Exceptional service in the national interest

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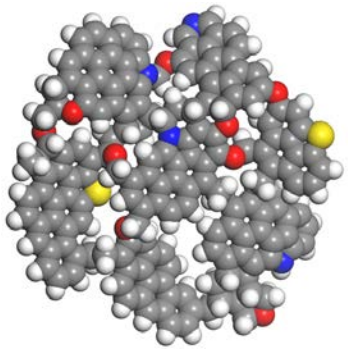

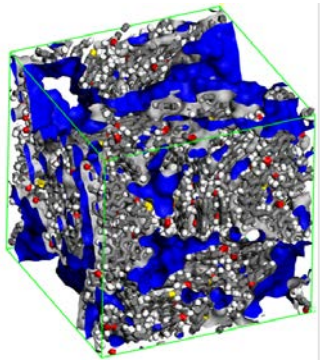

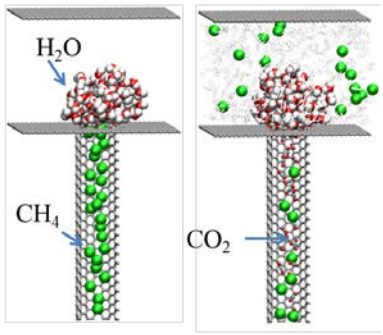

Fundamental Understanding of Methane-Carbon Dioxide-Water (CH_4-CO_2-H_2O) Interactions in Shale Nanopores under Reservoir Conditions

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

Sandia National Laboratories, Albuquerque, New Mexico

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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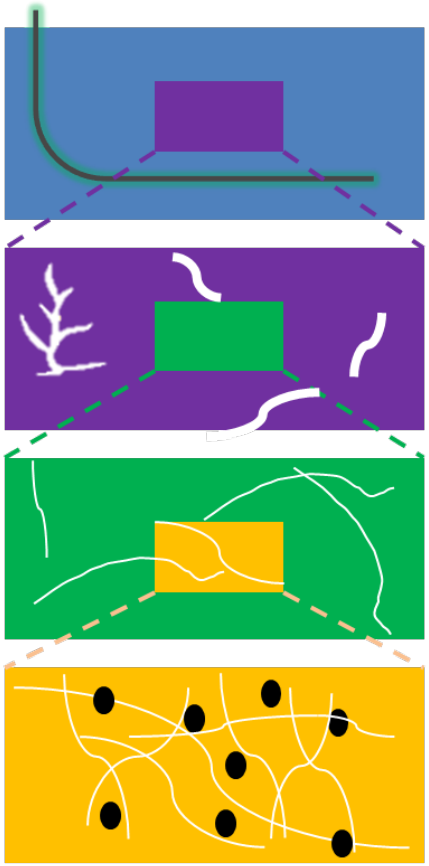
Acknowledgments

- DOE NETL for financial support
- Bruce Brown, Adam Tew, Joe Renk, Henry Stephen, Jared Ciferno, (NETL) for management support
- MSEEL for shale samples
- Mei Ding (LANL) for neutron scattering experiments

Shale gas production: A multi-scale problem



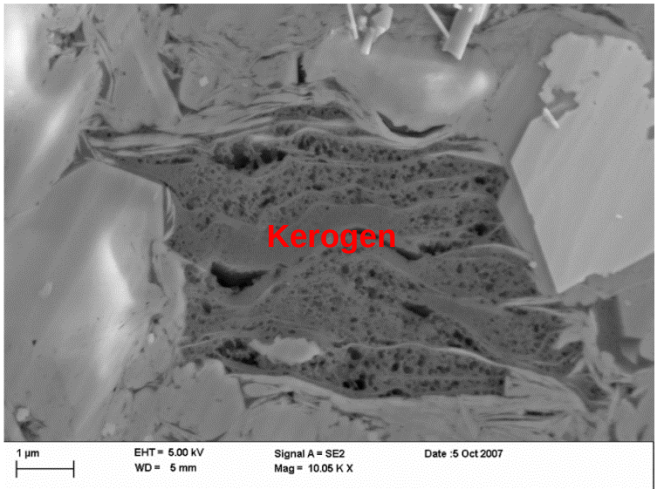
Macroscale:
gas flow to
the wellbore

Mesoscale:
micro-fractures
network

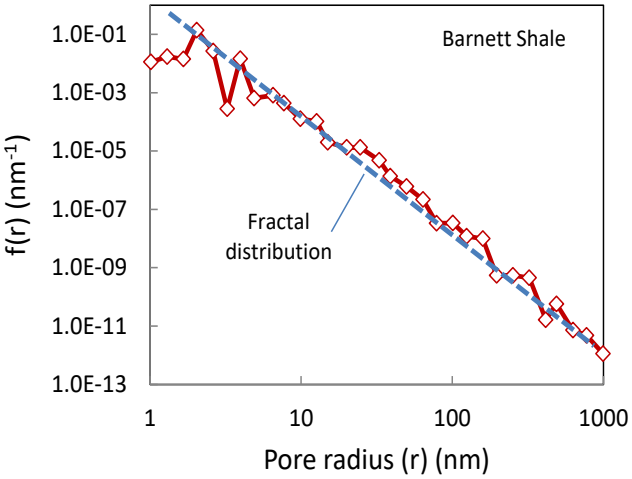
Microscale:
nanopores
network

Nanoscale/Sub-nanoscale:
Gas diffusion from
kerogen/clay porous
structure to nanopores.

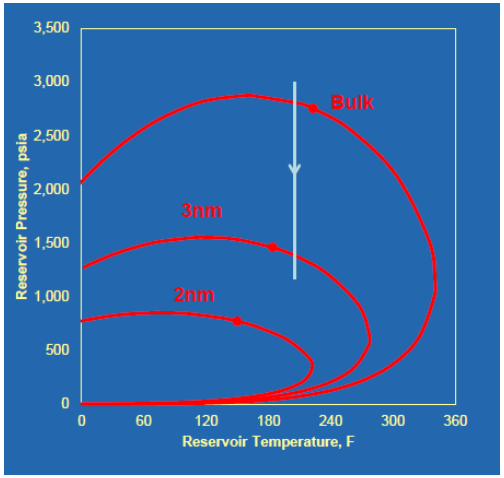
JCPT 46, 55 -61 (2007)



SPE 124253 (2009)



Nanopore confinement and emergent properties

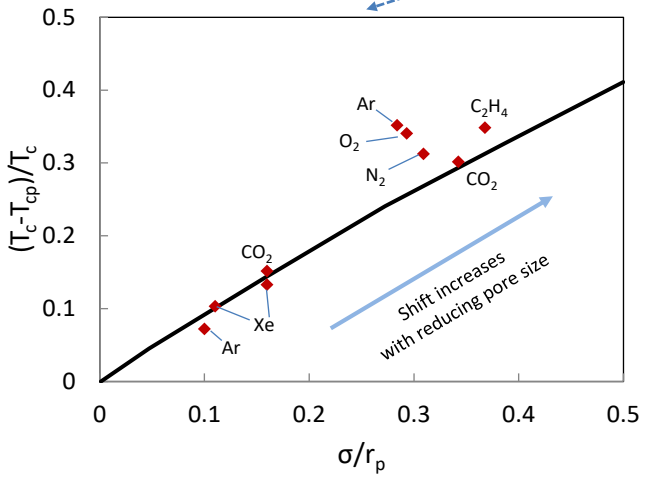


Akkutlu, 2013

Bulk phase fluids
(Unconfined or pore size > ~100 nm)
EOS = f(P, T, composition)

Nanoconfinement

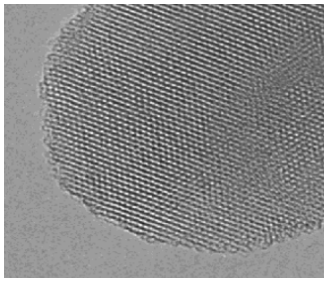
Nanofluids
(Confined in nanopores, pore size < ~100 nm)
EOS = f(P, T, composition, pore size, surface chemistry)



Wang (2014); Zarragoicoechea and Kuz (2004)

Overall goal: (1) Obtain a fundamental understanding of CH_4-CO_2-H_2O (or other fluid component) interactions in shale nanopores under high-pressure and high temperature reservoir conditions, and (2) integrate this understanding into reservoir engineering for efficient resource recovery and subsurface carbon sequestration.

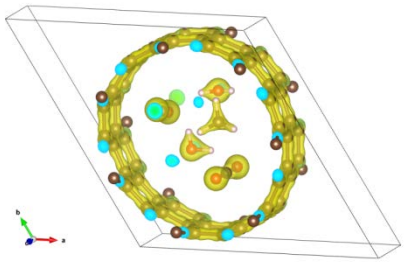
Capabilities for Nanogeochemical Studies at Sandia National Laboratories



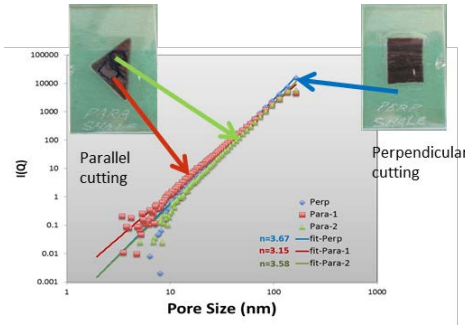
Synthesis of nanoporous materials

Isolation of kerogen from Mancos shale

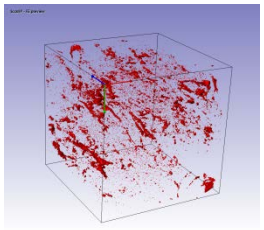
Pioneering work in nanogeochemistry. Access to DOE Center of Integrated Nanotechnology



Density functional theory (DFT) modeling



Pore structure characterization



Pore structure characterization (FIB)

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

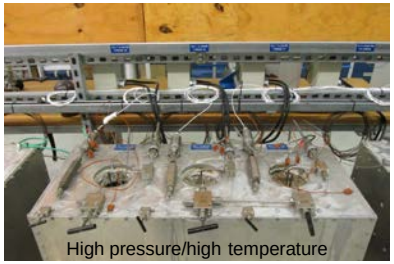
Gas disposition & release
- Gas in place (GIP)
- Gas migration from matrix into fractures
- Stimulated volume
- Gas for secondary recovery

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

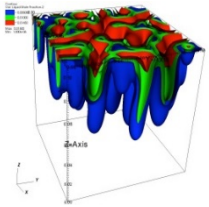
Nanoscience
- Effects of nanopore confinement on fluid thermodynamic properties
- Effects of nanopore confinement on methane transport (microfluidics in shale)

Upscaling
- Percolation theory
- Fractal representation
- Lattice Boltzmann modeling

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

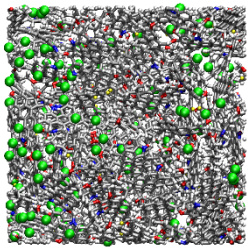


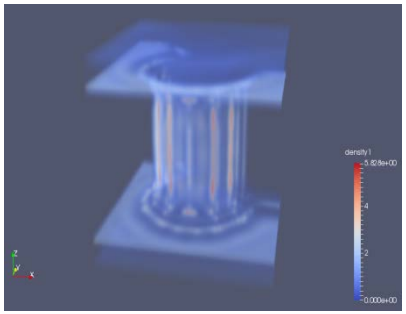
High pressure/high temperature sorption/desorption measurements



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

PFLOTRAN: Reactive transport modeling





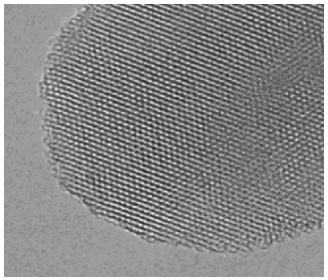
TRAMANTO: Classical Density Functional Theory

Material preparation & characterization

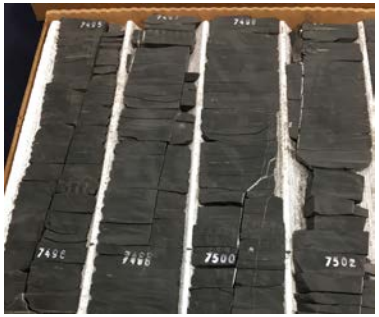
- About 10 shale core samples obtained
  - Focus on Mancos, Marcellus & Woodford
- Pure kerogen isolated from Mancos, Woodford & Marcellus shale
- About 5 model materials synthesized or purchased
- Major material characterization completed (BET, SANS, FTIR)

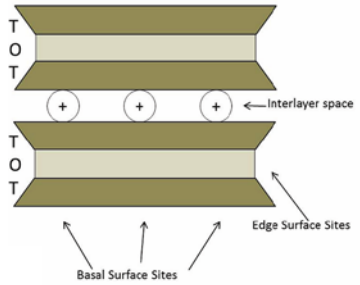
Surface area and pore size of activated carbon materials

Activated carbon	Surface area (m^2/g)	Average pore size (nm)	Total volume (cc/g)
INSUL	489	4.6	0.56
HYDRO-B	468	4.3	0.50
HYDRO-4000	750	4.1	0.76
12X20DC	538	4.9	0.66
MRX	557	5.4	0.76
S-51HF	640	4.8	0.77



Synthesis of nanoporous materials





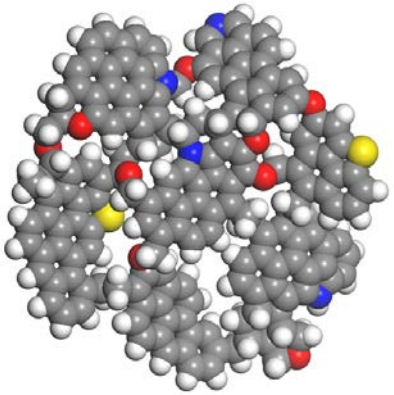
Gas sorption measurements

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

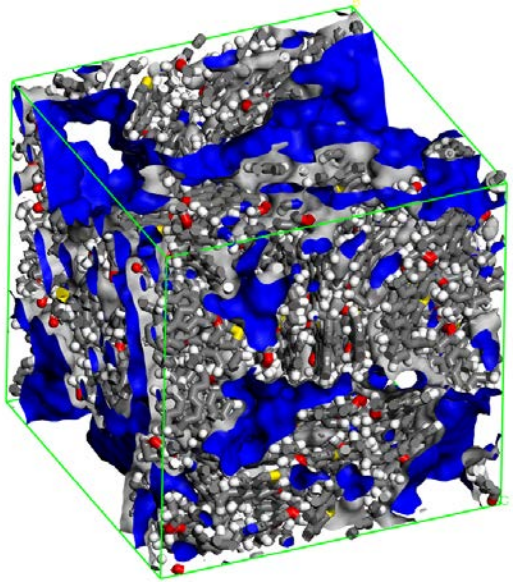
Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min^{-1}
DARCO activated carbon	25	85% CH_4 + 15% CO_2	1	28	0.68
	50	85% CH_4 + 15% CO_2	1	11	0.59
	75	85% CH_4 + 15% CO_2	1	9.0	0.31
	100	85% CH_4 + 15% CO_2	1	2.1	0.14
	125	85% CH_4 + 15% 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}

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, PSI	Sorption Capacity (mixture) mg/g	Sorption Rate, mg/g min^{-1}
Illite, <75 mm	50	90% CH_4 + 10% CO_2	300	190	1.5

Kerogen



Over-mature kerogen molecules



Density

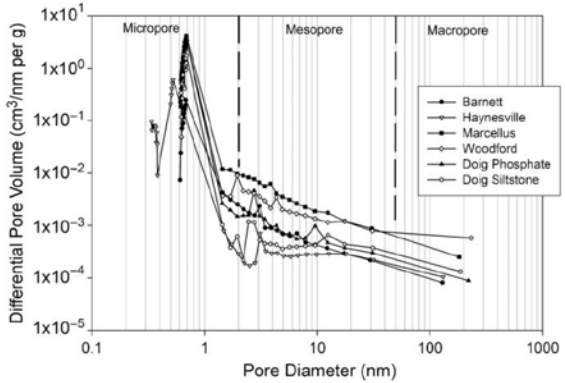
Sample 1: 1.172g/cm^3
Sample 2: 1.287g/cm^3

Average :1.22±0.04 g/cm^3
Experiment: 1.28±0.3g/cm^3

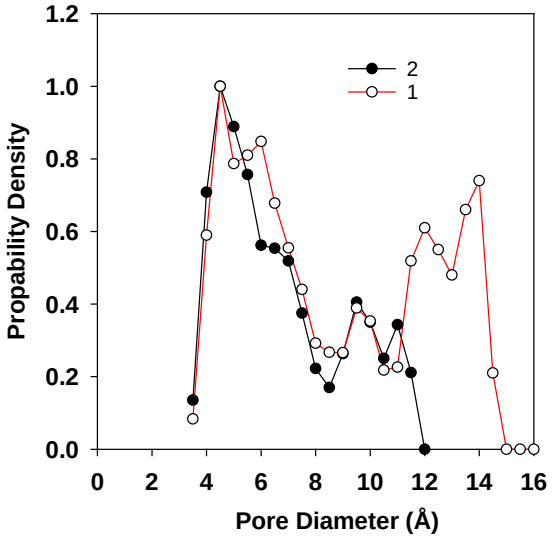
Stankiewicz A, *et al.* (2015) Kerogen density revisited – lessons from the Duvernay Shale. *In: Paper URTeC 2157904 at the Unconventional Resources Technology Conference, San Antonio, Texas, July 2015*

Pore size distribution

Ho et al, Scientific Reports 28053

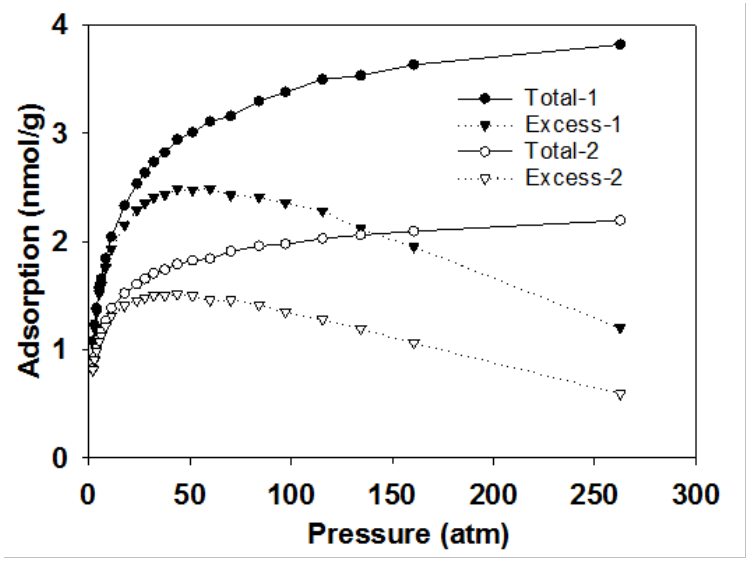


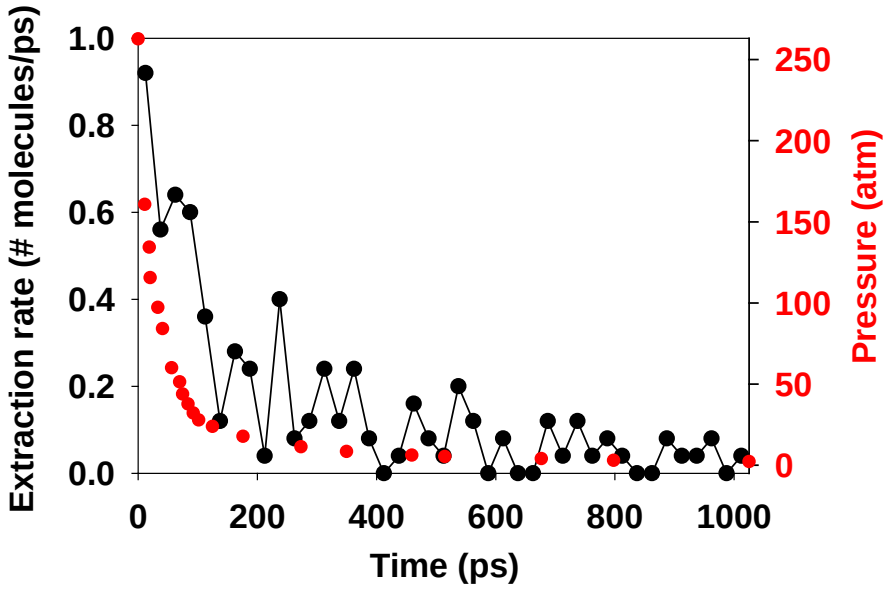
AAPG 96 (2012), 1099-1119

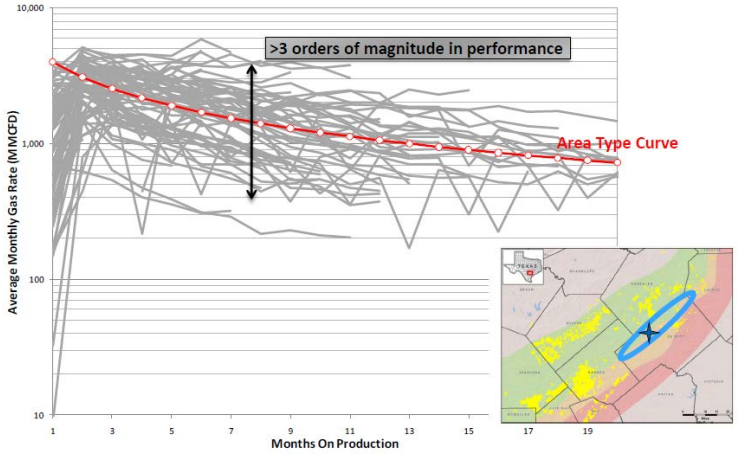


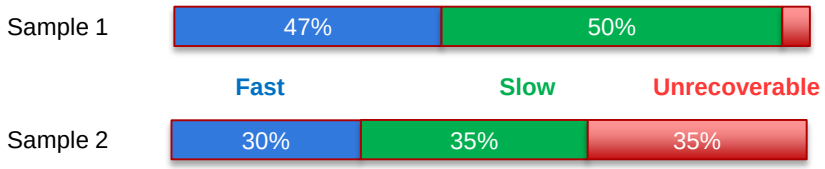
Method: Bhattacharya S & Gubbins KE (2006) *Langmuir* 22:7726-7731

Methane sorption and extraction from kerogen

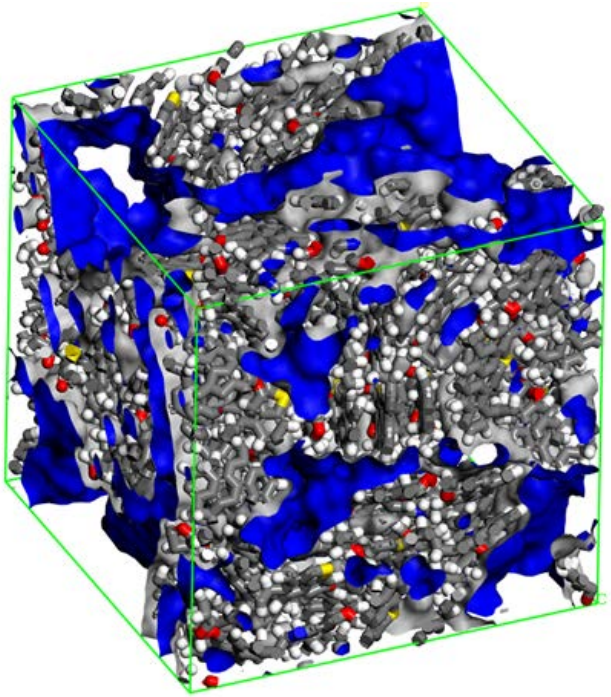




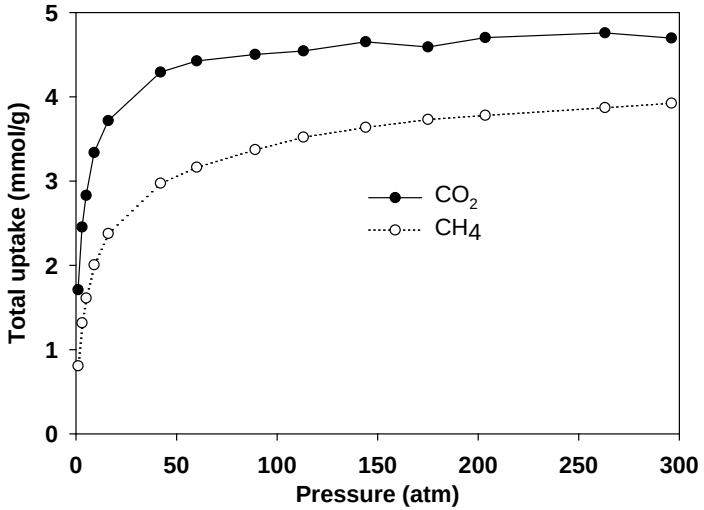




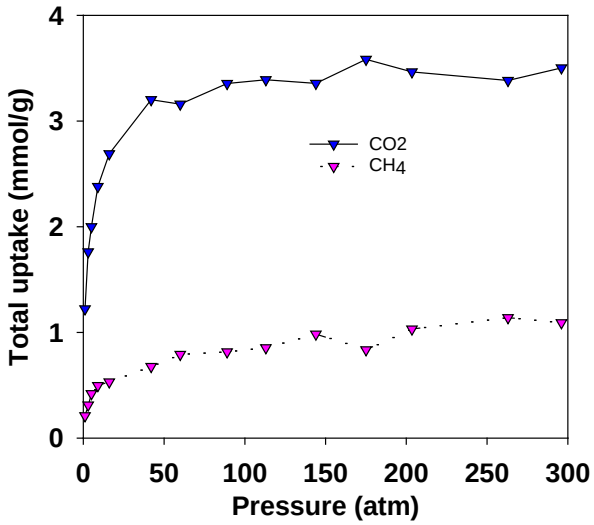
Gas adsorption



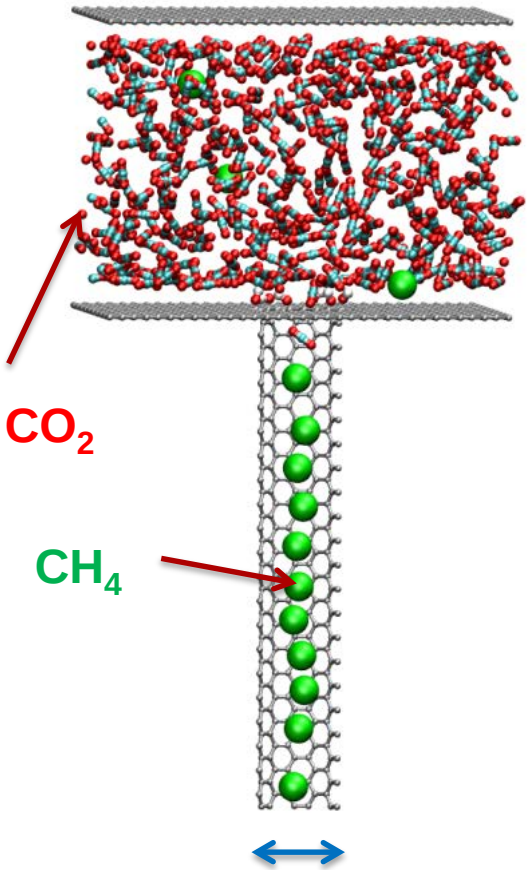
Scenario 1: Pure CH_4 and pure CO_2



Scenario 2: 1:1 binary mixture CH_4 and CO_2



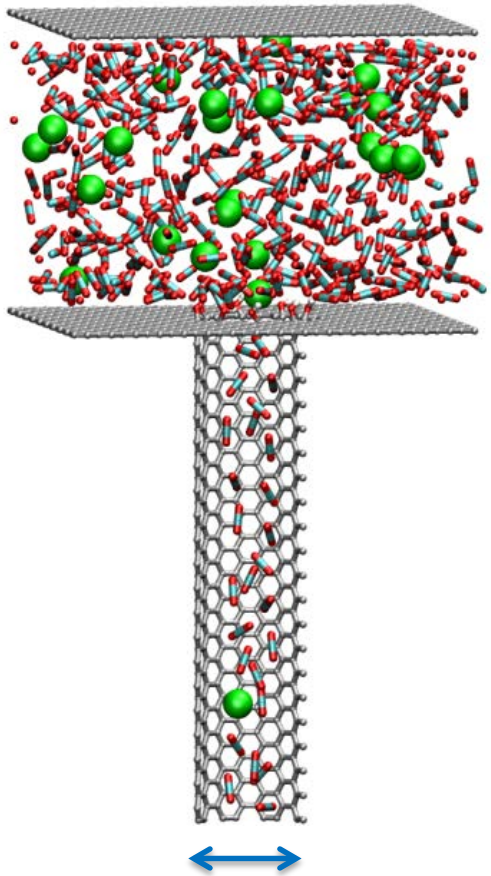
Pore specific effects on enhanced gas recovery



0.814 nm CNT

Pore is too small for the invasion of CO_2

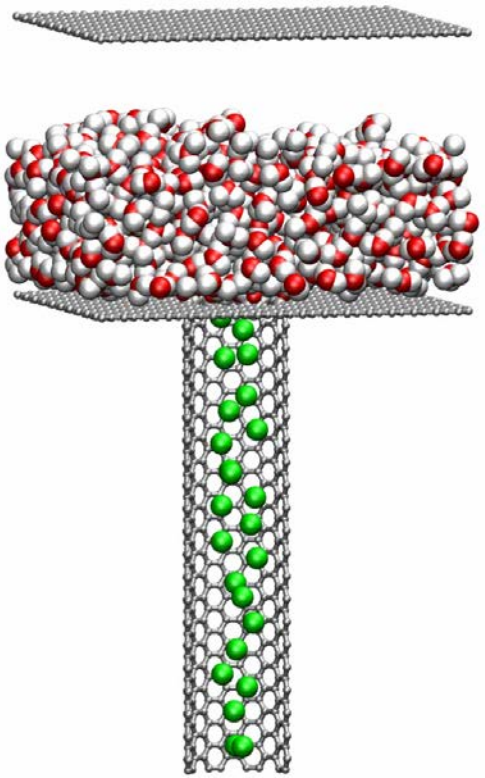
Pore size effect



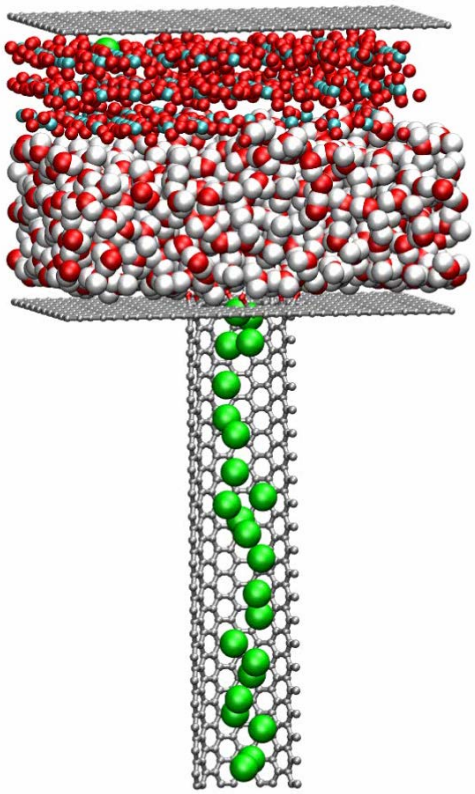
1.085 nm CNT

Pore is big enough for the invasion of CO_2

Pore specific effects on enhanced gas recovery



Water effect



Assume that water thin films block the pore entrance.

CO_2 invades through water and replaces CH_4 in the nanopore.

Model Molecular Structure of kerogen

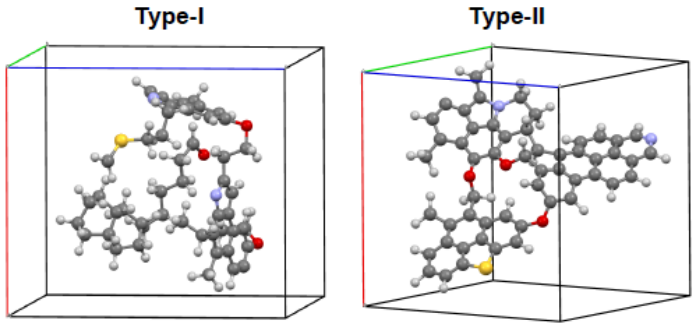


Figure 1: Structures of 3D-periodic type-I (*left*) and type-II (*right*) kerogen models used in DFT/DFPT calculations at the GGA/PBE level of theory. The simulation cells are indicated by solid lines. Color legend: grey, C; white, H; purple, N; red, O; yellow, S.

Ungerer et al. (2015)

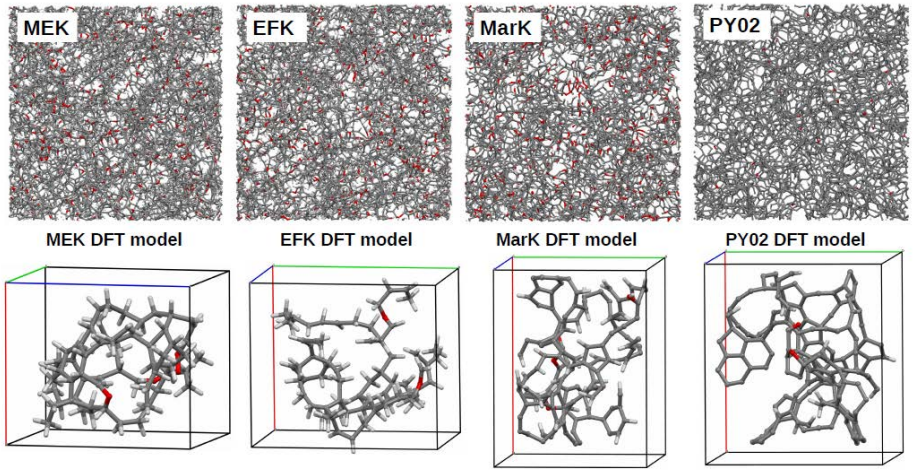
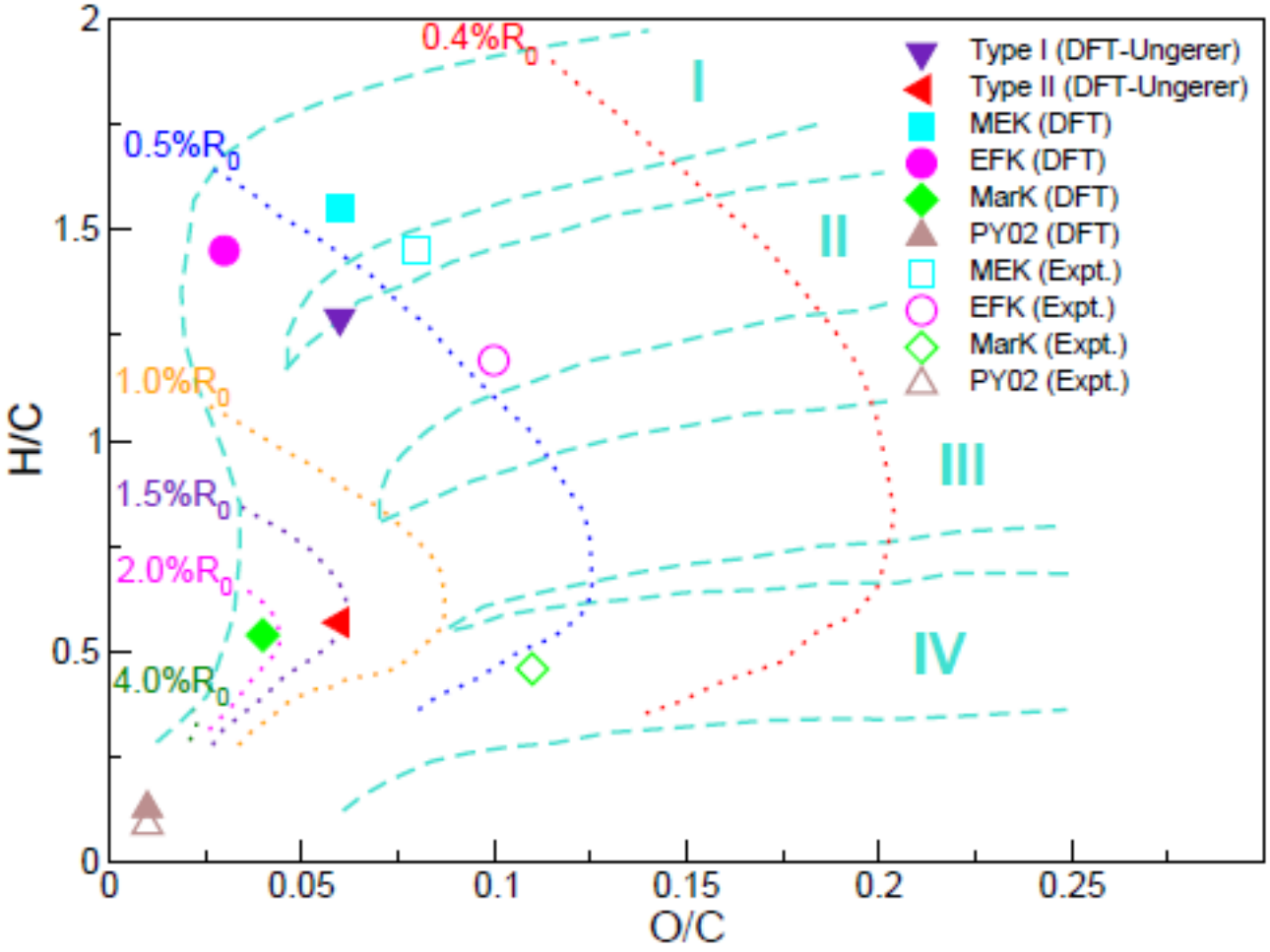


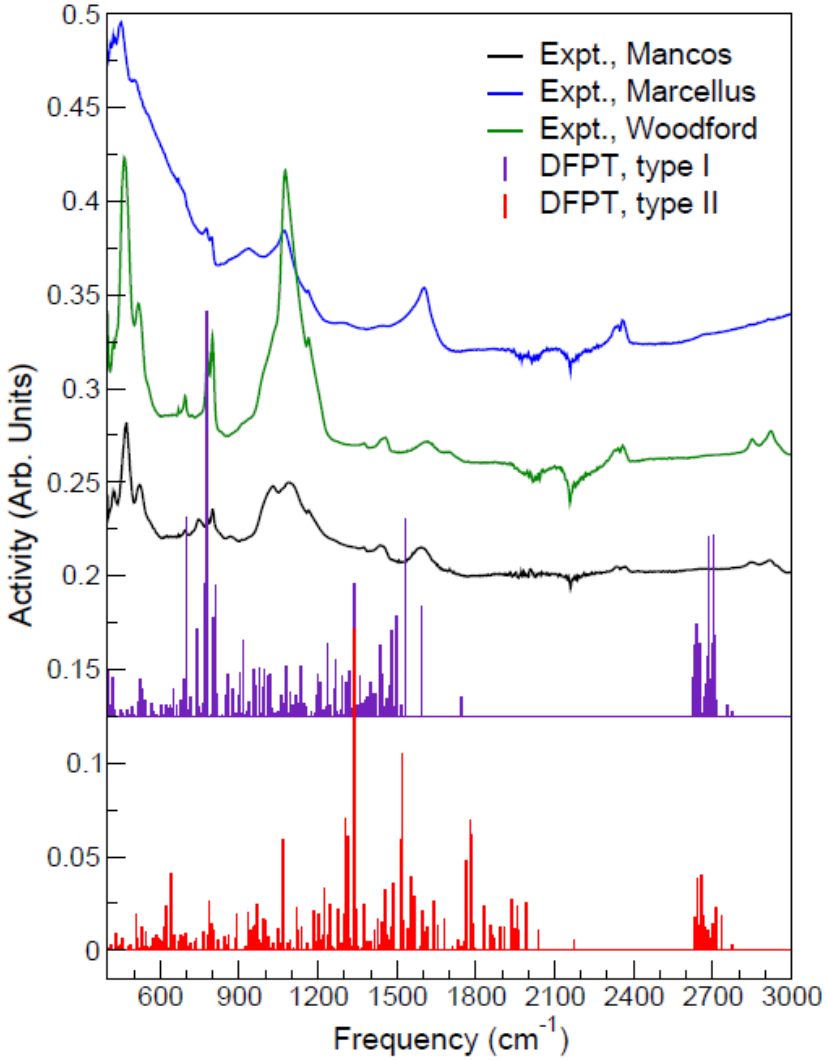
Figure 3: *Top*: Stuctures of the EFK, MEK, MarK and PY02 models (cubic box size of $50 \times 50 \times 50$ Å^3); *Bottom*: representative 3D-periodic portions of EFK, MEK, MarK and PY02 models used in the present DFT/DFPT calculations at the GGA/PBE level (simulations cells are indicated by solid lines). Color legend: grey, C; white, H; red, O.

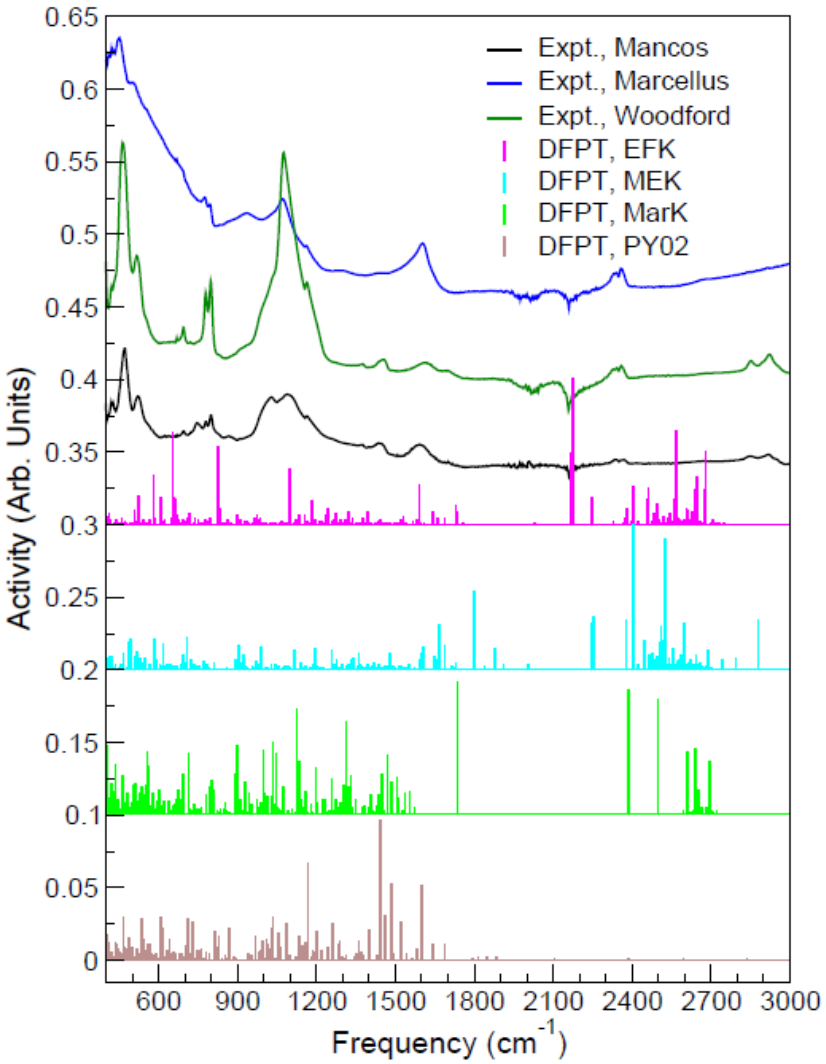
Weck et al, Scientific Reports (2017)

Kerogen Models

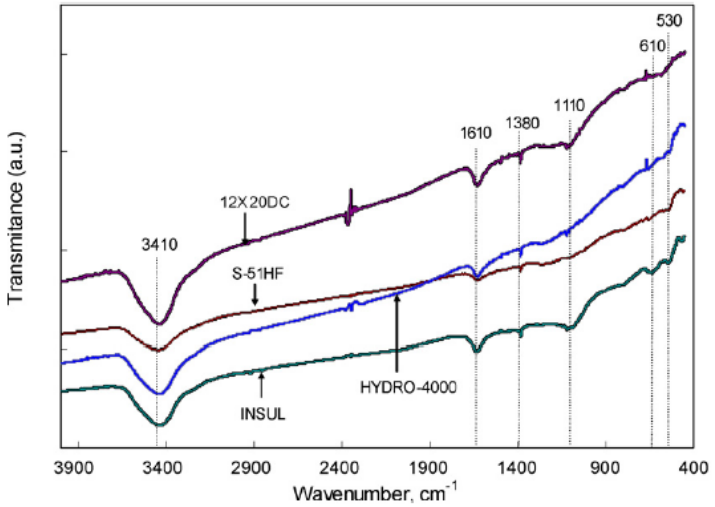


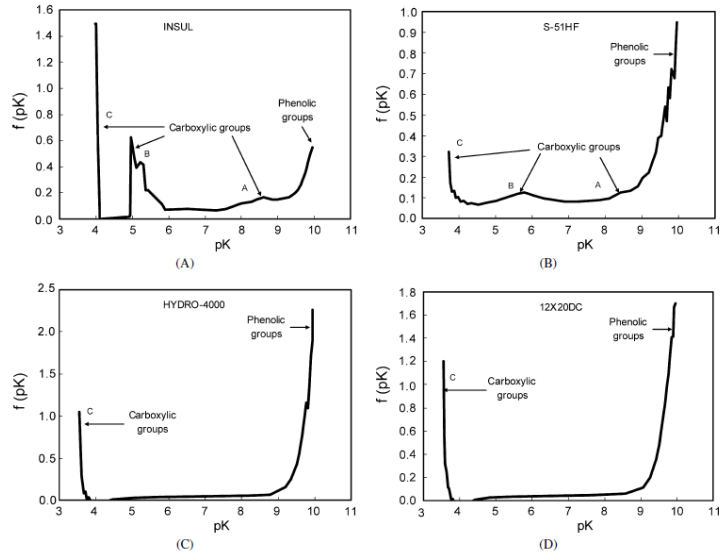
Comparison of DFT results with measurements





Activated carbon: pH titration, surface functional groups, gas sorption and metal sorption and release





Surface area and pore size of activated carbon materials

Activated carbon	Surface area (m^2/g)	Average pore size (nm)	Total volume (cc/g)
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MRX	557	5.4	0.76
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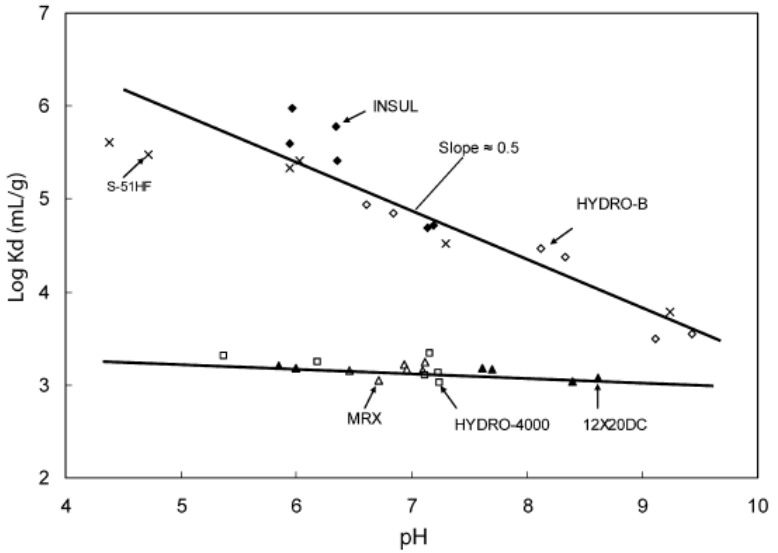


Wang et al. (2007)

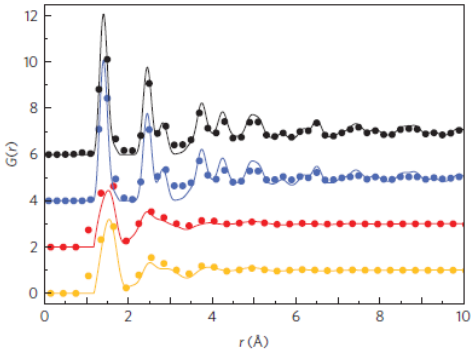
New kerogen models?

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

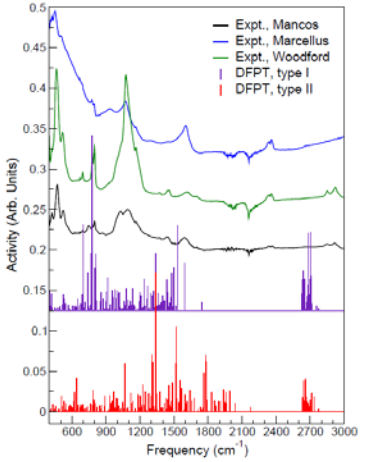
Property	Quantity	Immature		Oil window		Postmature	
		Analytical data	Model unit	Analytical data	Model unit	Analytical data	Model unit
Composition	H/C	1.17	1.17	0.89	0.905	0.56	0.58
	O/C	0.097	0.095	0.05	0.054	0.047	0.051
	N/C	0.029	0.024	0.021	0.021	0.021	0.023
	S/C	0.014	0.012	0.006	0.008	0.01	0.011
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].

New structural models



Bousige et al. (2016)



Nanoconfinement & emergent transport properties

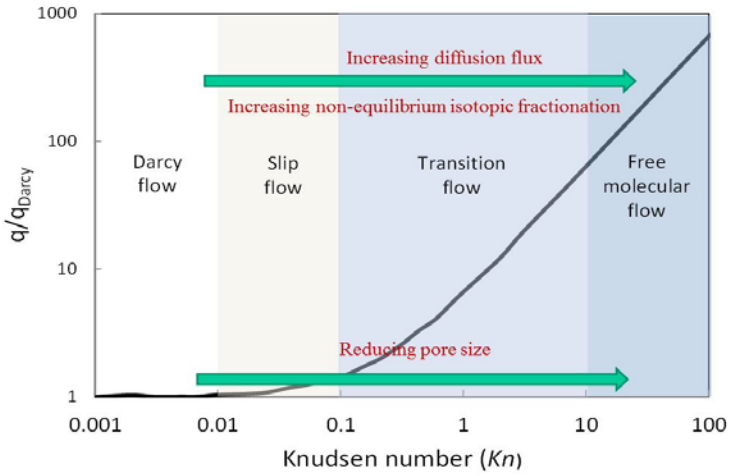
- Slip flow
- Knudsen diffusion

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

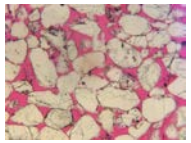
Wang (2017)

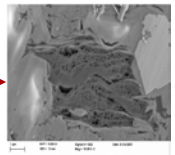
M - Molecular weight

Mass dependent transport



Conventional reservoir



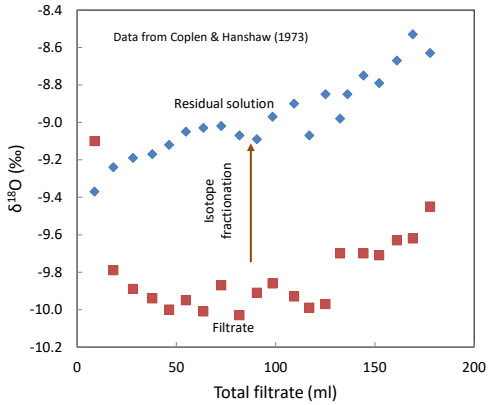


Shale formation

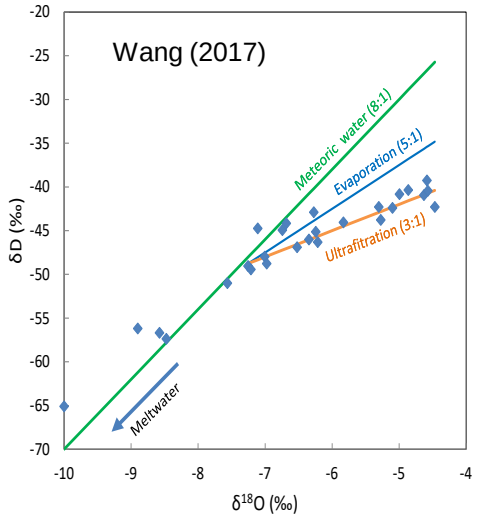
SPE 124253 (2009)

Nanoconfinement & emergent transport properties: isotope fractionation

- Chemical species confined in nanopores behave differently from those in a bulk system.
- Interaction of chemical species with pore surfaces is much enhanced due to a high surface/fluid volume ratio.
- Nano-confinement also manifests the discrete nature of fluid molecules in transport, therefore enhancing mass-dependent isotope fractionations.
- All these effects combined lead to a distinct set of tracer signatures that may not be observed in a conventional hydrocarbon reservoir or highly permeable groundwater aquifer system.

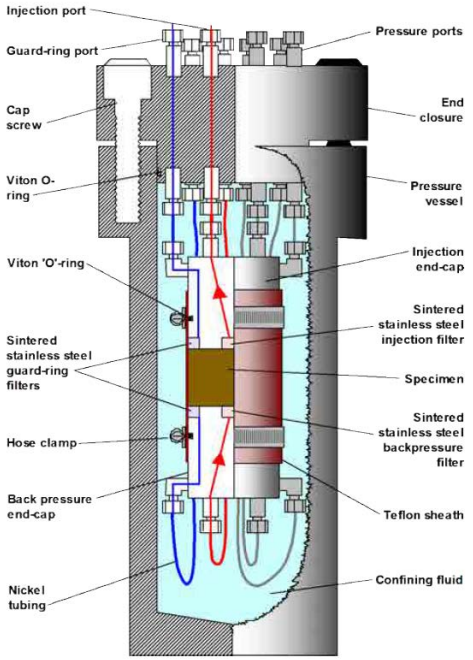


Isotope fractionation of water by ultrafiltration across a compacted clay membrane (Coplen and Hanshaw, 1973)

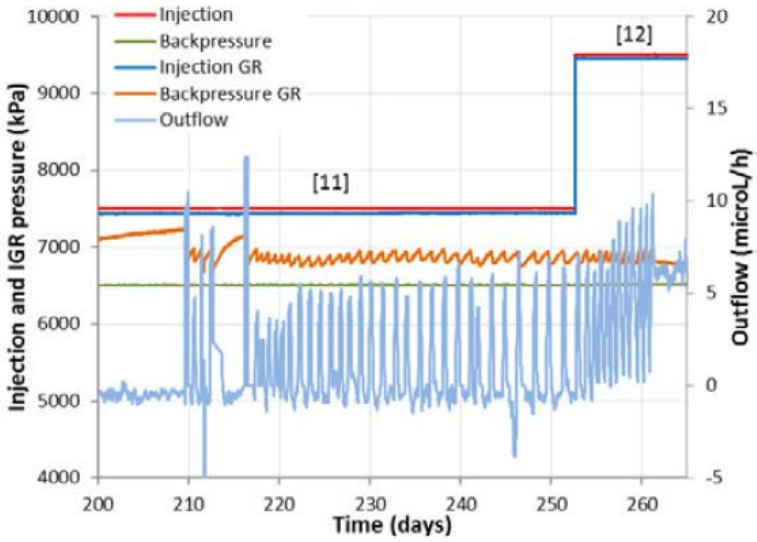


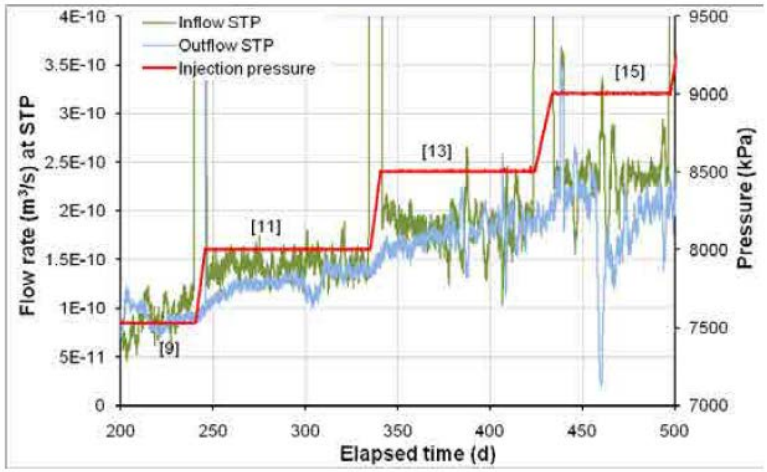
Waters extracted from Opallinus Clay at Benken (Switzerland) (Mazurek et al., 2009)

Chaotic behavior of gas migration in compacted clay

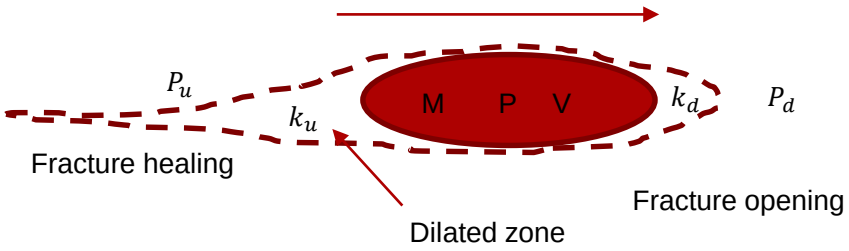


FORGE Report D4.17 (Harrington, 2013)



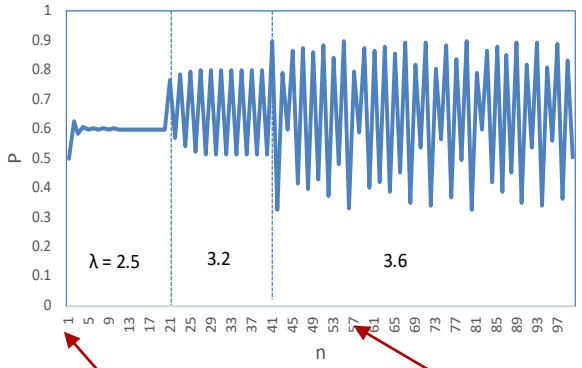


Bubble migration under a pressure gradient



Logistic map

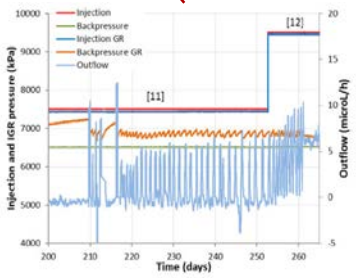
$$p_{n+1} = \lambda p_n(1 - p_n)$$

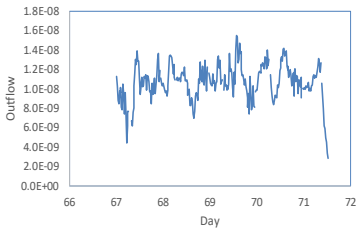


Delay logistic equation

$$\frac{dP}{dt} = \lambda_1 \left(1 - \frac{P}{K}\right) \int_{-\infty}^{t} G(t-s)p(s)ds$$

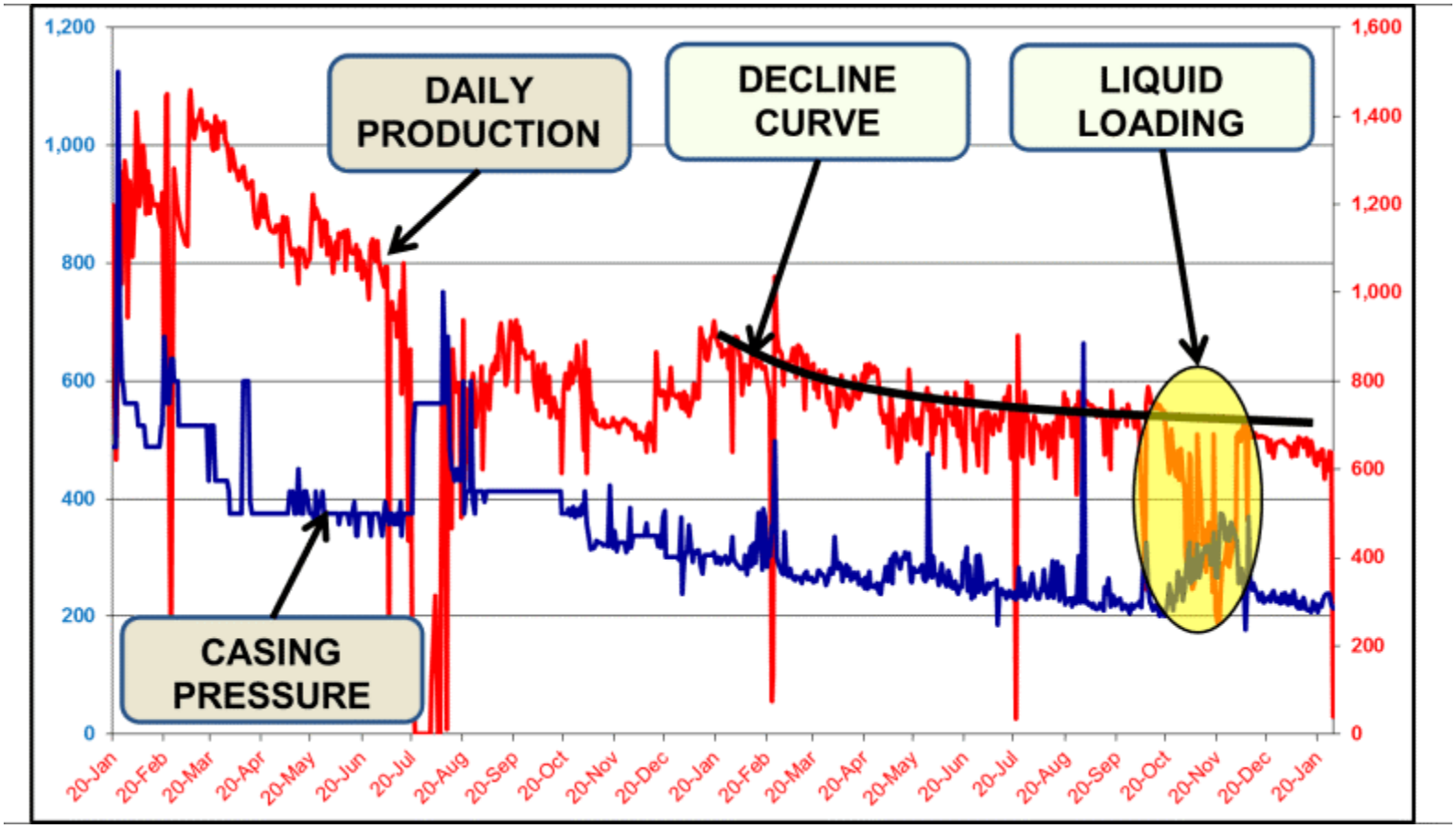
$$\frac{dP}{dt} = \lambda_1 \left(1 - \frac{P}{K}\right) \int_{-\infty}^{t} \alpha e^{-\alpha(t-s)} p(s)ds$$





$$\lambda_1 = \frac{\left(k_u^0 P_u + k_d^0 P_d\right) RT}{V} \qquad \lambda_2 = \frac{\left(k_u^0 + k_d^0\right) RT}{V} \qquad K = \frac{\lambda_1}{\lambda_2}$$

Chaotic behavior of well production?



https://www.shaletec.com/files/Production-below-decline-curve.png

Future work

- Performing additional high pressure and high temperature sorption measurements on crushed shale samples.
- Perform sorption measurements more on multicomponent systems to clarify the interactions among different components (CH_4-CO_2-H_2O).
- Develop new structural models for kerogen that correctly account for both atom correlations and functional group distributions.
- Understand the effects of surface functional groups on gas sorption and release in kerogen.
- Perform MD (or MC) simulations for understanding CH_4-CO_2-H_2O interactions in nanoporous clay matrix.
- Extend the research to include other hydrocarbon components.
- Develop a nanofluidic model for gas transport and isotope fractionation in shale.
- Based on the existing experimental and modeling results to formulate new gas disposition and release model for well-borehole production.
- Collaboration on kerogen study: Schlumberger, MIT