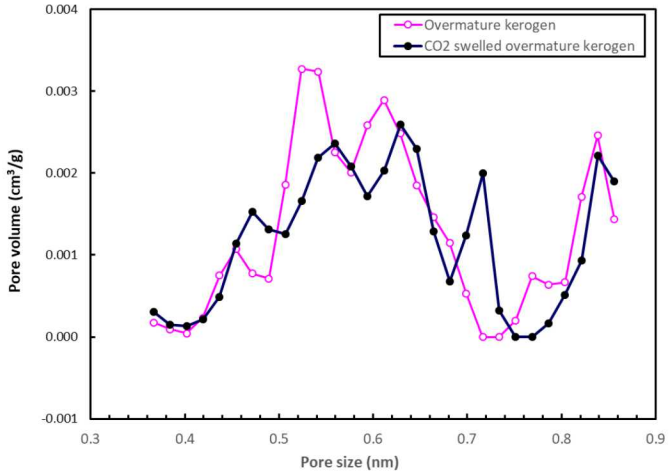
Gas adsorption and desorption on kerogen: High pressure measurements

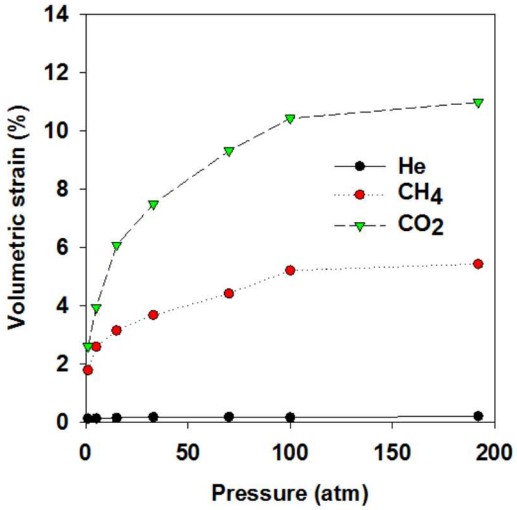


Hysteresis loop exists for very high pressure adsorption.

Understanding adsorption-desorption hysteresis





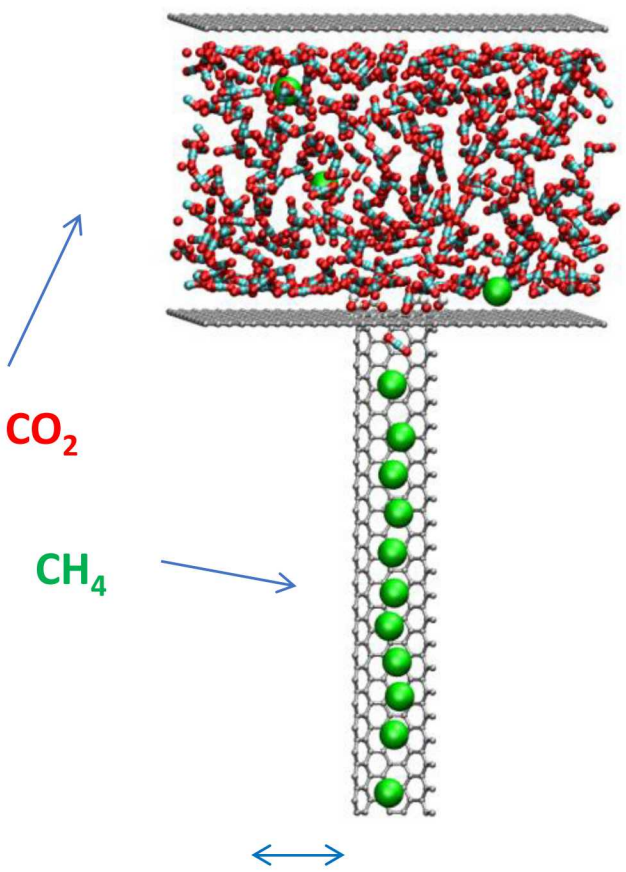


Hysteresis loop %		BET surface area (m^2/g)	Pressure from 0 to 1 atmosphere					Pressure: 0 to 100 bar	
			N_2 77K	27 °C CO_2	57 °C CO_2	27 °C CH_4	57 °C CH_4	27 °C CH_4	57 °C CH_4
Marcellus	immature	54	21.3%	18.6%		4.8%			
	mature	205	38.1%	9.5%		0.9%			
	overmature	301.5	14.0%	27.1%	44.8%	6.2%	11.8%	2.8%	3.5% / 5.6%*
Woodford	immature	50	12.6%	16.2%	23.0%	2.9%	4.3%		
Carbon Black		31	7.9%	74.9%		9.5%			
Activated carbon		474	9.6%	5.2%		3.1%			
* from 0 to 72.5 bar and curves overlap from 72.5 to 100 bar									

Hysteresis loop % increases with temperature; the loop % is much higher for CO_2 compared to CH_4.

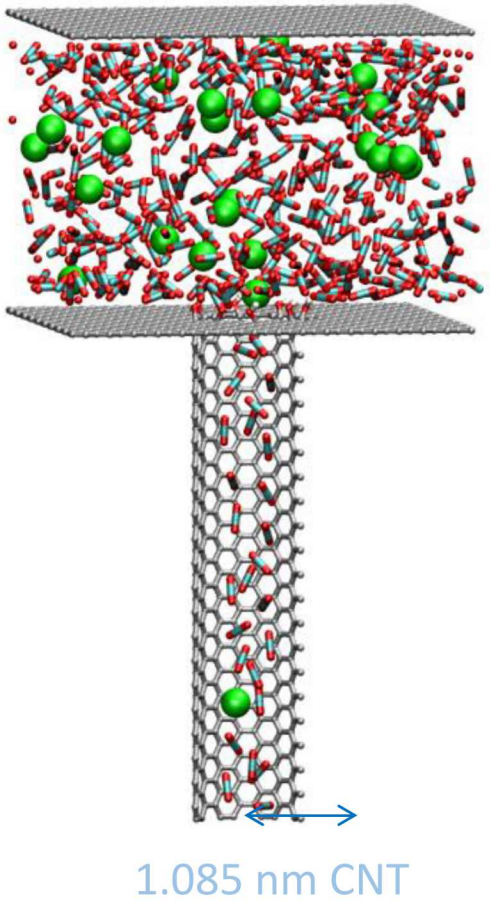
~~Current capillary condensation and pore neck snapping mechanism~~

More on CH_4-CO_2-H_2O in nanopores (Fuel 220, 1-7, 2018)



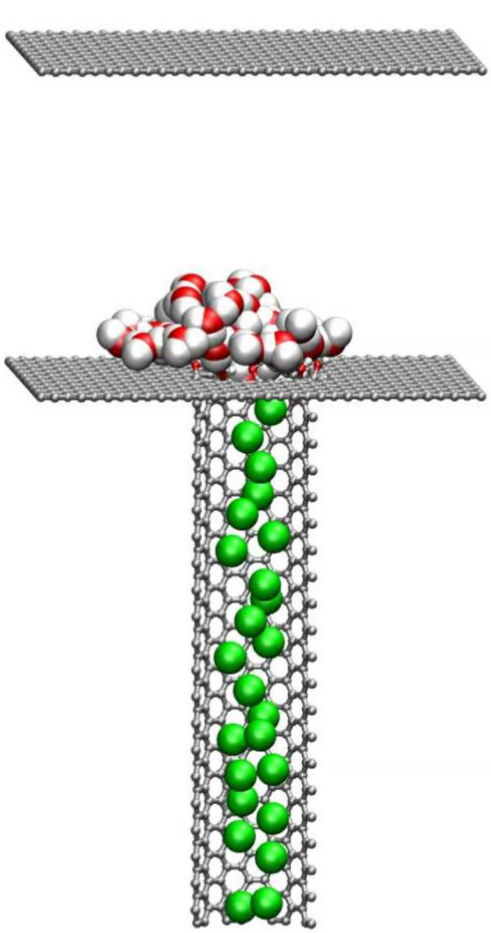
Pore is too small for the invasion of CO_2

Pore size effect

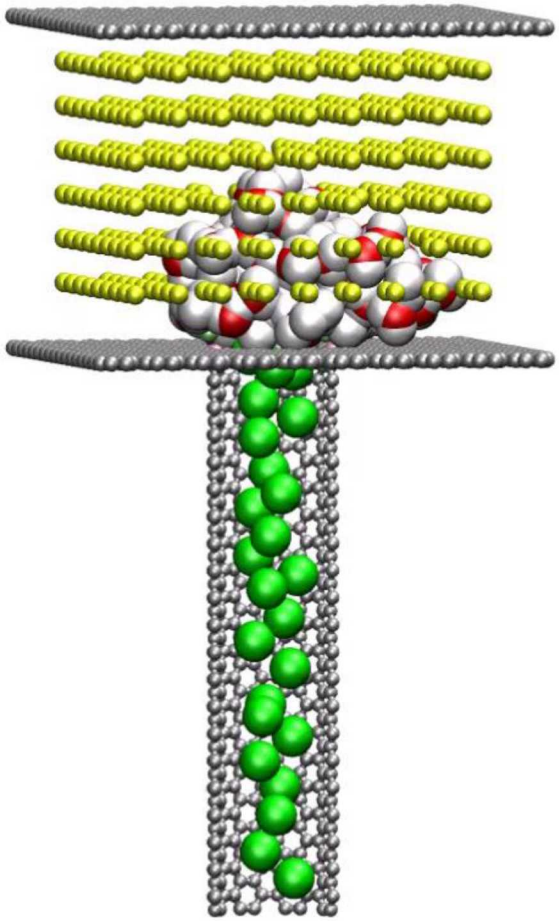


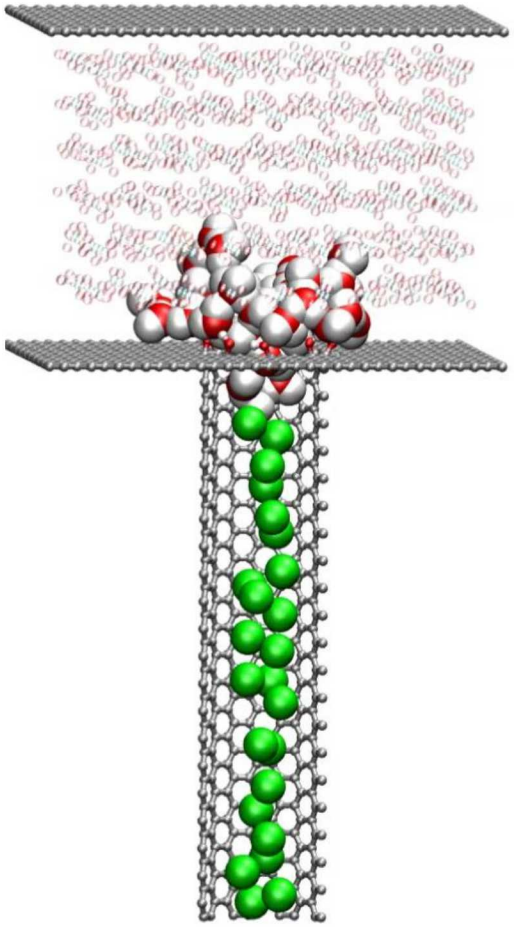
Pore is big enough for the invasion of CO_2

More on CH_4-CO_2-H_2O interaction in nanopores (cont.)



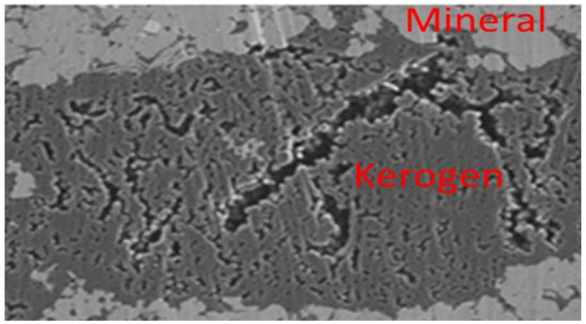
Water drop blocks the pore entrance.

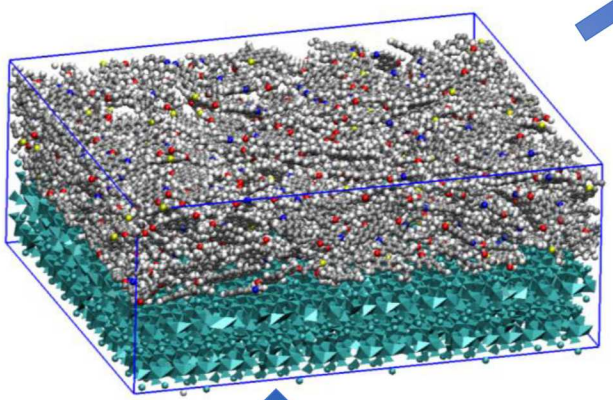


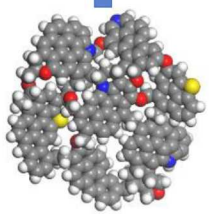


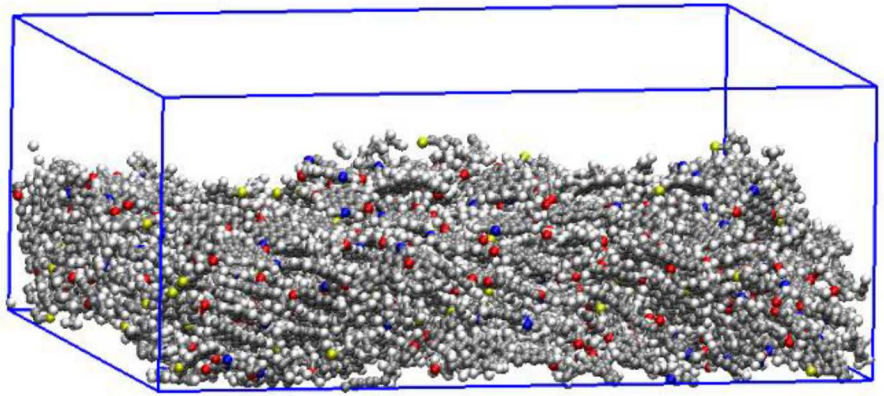
CO_2 invades through water and replaces CH_4 in the nanopore.

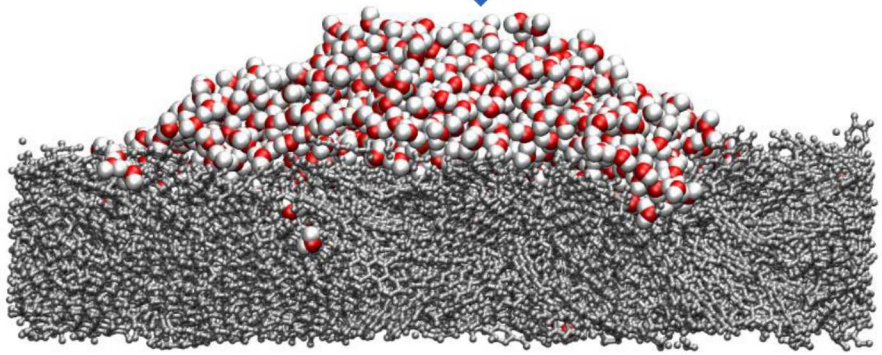
CH_4-CO_2-H_2O interaction in a kerogen microfracture: Wettability (Nanoscale, 2018)







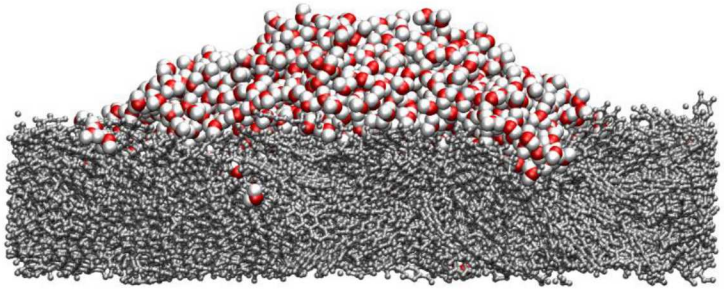




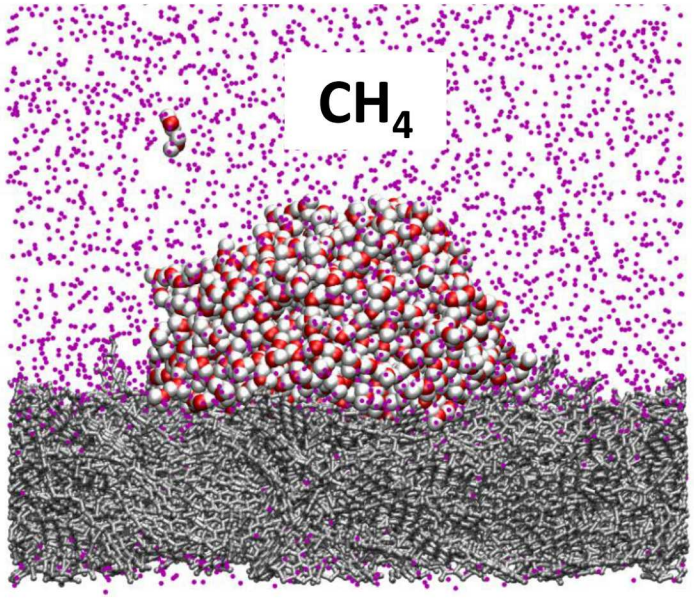
Contact angle: 42.8°±6.5°

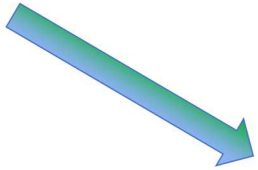
Wettability (cont.)

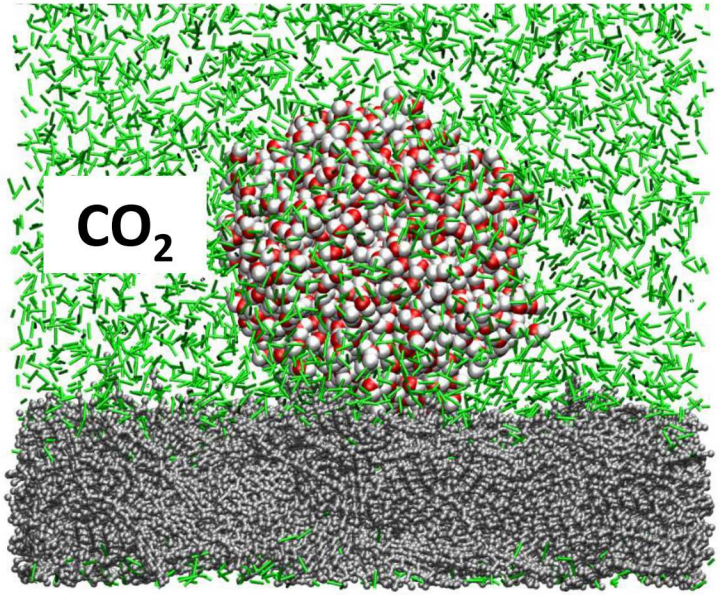
42.8°±6.5°



79.18°±1.97°

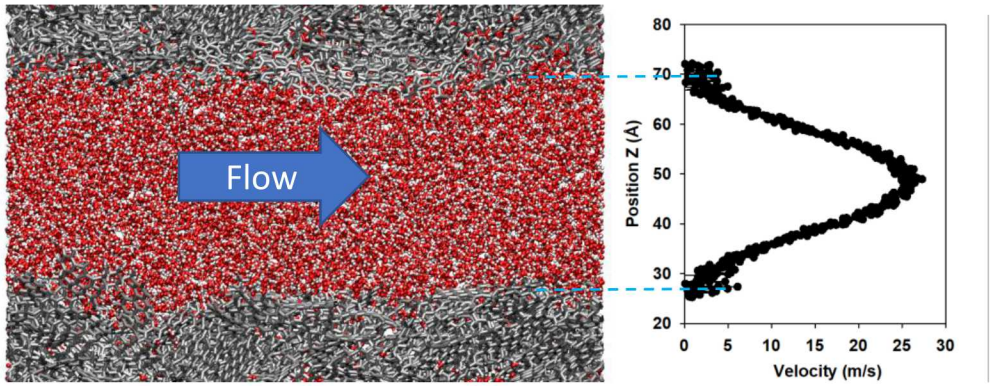






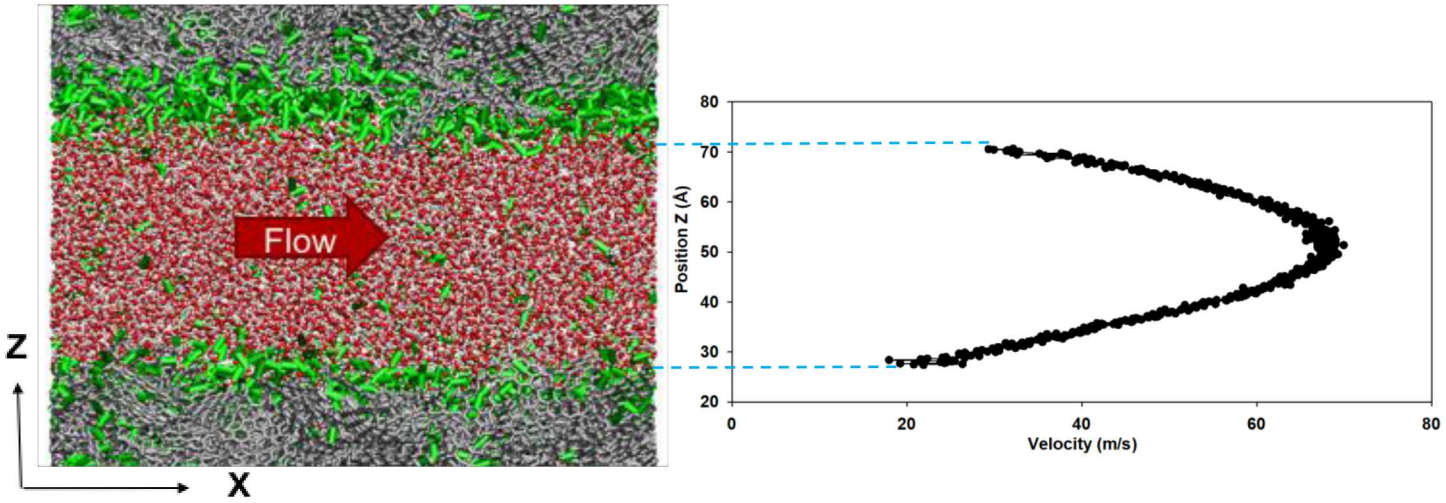
Hydrophilic to hydrophobic transition

CH_4-CO_2-H_2O interaction in a kerogen microfracture: Fluid flow (Nanoscale, 2018)



$$\frac{\text{Flow Rate (w } CO_2\text{)}}{\text{Flow Rate (w/o } CO_2\text{)}} \sim 4$$

CO_2 thin layer → Lubricant



Implications:

- Water release and removal
- Lubrication for hydrocarbon fluid flows?

Kerogen reaction with supercritical CO_2

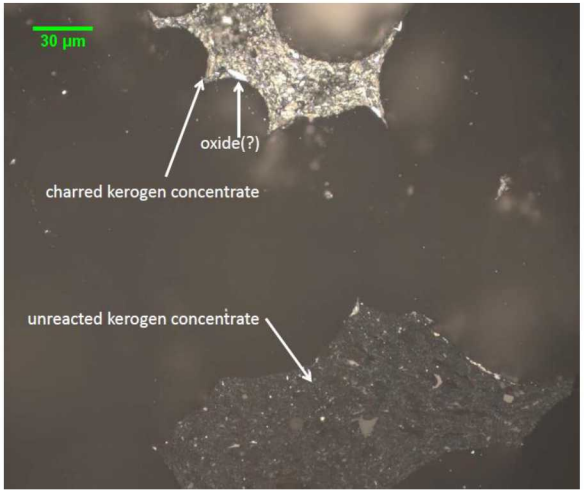
Experiment: 0.13 gram immature kerogen reacted with supercritical CO_2 saturated brine (1M) at 90 °C and 2800 psi for 30 days

Observation: Some kerogen grains are reacted and coated by char, while others grains are not, indicating the heterogeneity (or selectivity) of the reaction.

Original kerogen

Reacted kerogen

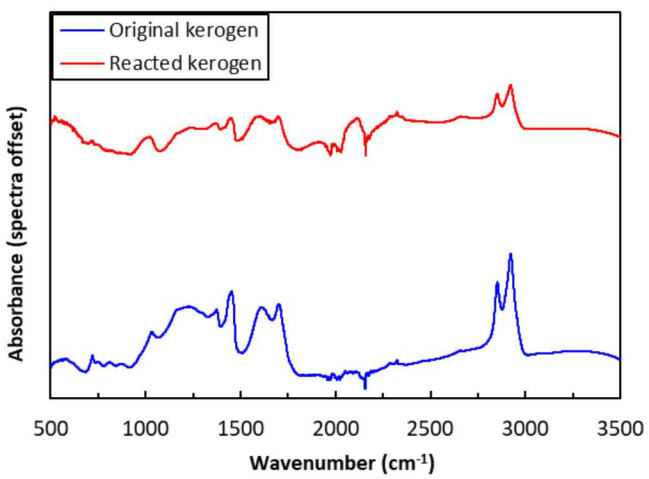
Reacted kerogen

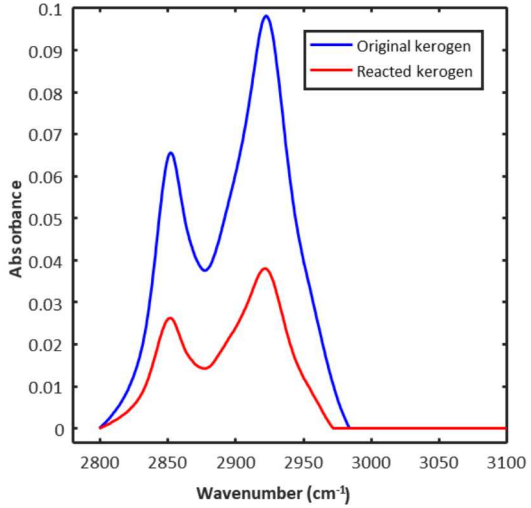


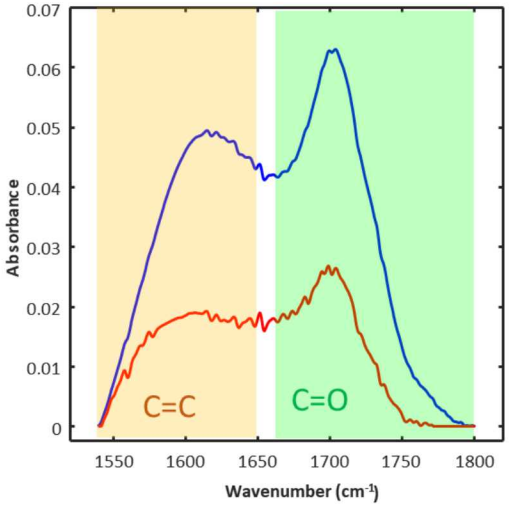
Kerogen reaction with supercritical CO_2: Change of functional groups

Observations:

- IR intensity of reacted kerogen decreases significantly, indicating the decrease in functional group abundance.
- At interval 2800 – 3100 cm^{-1}, the decrease is proportional, whereas at interval 1550 -1800 cm^{-1} aromatic C=C decrease more than C=O functional groups







Kerogen reaction with supercritical CO_2 : Compositional changes

Observations:

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

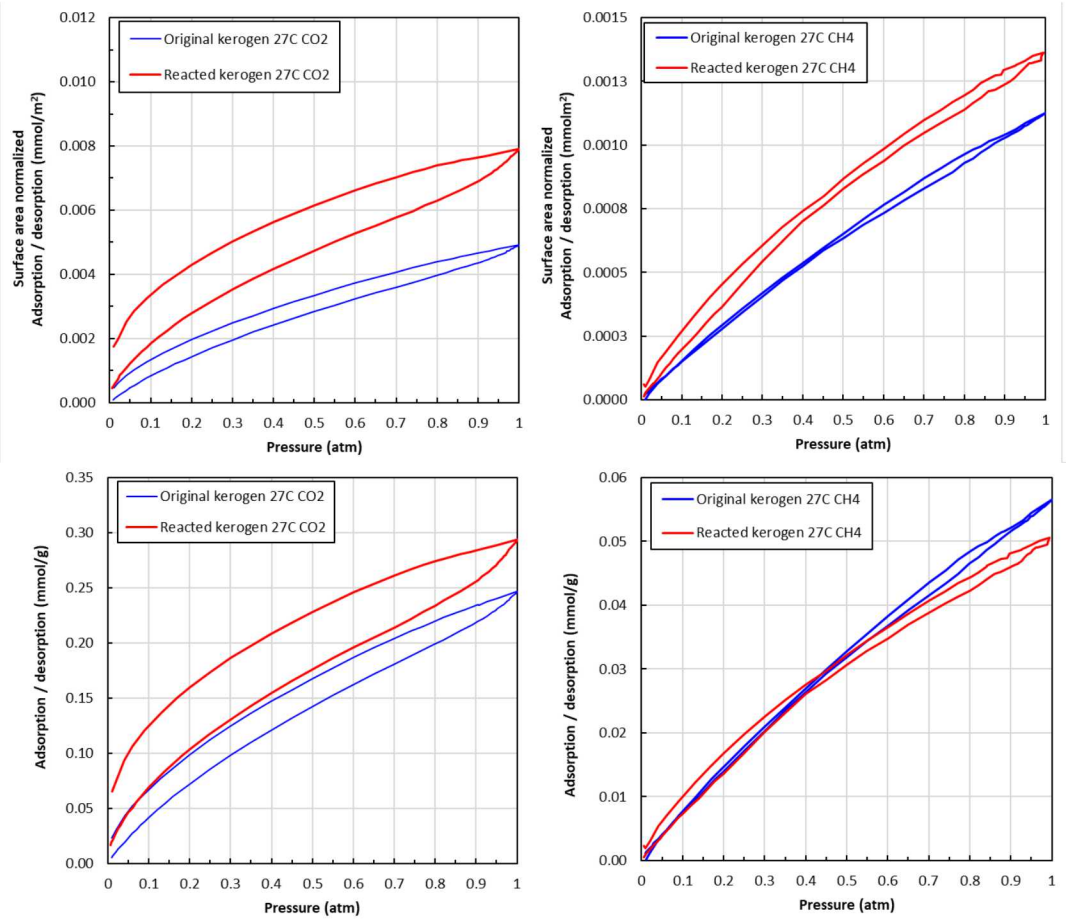
Implication: Chemical reaction with supercritical CO_2 as an alternative maturation?

	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

Kerogen reaction with supercritical CO_2 and its effect on gas adsorption

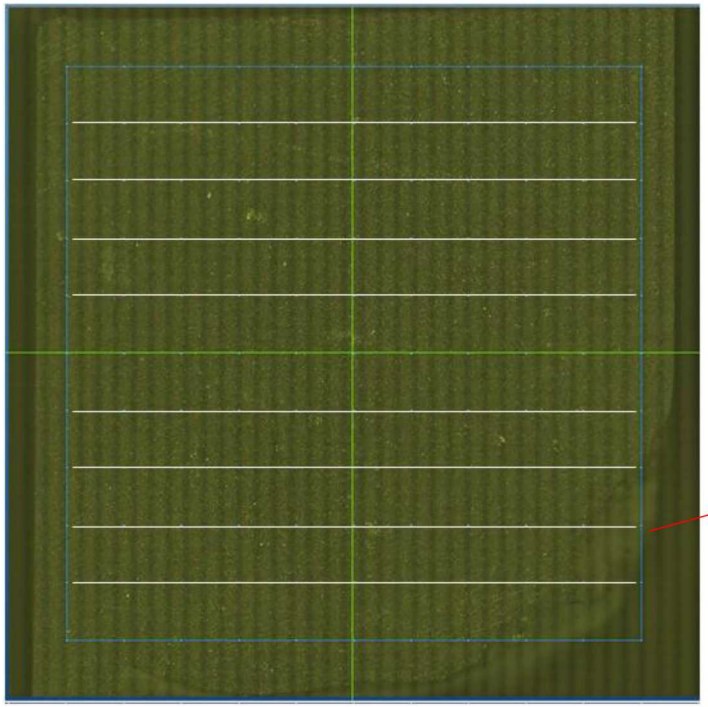
- After reaction, BET surface decreases from 50 to 37 m^2/g.
- Reacted residual kerogen adsorbs more CO_2 than original kerogen.
- Surface adsorption ability activation?
- CO_2 preferentially adsorbs to both reacted and unreacted kerogen.

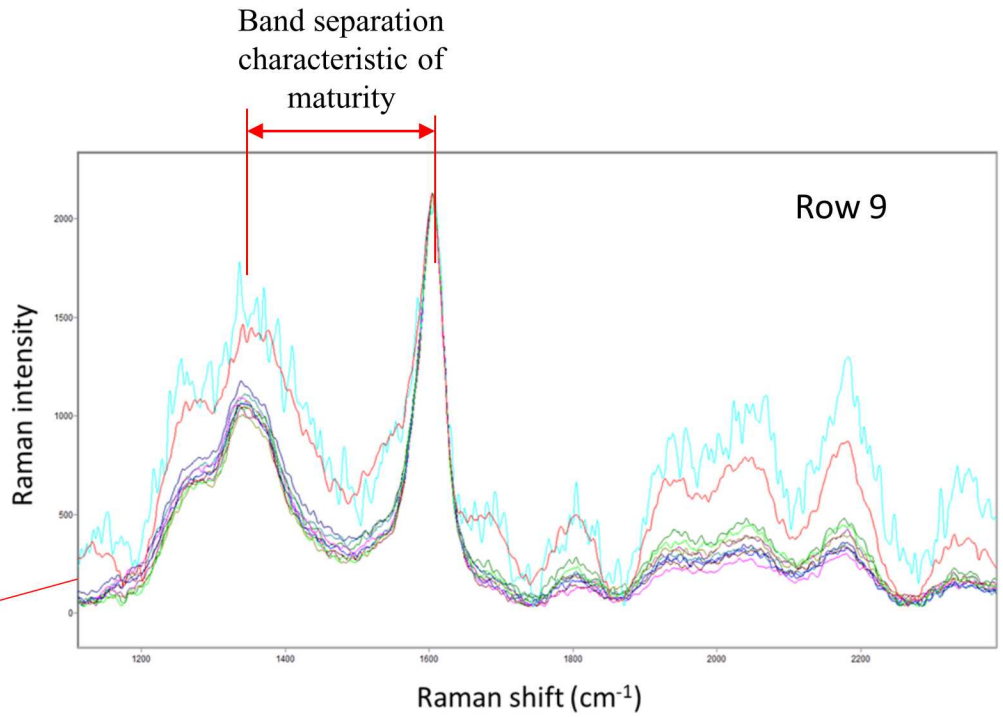


Physics-based, data-driven machine learning

Kerogen compositional variation by micro-Raman analysis

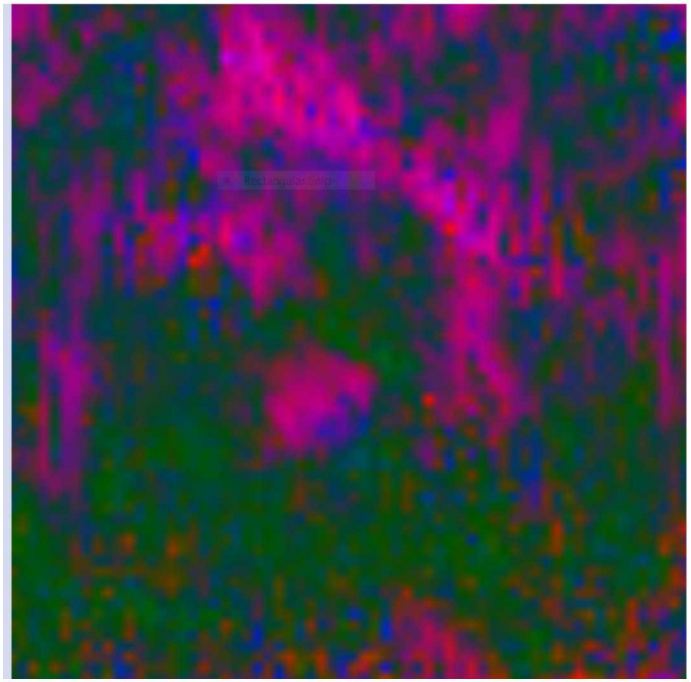
Shale sample





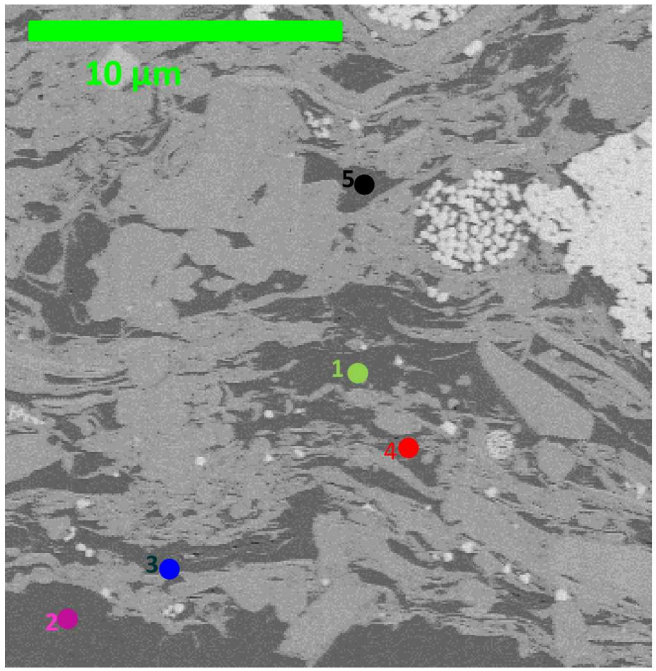
Micron- to Nano- scale kerogen compositional analyses

Kerogen compositional variation by micro-FTIR analysis



Green - organic
Pink - silicates

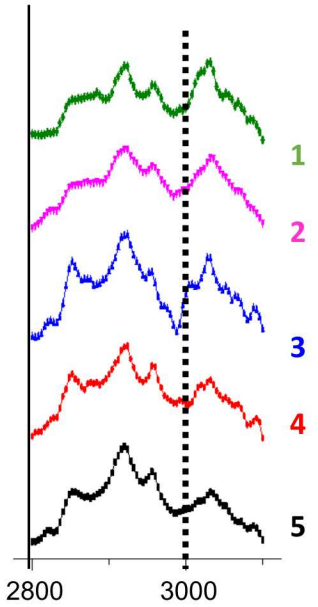
Kerogen compositional variation by NanoIR analysis



Collaborated with
Schlumberger –Doll Research

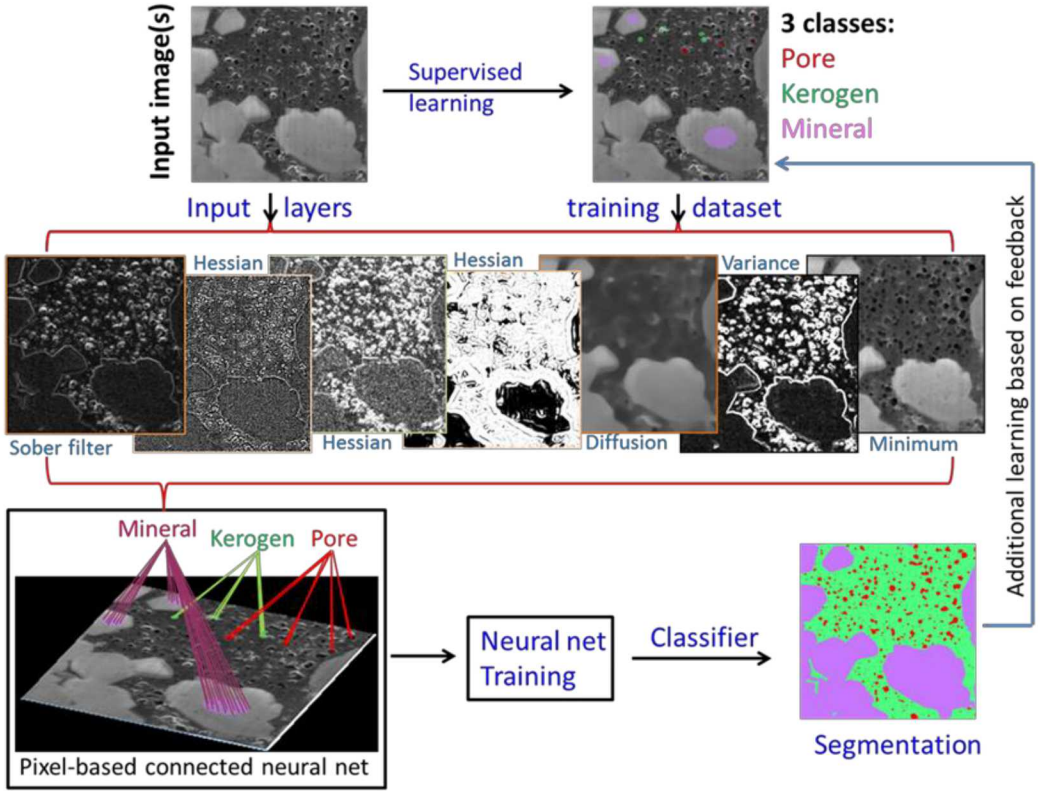
NanoIR spectra of different kerogen grains

- Strong aromatic absorption – mature kerogen
- Chemical composition variation between kerogen grains



Wavenumber (cm^{-1})

Machine learning assisted microscopic image analysis

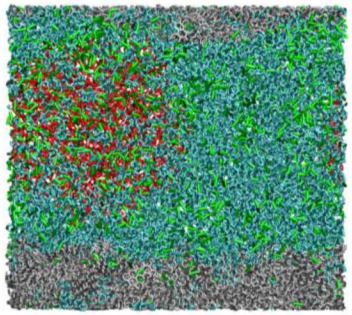


Goal:

- Unravel the functional relationship between kerogen maturity and local texture/composition.
- Construct 3-D nanopore networks.
- Develop continuum-scale constitutive relationships based on pore scale simulations.

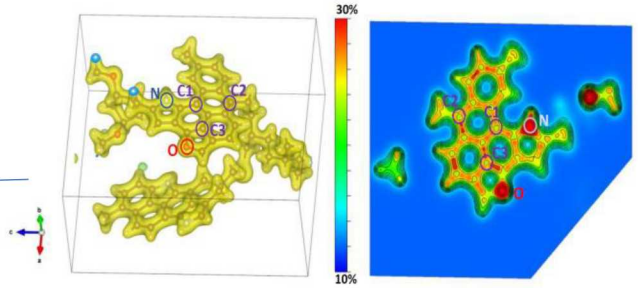
Future work

- Develop new kerogen models with better representation of functional groups (in progress).
- Extend the work to include other chemical components (e.g. LNG as a stimulating agent) (in progress).
- Understand CH_4-CO_2-H_2O interactions in clay matrix (progress made, Sci. Rep., 2017)
- Use classical density functional theory (cDFT) to simulate and upscale molecular simulations (initiated).
- Develop EOS for CH_4-CO_2-H_2O in nanoconfinement (to be initiated)
- Use DFT simulations to understand redox properties (e.g. electron transfer) of kerogen (initiated). (SNL-NETL-WVU)
- Understand isotope fractionation in nanoconfinement (initiated). (SNL-WVU)
- Use machine learning for image analysis and process model upscaling (initiated).

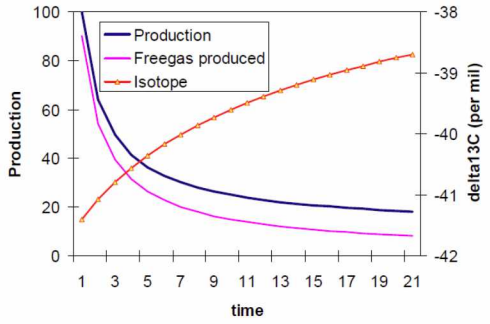


Red: Water
Green: CO2
Cyan: Octane
Silver: Kerogen

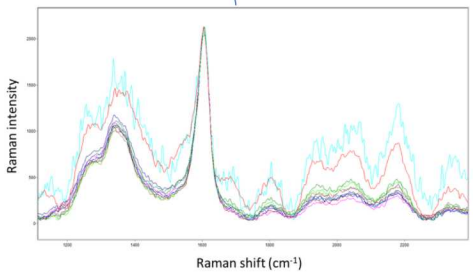
Charge density isosurface of kerogen (type IIB) calculated using DFT



Using Real Time Gas Isotope to Model Gas Production Decline Curve



Data-driven ML



From REPSEA presentation: *Novel Gas Isotope Interpretation Tools to Optimize Gas Shale Production*; YongchunTang; PEERI