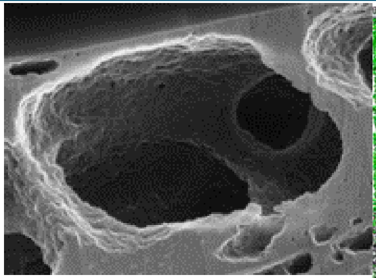
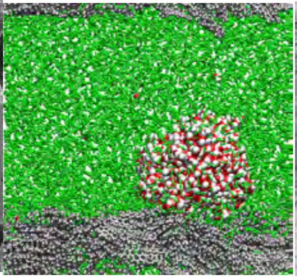
Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfers





PRESENTED BY

Yifeng Wang

SAND2018-9465PE for UUR

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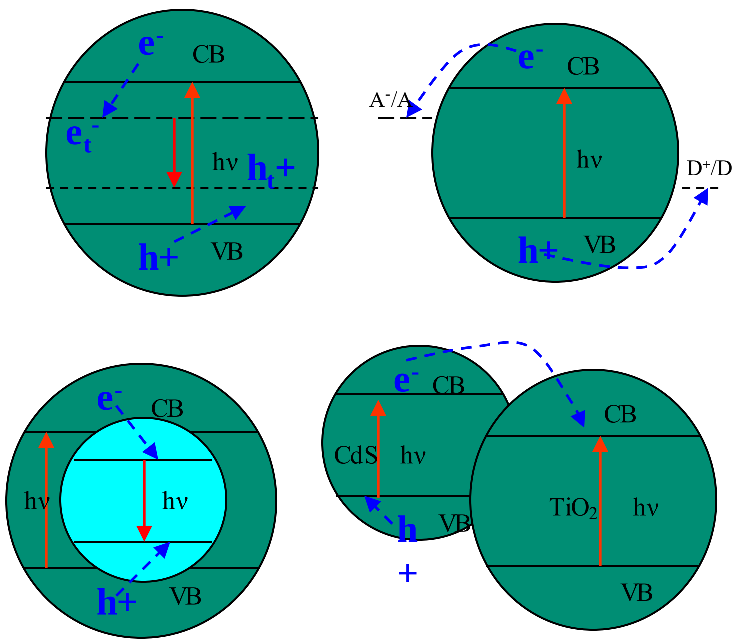
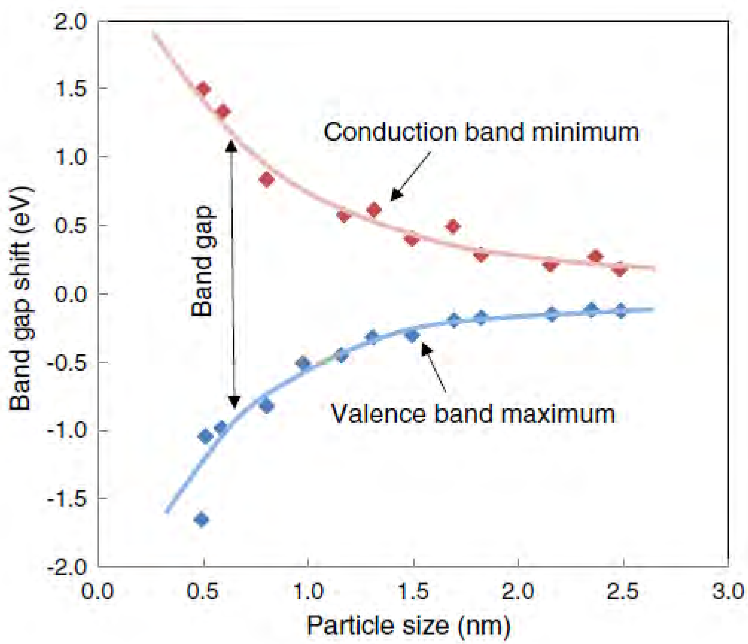
Nanoscience: Size-Dependent Material Properties

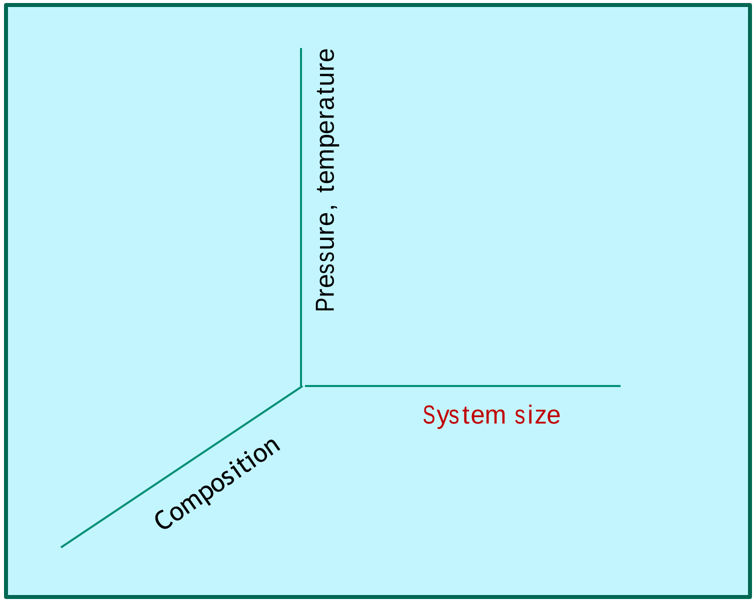


Photophysical/Photochemical Processes in Semiconductor Nanoparticles
(Roduner, 2006)



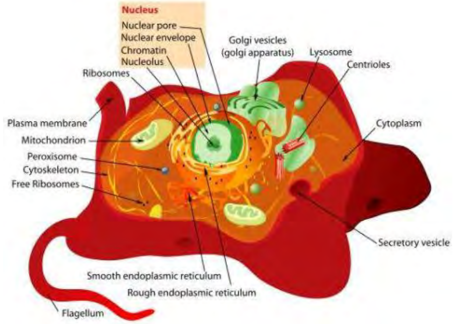
Size-dependent CdS band gap
(Lüning et al., 1999, Sold State Communication)

Nanogeochemistry

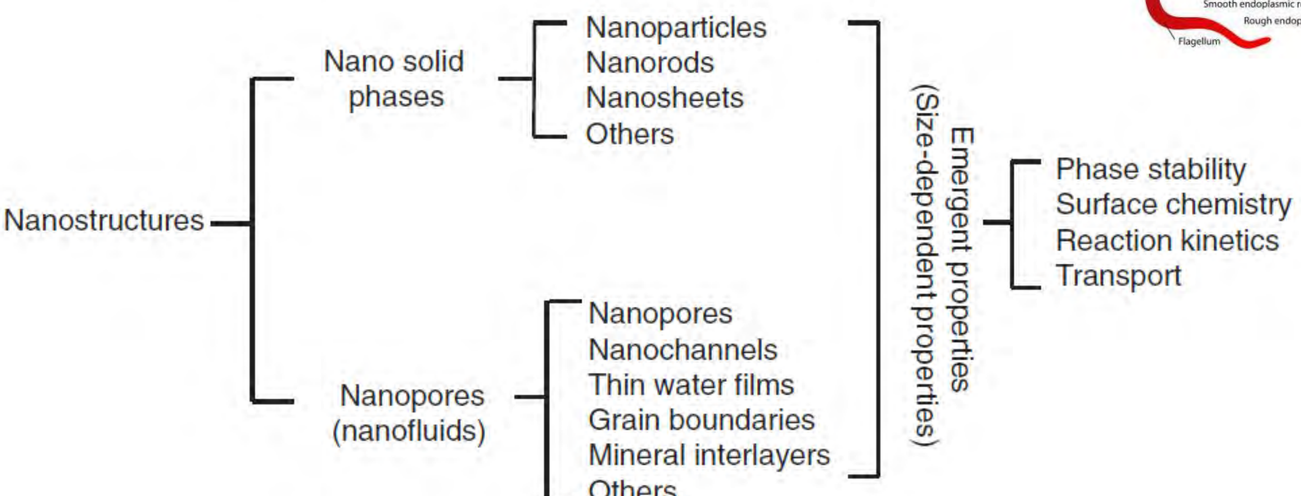


Nanogeochemistry: Understand emergent properties of geochemical systems under nano-scale structural constraints or organizations.

Rule of thumb: <100 nm

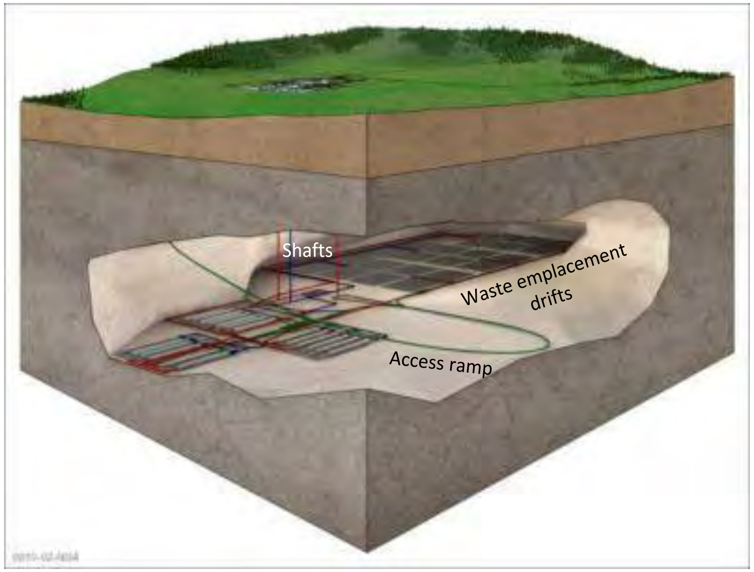


http://tamiport.hubpages.com/hub/Cell-Biology-Differences-Between-Prokaryotic-and-Eukaryotic-Cells#slide2150310

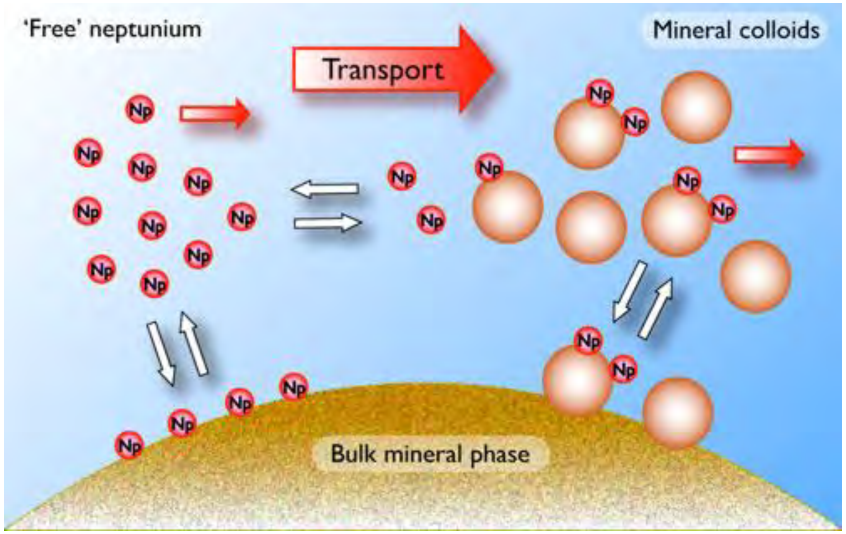


Wang (2014) Chemical Geology

Colloid-facilitated radionuclide transport



http://www.bbc.com/news/uk-england-cumbria-21253673

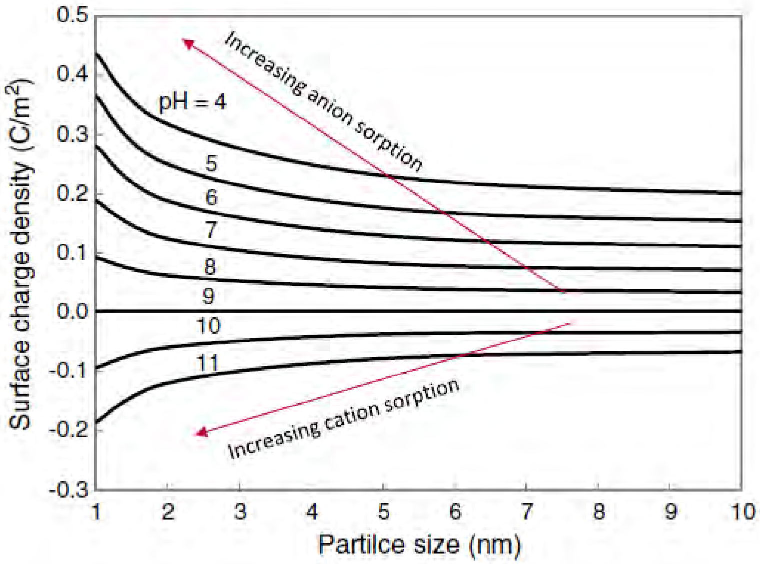


https://eesa.lbl.gov/radioactive-contamination-over-geologic-time/

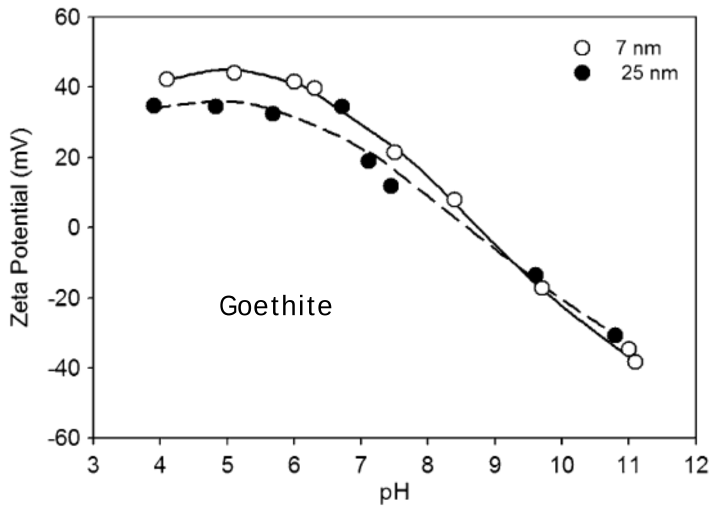
Key radionuclides:
Pu-239, Th-230, Am-241 - Strong interaction (colloids)
U-238, Np-237 - Moderate interaction
I-129, Tc-99 - Weak interaction (anions)

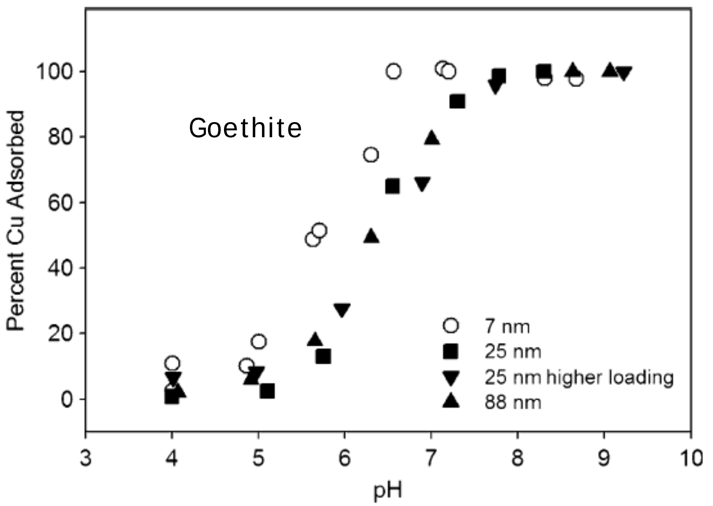
Colloids: ~1 - 1000 nm
Nanoparticles: ~1 - 100 nm

Surface charge and sorption capability of nanoparticles



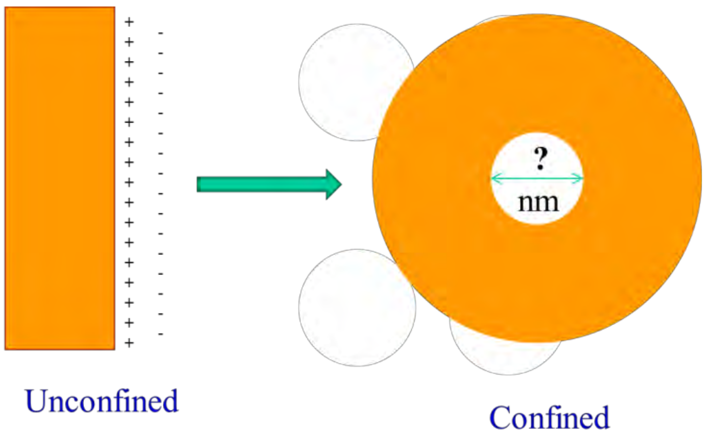
Surface charge density predicted by Monte-Carlo simulations for goethite nanoparticles (Abbas et al., 2008)

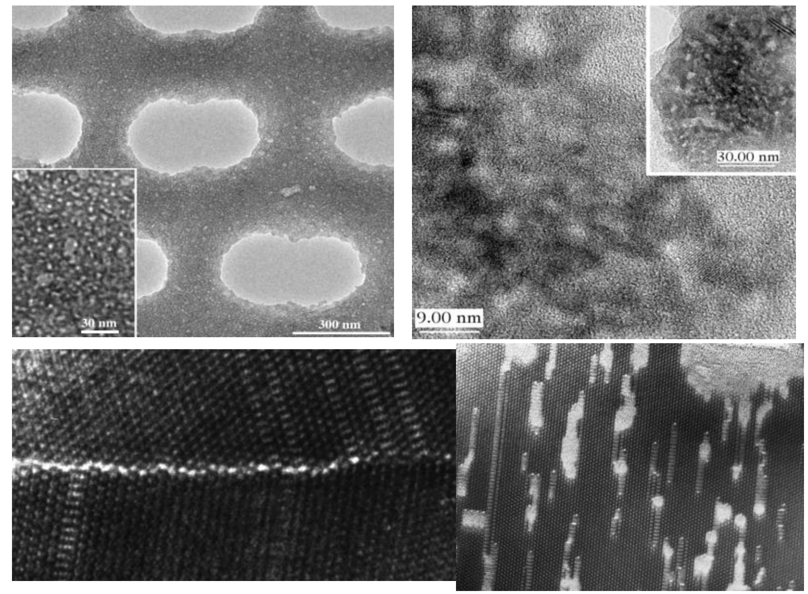




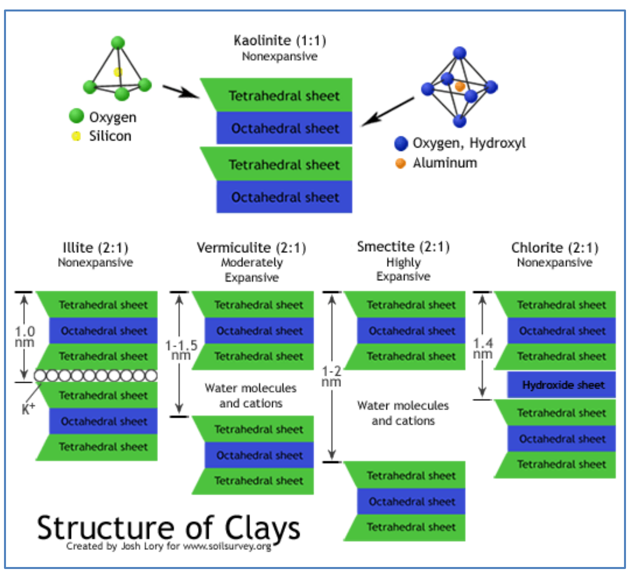
Madden et al., 2006, GCA

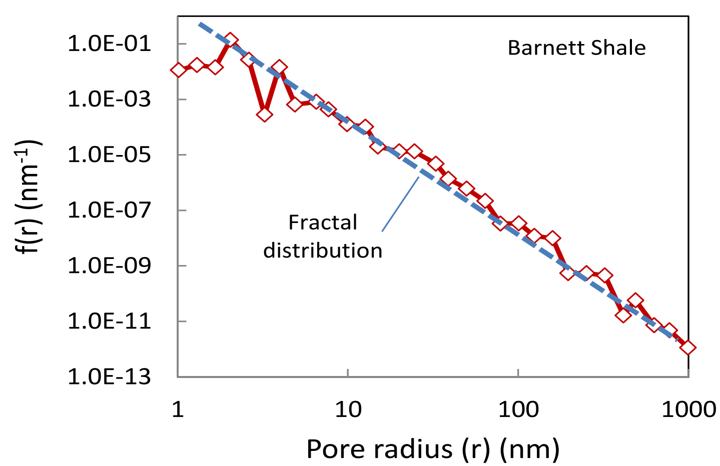
Effects of Nanopore Confinement





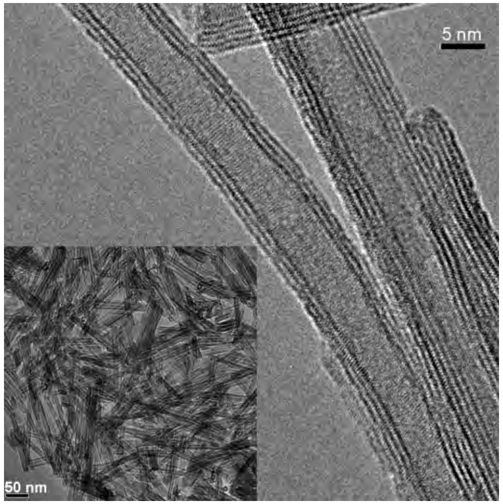
Wang et al., 2003, Geology

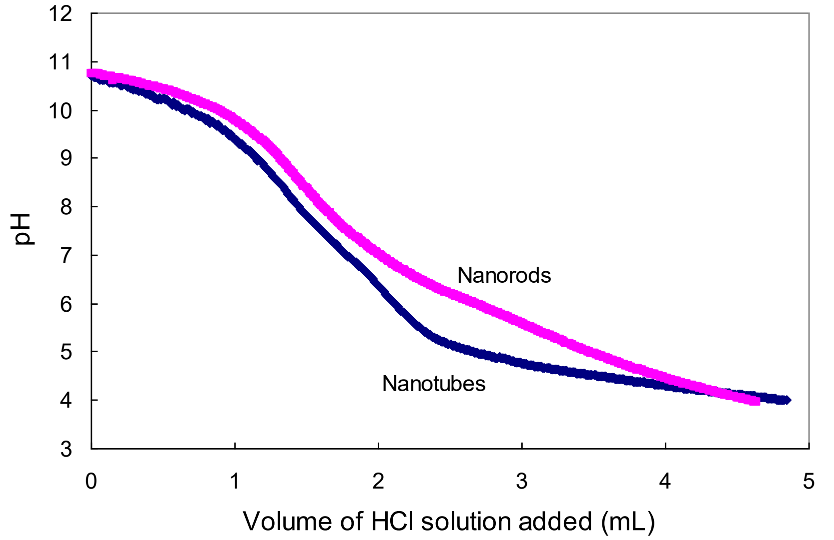


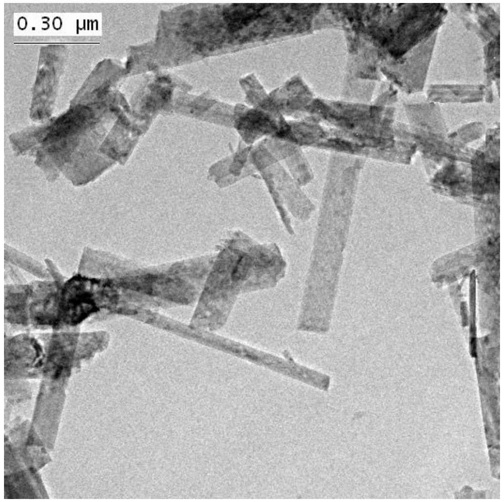


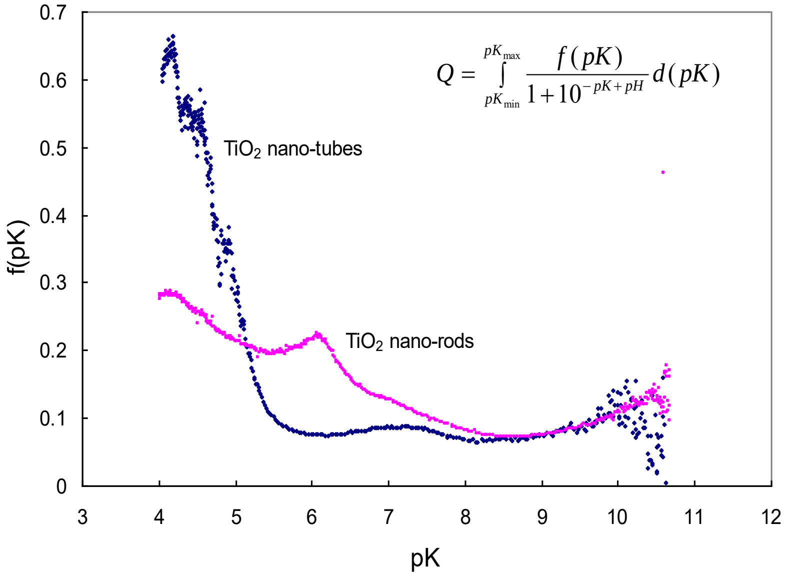
Clarkson et al. (2012)

Model Systems for Studying Nanopore Confinement



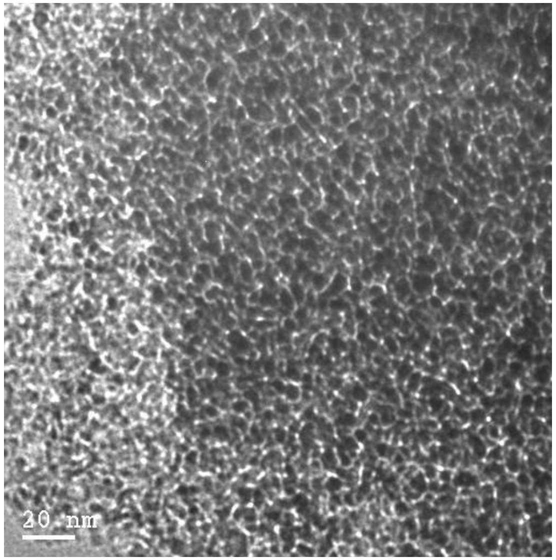


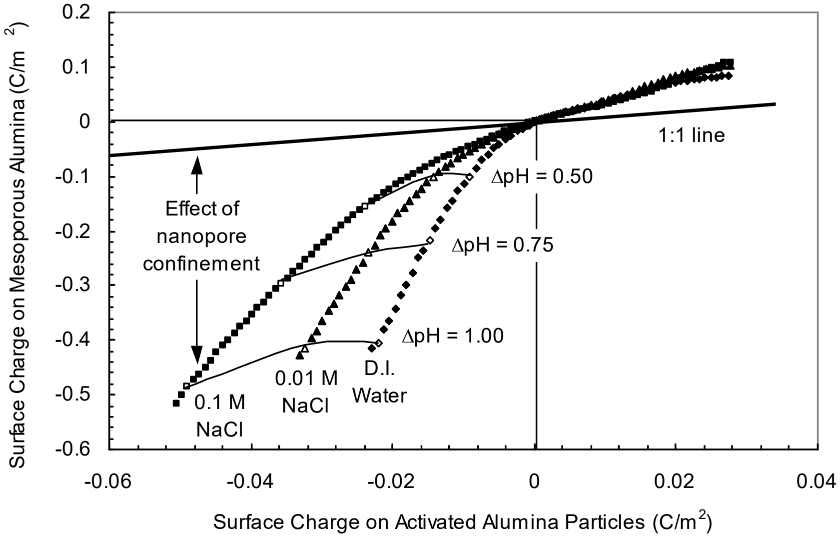


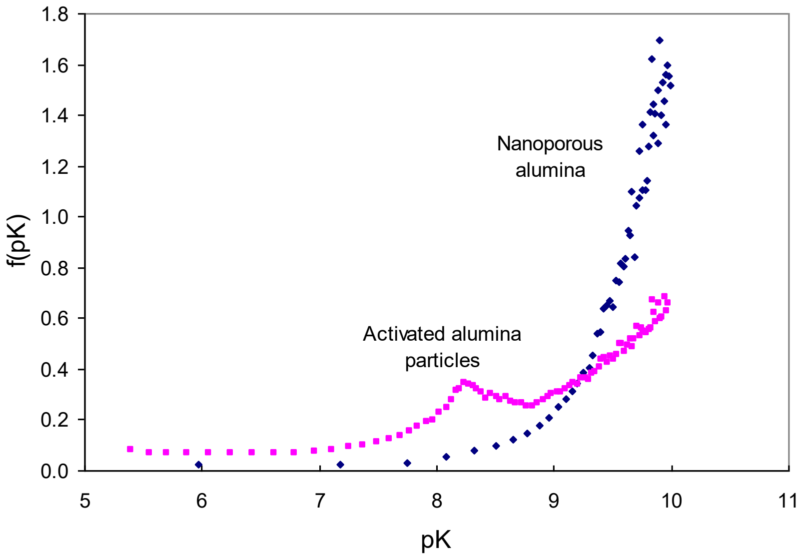


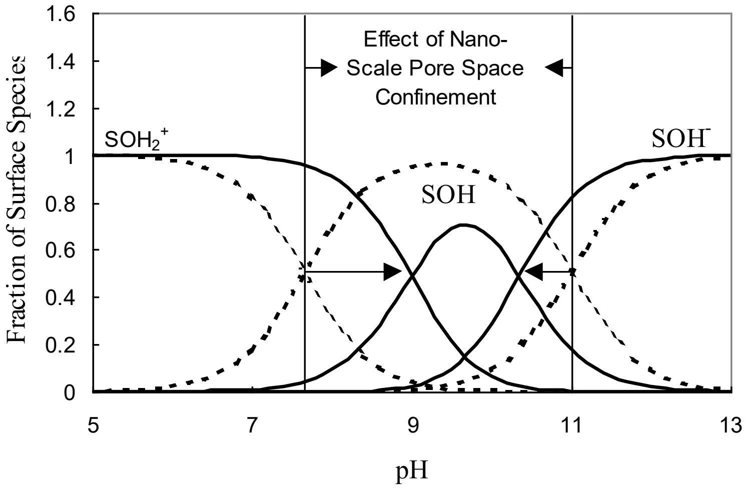
Wang et al. (2008)

Model Systems for Studying Nanopore Confinement (cont.)



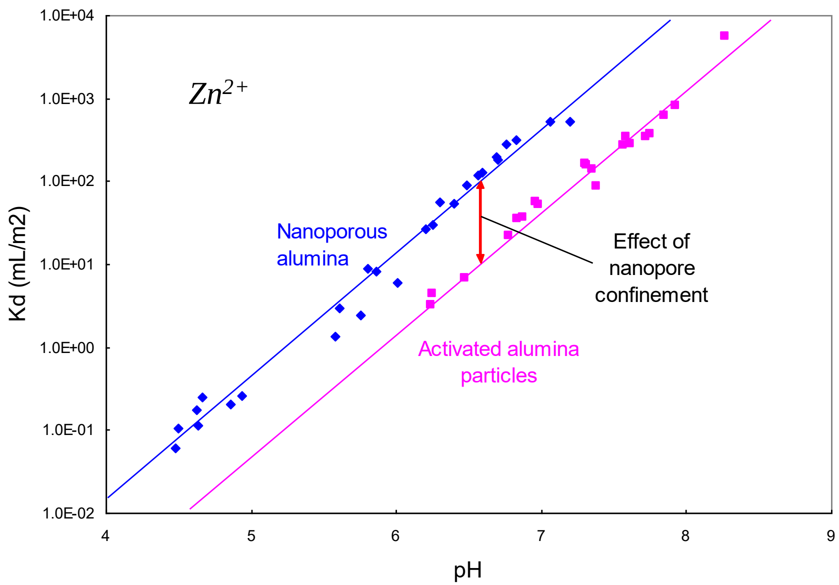


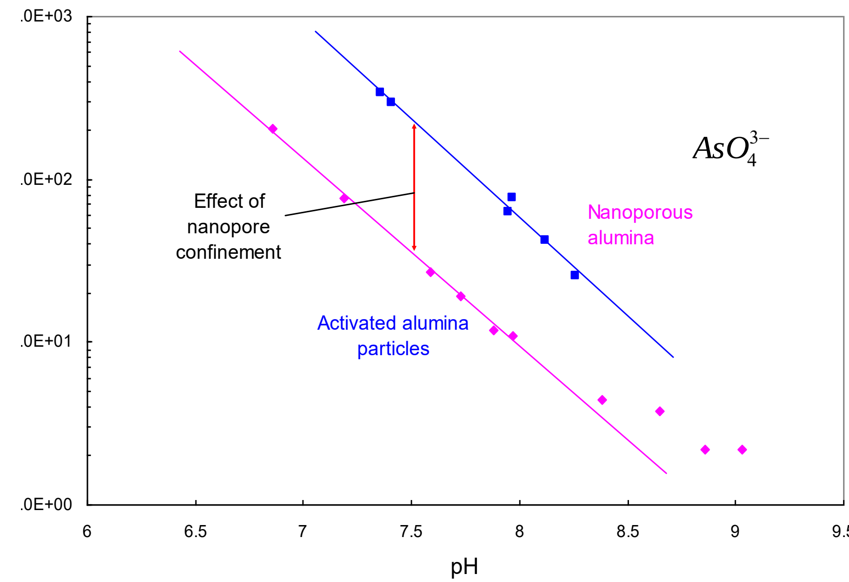




Wang et al., 2002, JCIS; 2003, Geology

Nanoconfinement and Ion Sorption

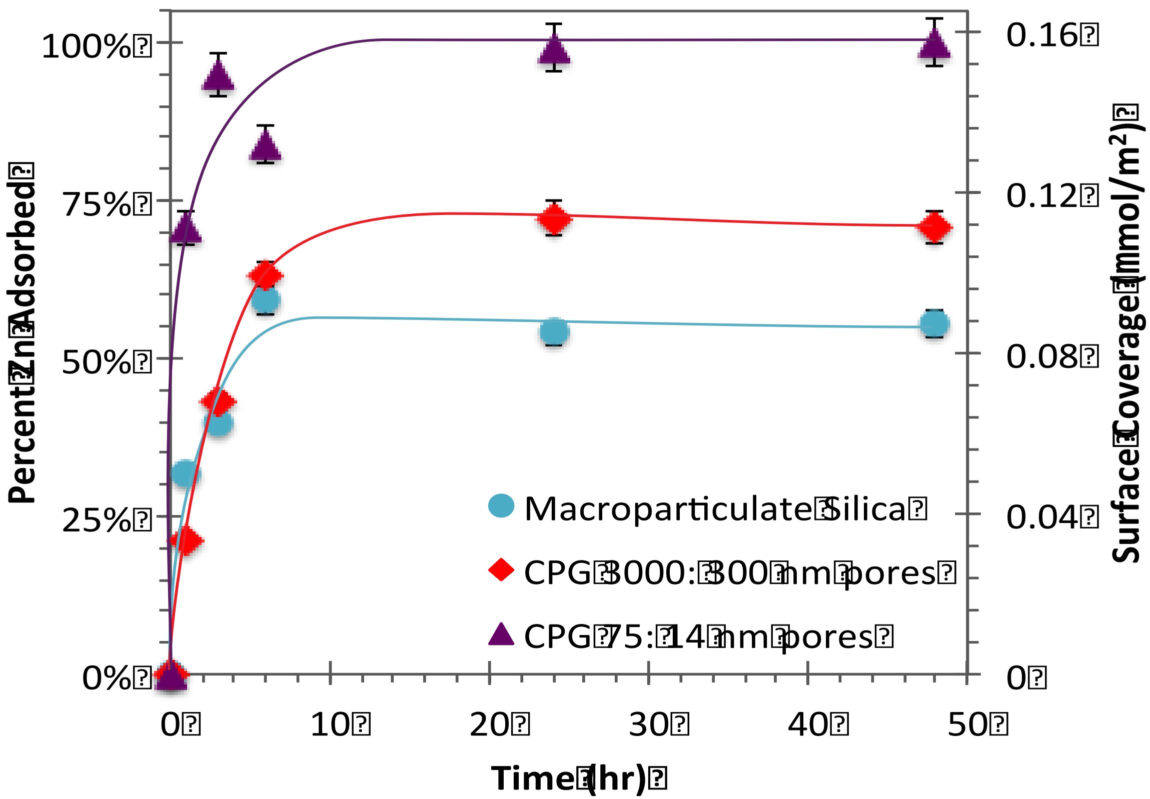




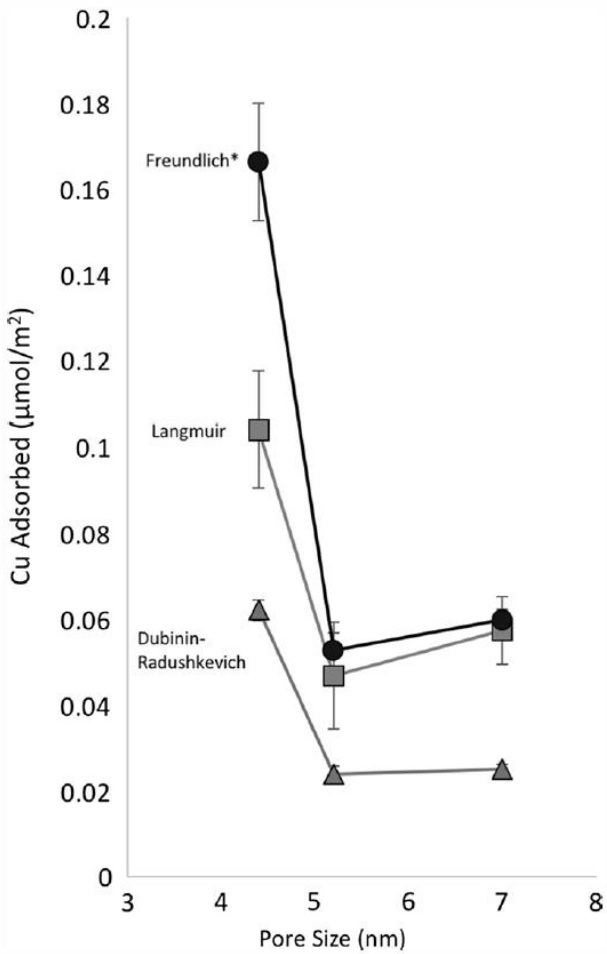
Nanopore confinement enhances ion sorption onto a solid-water interface for both cations and anions.

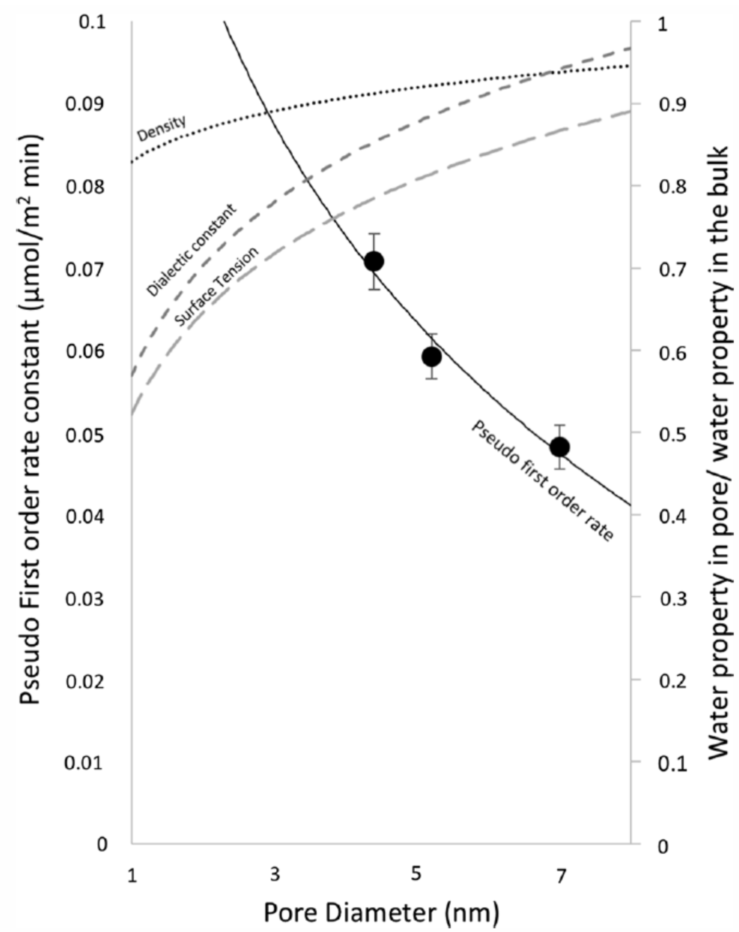
Wang et al., 2003, Mat. Res. Soc. Symp. Proc.; 2003, Geology

Zn^{2+} sorption on to controlled pore glass (Nelson et al., 2014)

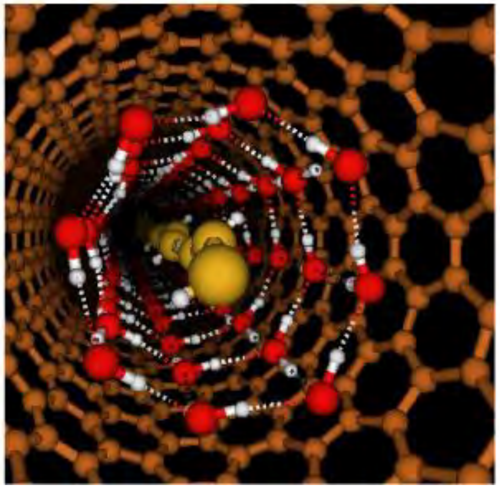


Cu(II) sorption onto mesoporous silica (Knight et al., 2018)

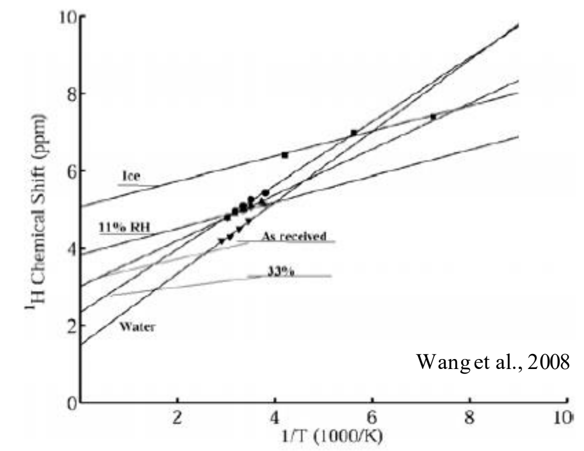




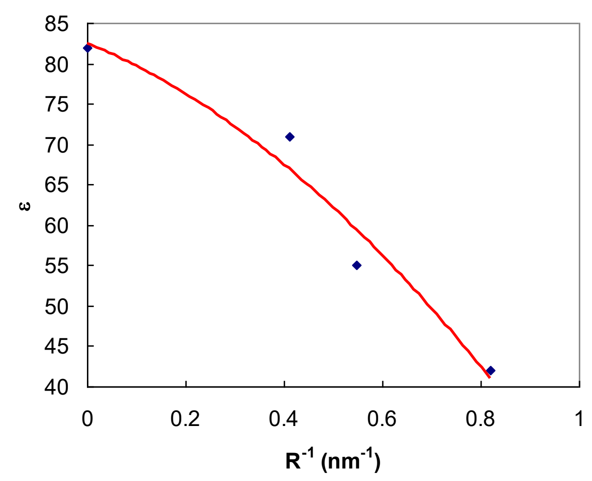
Effect of Nanopore Confinement on Water



Kolesnikov et al., 2004



Wang et al., 2008



Senapati & Chandra, 2001, J. Phys. Chem.

Postulations:

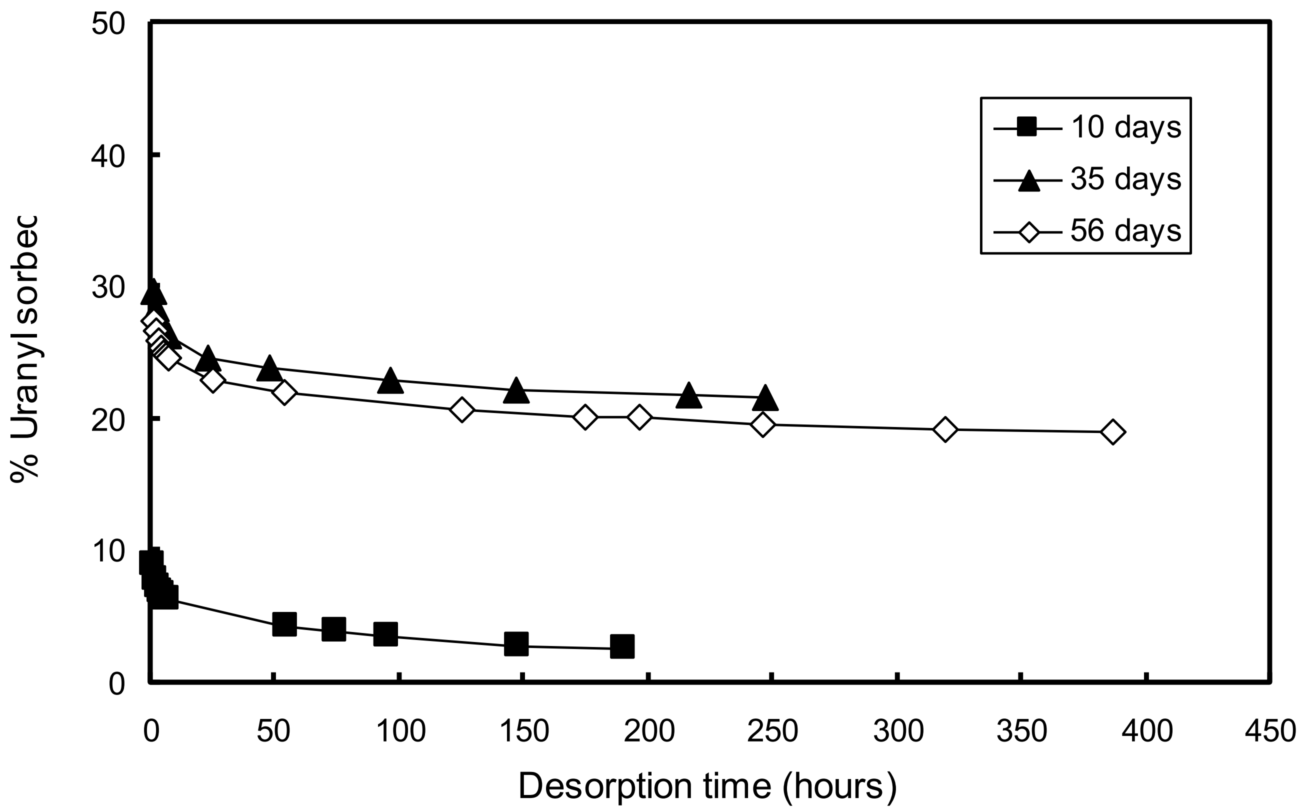
Water molecules in nanopores are more restrained.

$H_4SiO_4 = SiO_2(s) + 2H_2O$ pptn

$M(H_2O)_n^{z+} = M^{z+} + nH_2O$ inner sphere

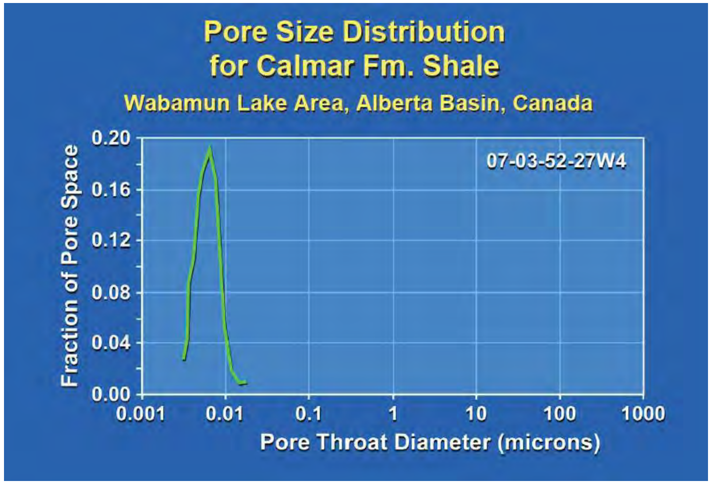
$Na^+ + Cl^- = NaCl^0$ ion pairing

Uranyl Desorption from Synthetic Porous Goethite

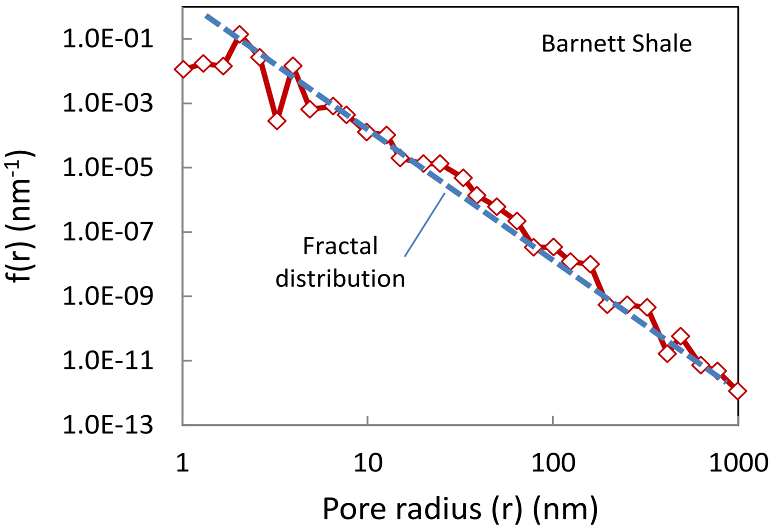


Wang et al., 2003, Geology

Shale as a nanocomposite material

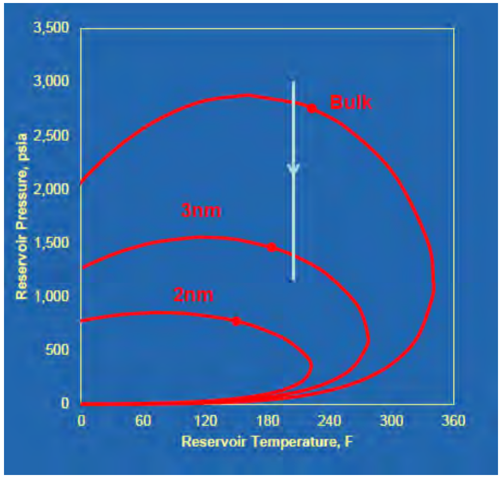


Bachu & Bennion (2006)



Clarkson et al. (2012)

EOS under Nanoconfinement

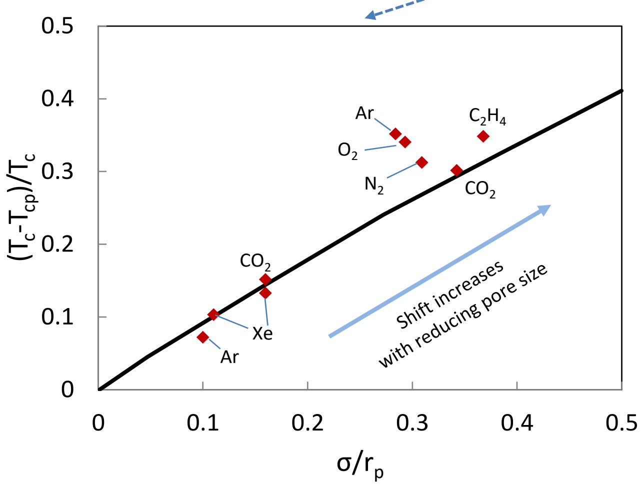


Akkutlu, 2013

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

Nanoconfinement →

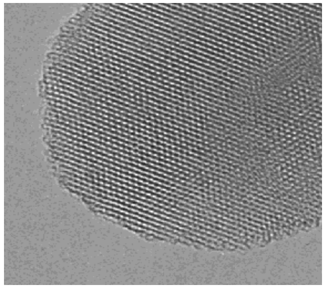
Nanofluids
(Confined in nanopores, pore size < ~100 nm)
EOS = f(P, T, composition, pore size, surface chemistry)



Wang (2014); Zarragoicoechea and Kuz (2004)

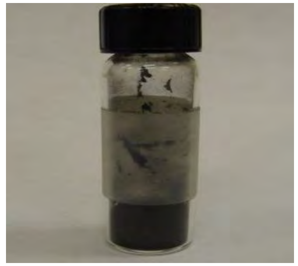
Overall goal: (1) Obtain a fundamental understanding of CH_4-CO_2-H_2O (or other fluid component) interactions in shale nanopores under high-pressure and high temperature reservoir conditions, and (2) integrate this understanding into reservoir engineering for efficient resource recovery and subsurface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

Capabilities for Nanogeochemical Studies at Sandia National Laboratories



A Synthesis of nanoporous materials

B



Isolation of kerogen from Mancos shale


Chemical Geology 370–376 (2014) 1–23

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/chemgeo

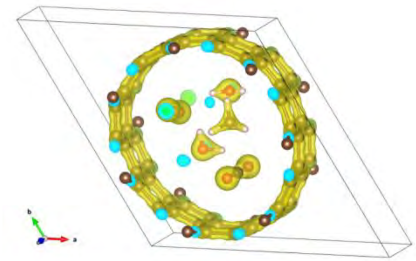
Nanogeochemistry: Nanostructures, emergent properties and their control on geochemical reactions and mass transfers

Yifeng Wang

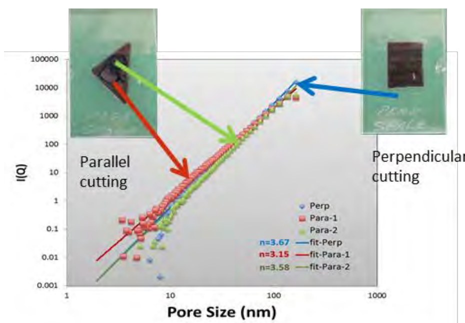
ARTICLE INFO

ABSTRACT

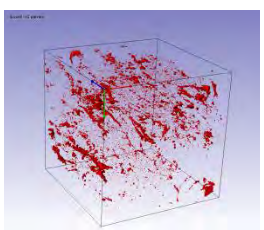
Pioneering work in nanogeochemistry. Access to DOE Center of Integrated Nanotechnology



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

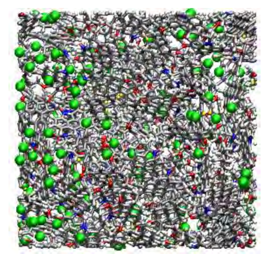
Gas disposition & release
- Gas in place (GIP)
- Gas migration from matrix into fractures
- Stimulated volume
- Gas for secondary recovery

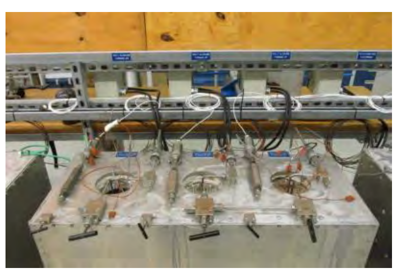
Molecular dynamic (MD) modeling
- Binding energies of methane sorption
- Diffusion rates

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

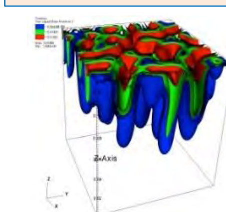
Upscaling
- Percolation theory
- Fractal representation
- Lattice Boltzmann modeling

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



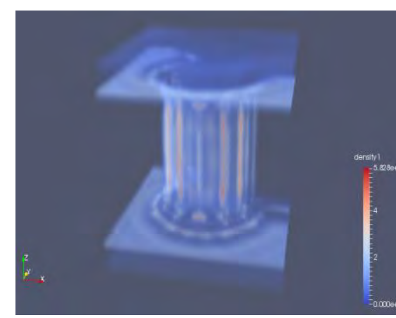


High pressure/high temperature sorption/desorption measurements



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

PFLOTRAN: Reactive transport modeling



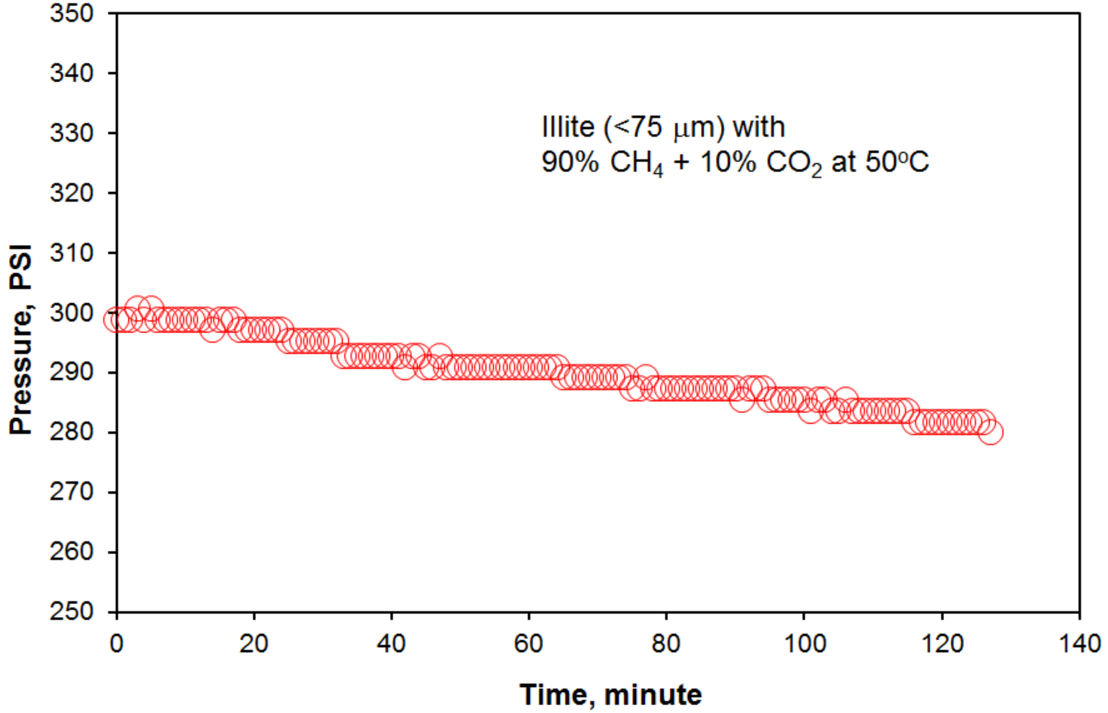
TRAMANTO: Classical Density Functional Theory

Low pressure gas sorption measurements

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

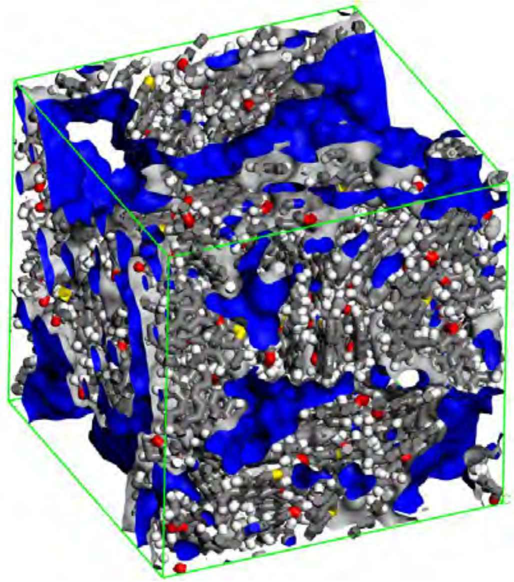
Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min^{-1}
DARCO activated carbon	25	85% CH_4 + 15% CO_2	1	28	0.68
	50	85% CH_4 + 15% CO_2	1	11	0.59
	75	85% CH_4 + 15% CO_2	1	9.0	0.31
	100	85% CH_4 + 15% CO_2	1	2.1	0.14
	125	85% CH_4 + 15%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

Experimental measurement of sorption capacity and sorption rate for a model substance at an elevated temperature and pressure



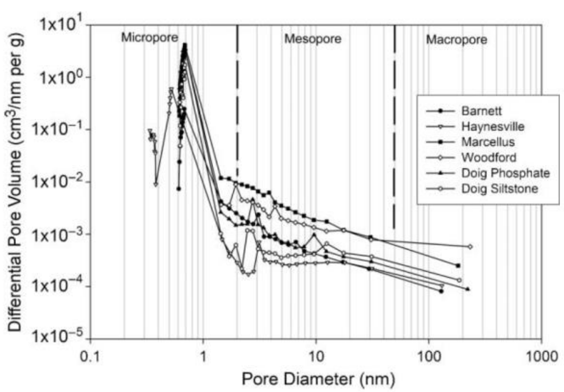
Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, PSI	Sorption Capacity (mixture) mg/g	Sorption Rate, mg/g min^{-1}
Illite, <75 mm	50	90% CH_4 + 10% CO_2	300	190	1.5

Kerogen



Over-mature
kerogen molecules

Ho, et al, Scientific Reports 28053



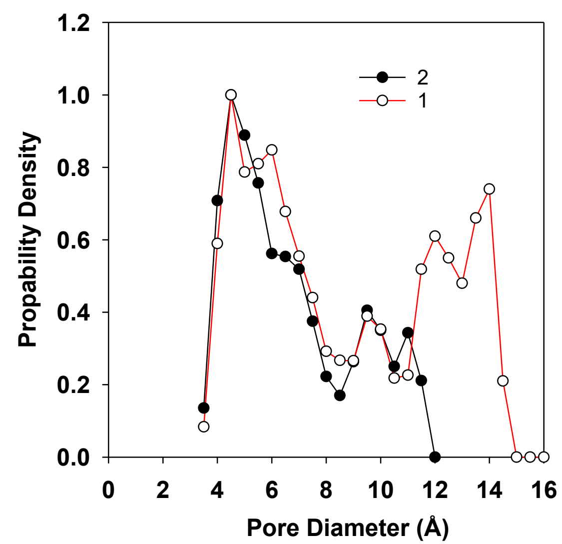
AAPG 96 (2012), 1099-1119

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

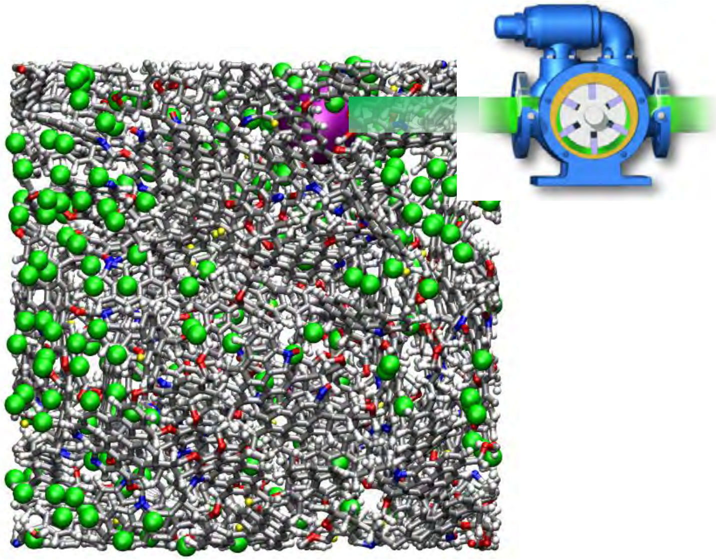
Stankiewicz A, *et al.* (2015) Kerogen density revisited - lessons from the Duvernay Shale. *In: Paper URTeC 2157904 at the Unconventional Resources Technology Conference, San Antonio, Texas, July 2015*

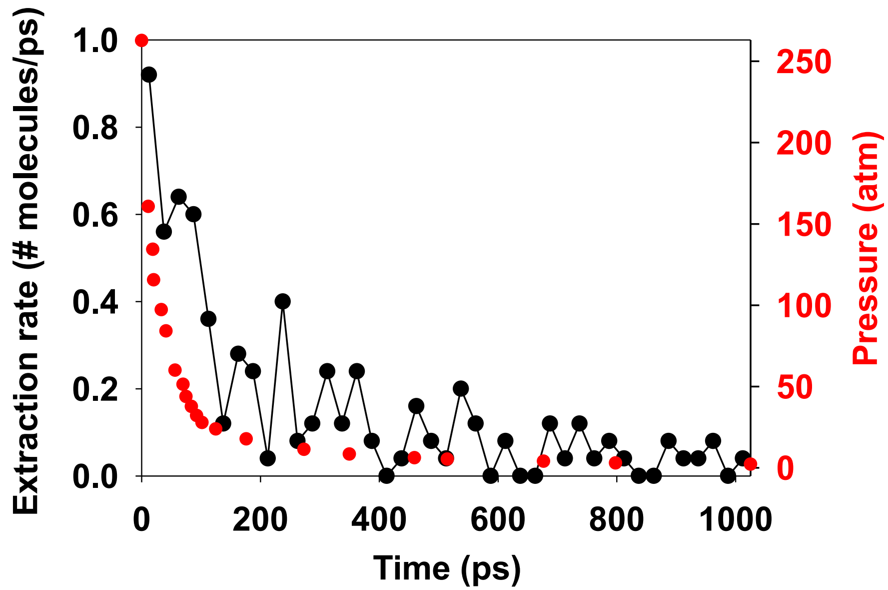
Pore size distribution

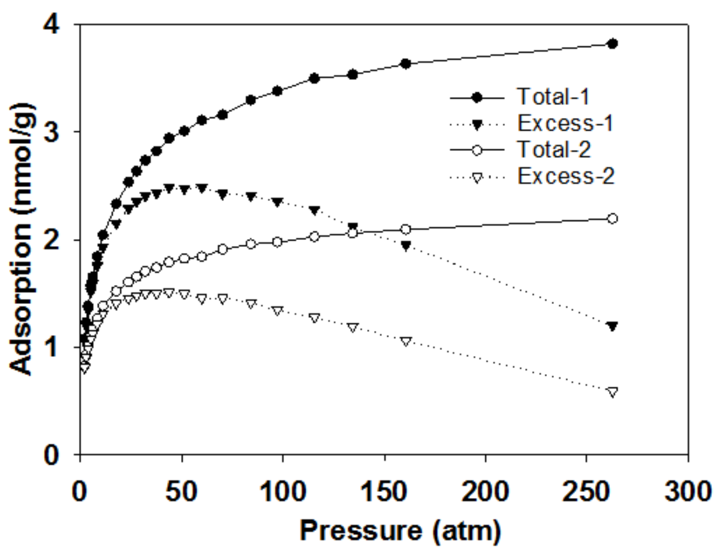


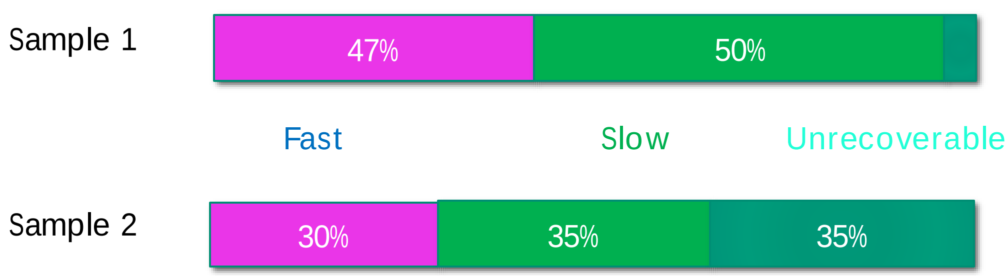
Method: Bhattacharya S & Gubbins KE (2006) *Langmuir* 22:7726-7731

Methane sorption and extraction from kerogen



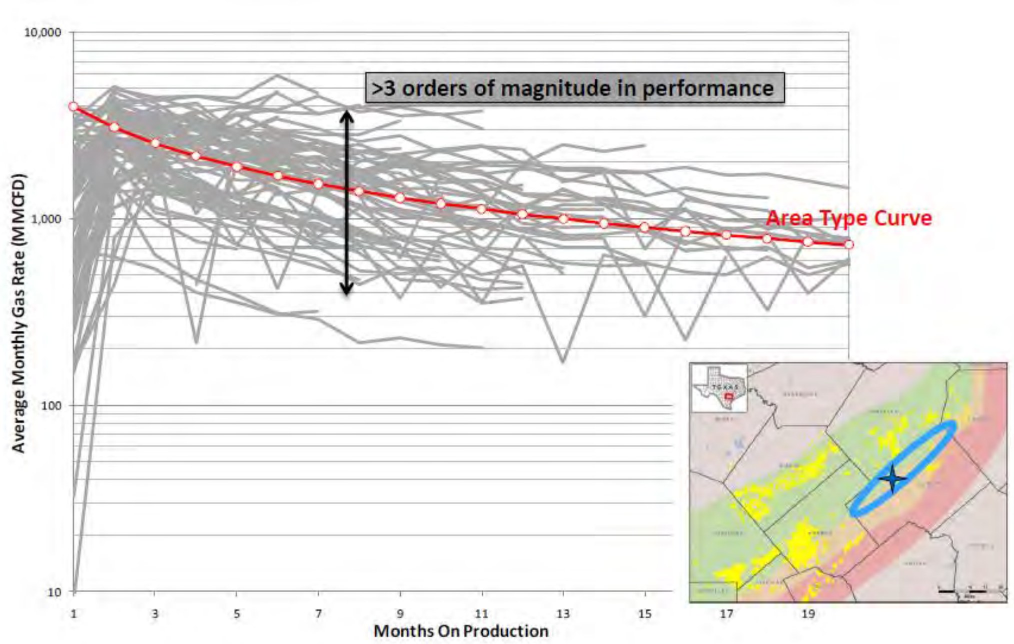






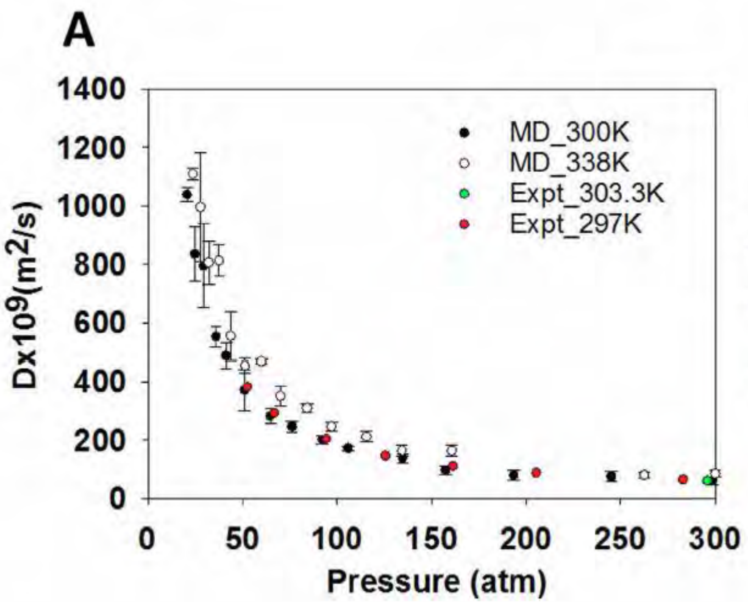
Implication to decline curve

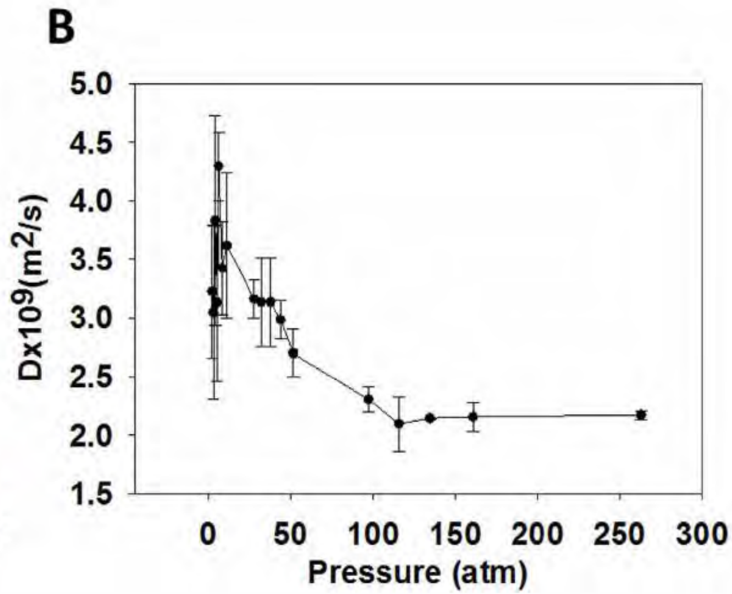
- Fractures shift the decline curves up and down.
- Matrix determines the slopes of decline curves.



Robertson (2013)

Methane Diffusion





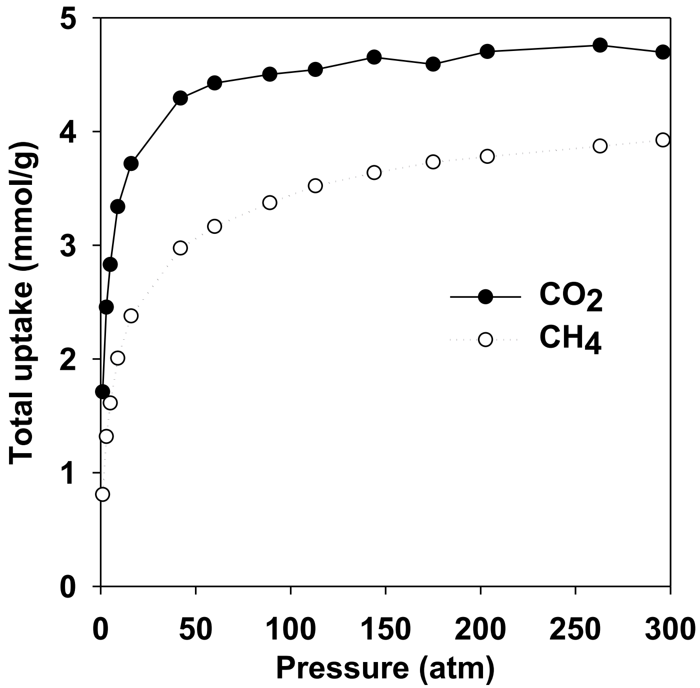
Bulk

In kerogen nanopores

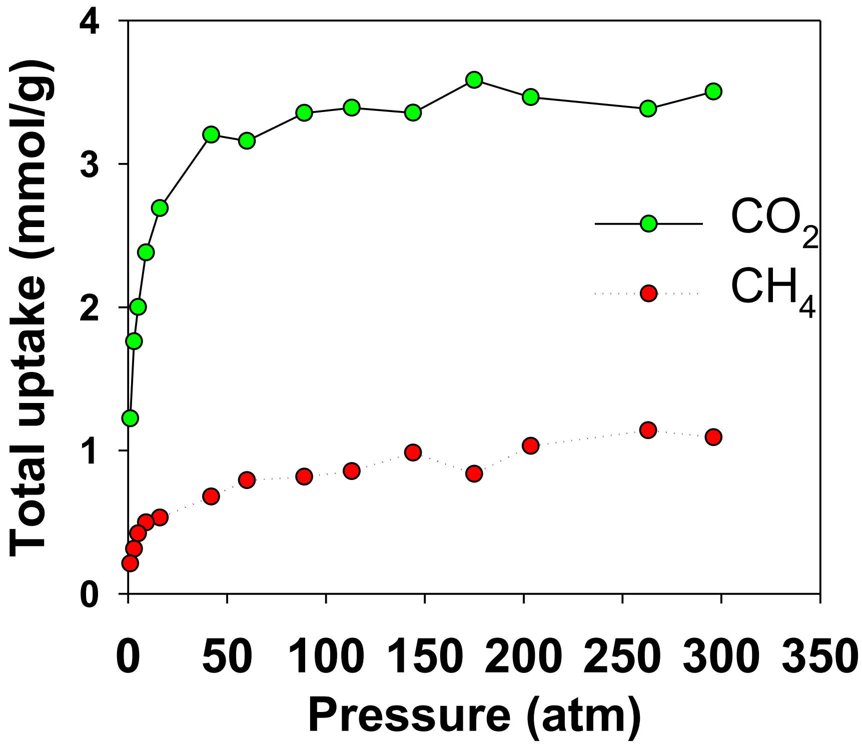
Differential retention of CO_2 and CH_4 in kerogen

Fuel 220, 1-7, 2018

Pure gas adsorption

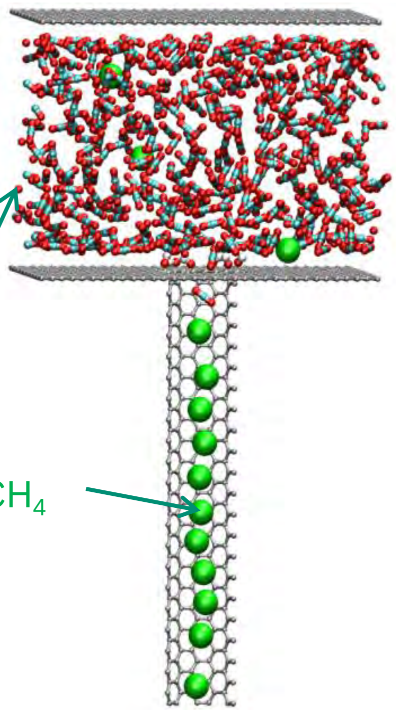


1:1 binary gas adsorption



Kerogen preferentially retains CO_2 over CH_4

Pore specific effects on enhanced gas recovery



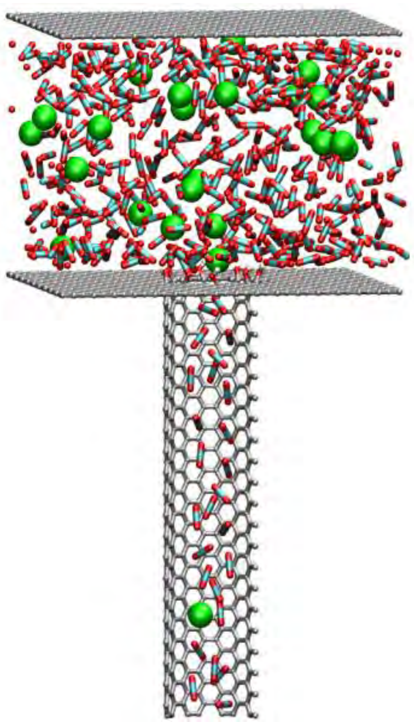
CO_2

CH_4

0.814 nm CNT

Pore is too small for the invasion of CO_2

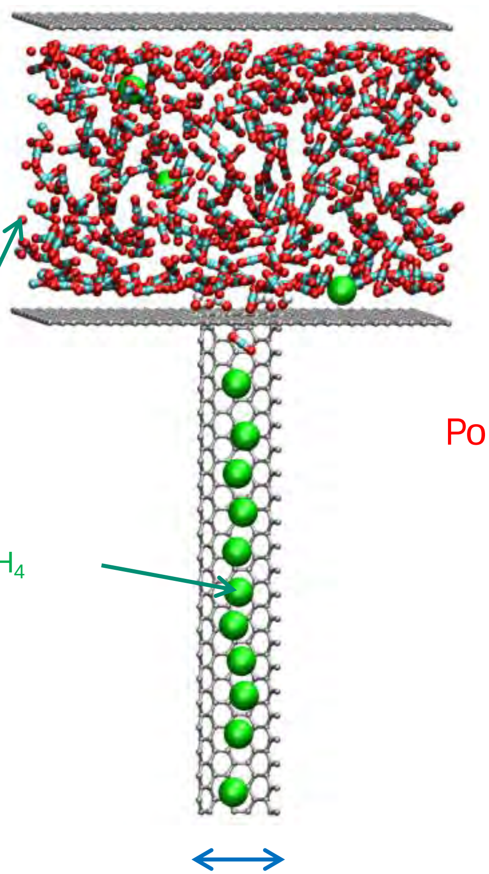
Pore size effect



1.085 nm CNT

Pore is big enough for the invasion of CO_2

Pore specific effects on enhanced gas recovery



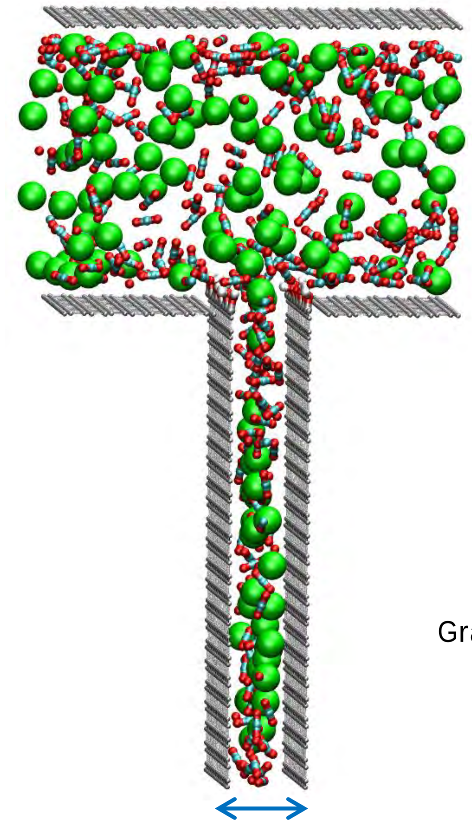
CO_2

CH_4

0.814 nm CNT

Pore is too small for the invasion of CO_2

Pore shape effect

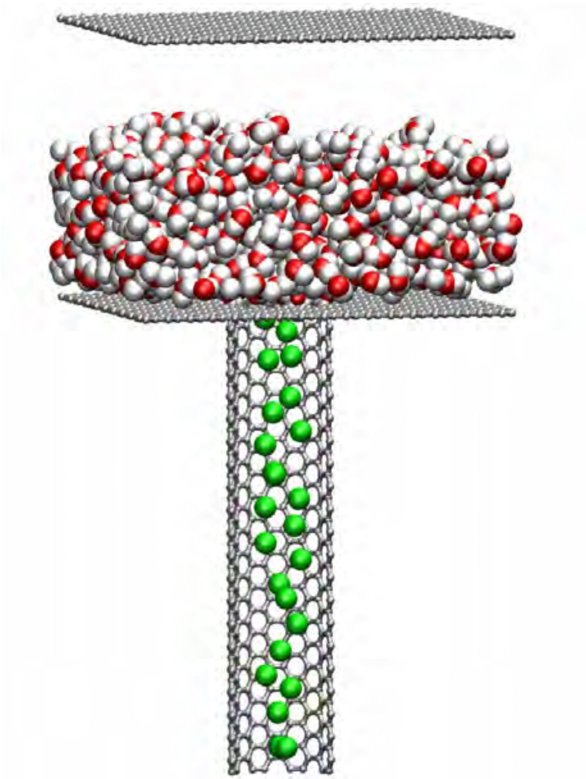


Graphene slit-pore

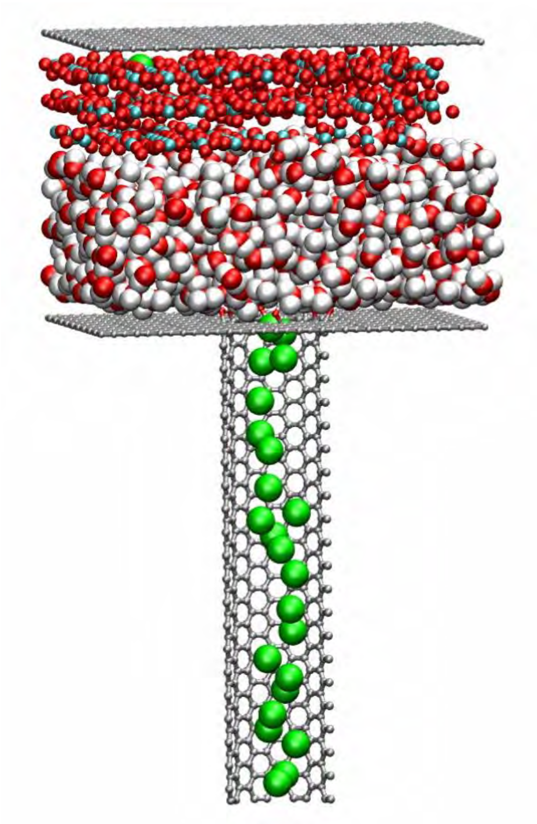
0.814 nm CNT

Methane and CO2 can diffuse in the direction parallel to the slit-pore surfaces

CH_4-CO_2-H_2O Interaction



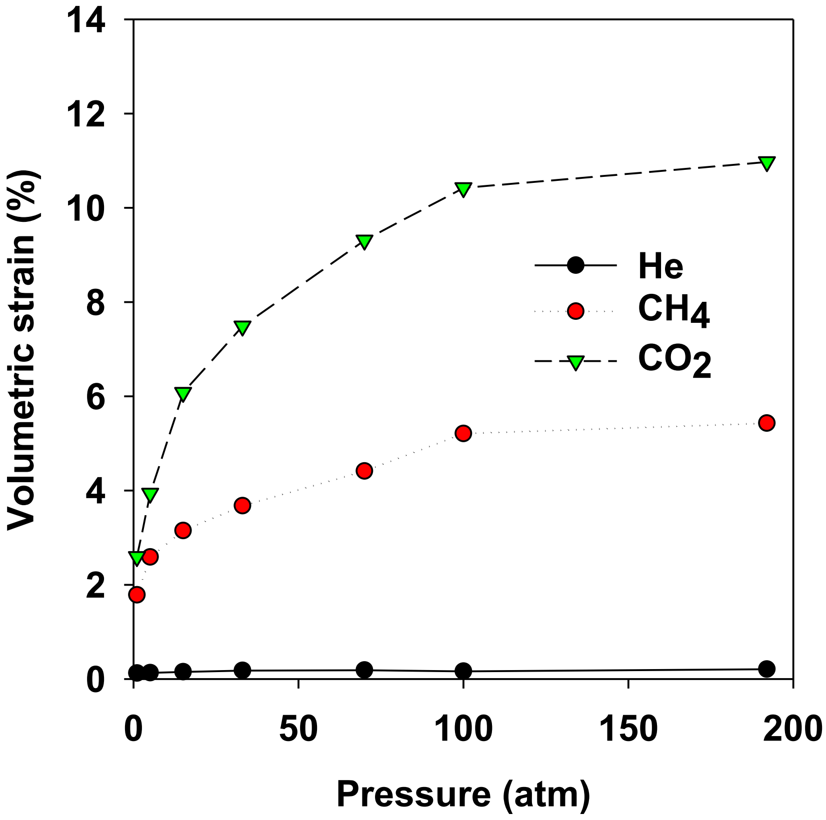
Water effect

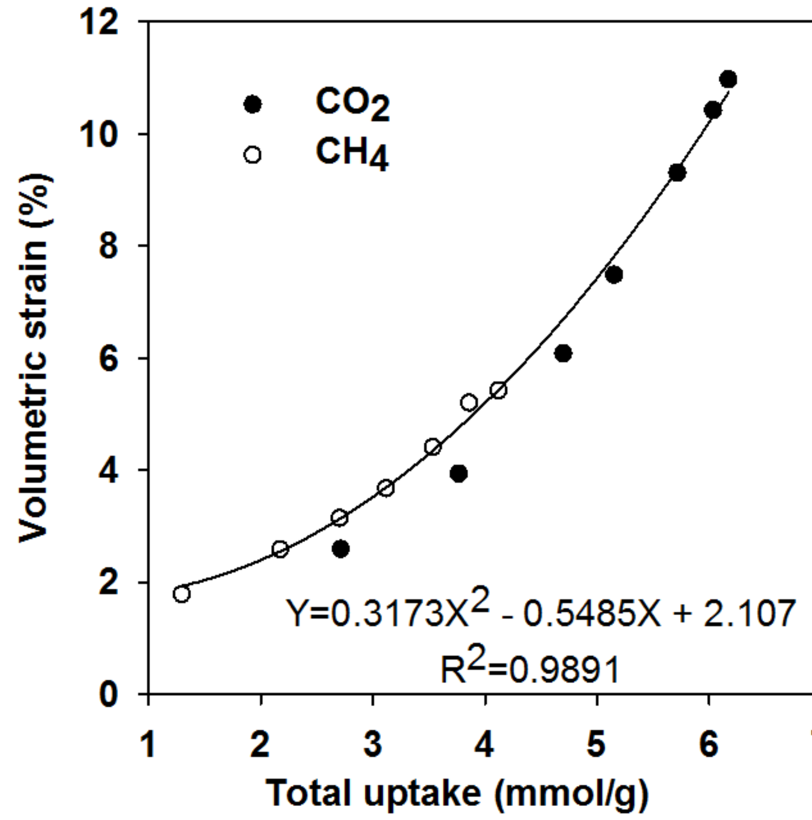


Assume that water thin films block the pore entrance.

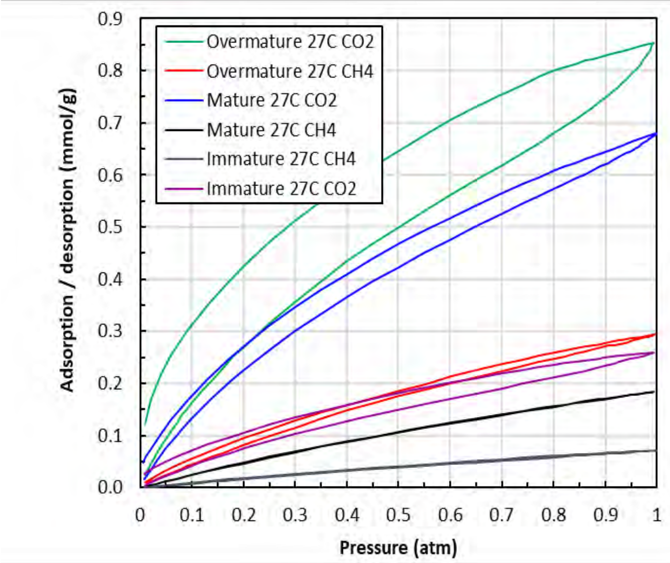
CO_2 invades through water and replaces CH_4 in the nanopore.

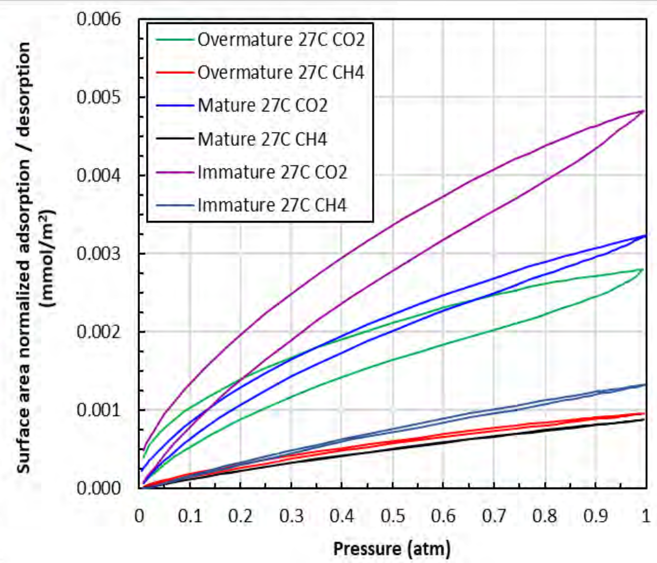
Kerogen Swelling upon Gas Sorption (PCCP, 2018)

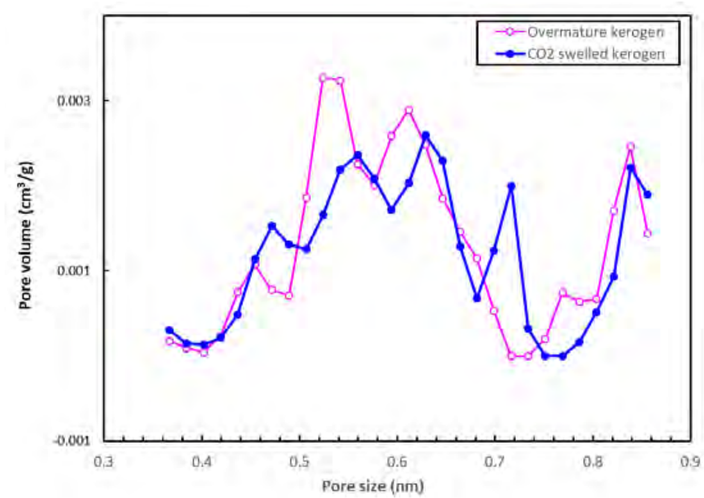


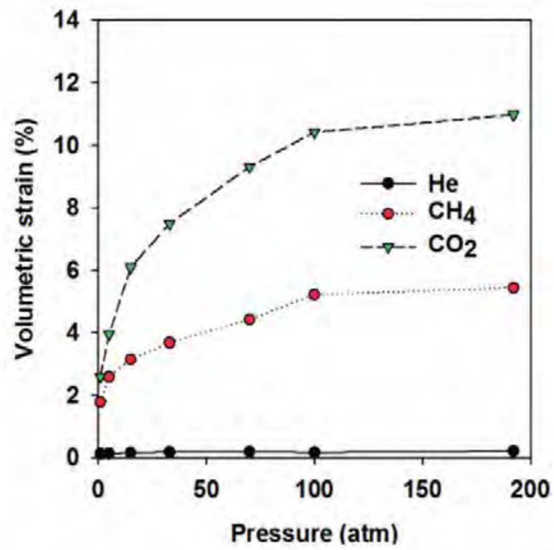


Sorption-desorption hysteresis and chemo-mechanical coupling (?)

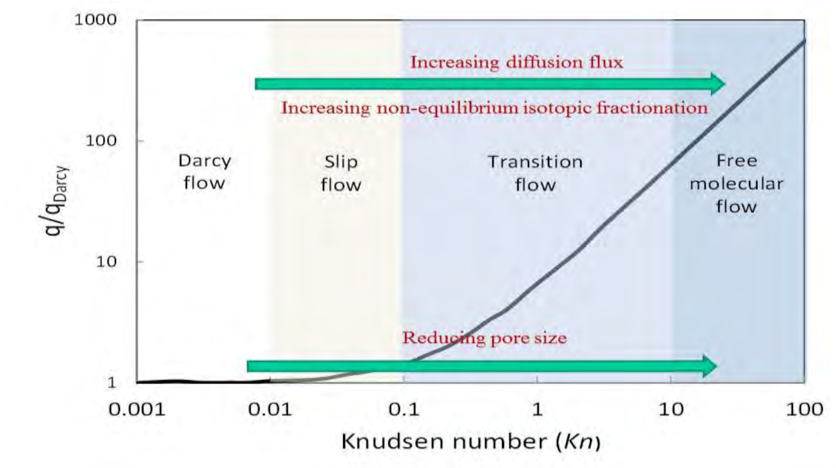


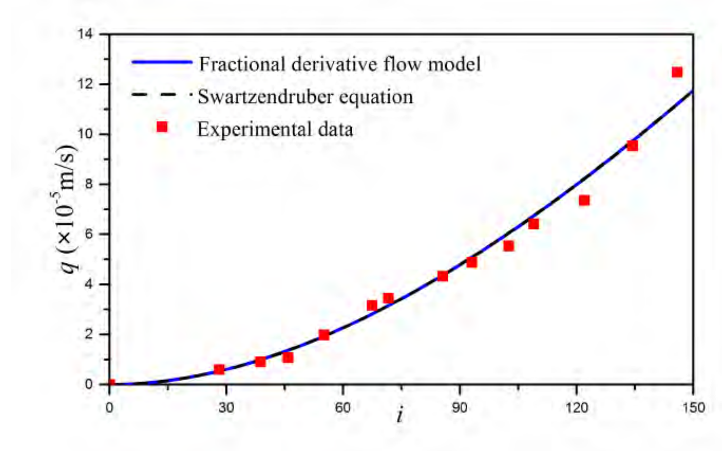






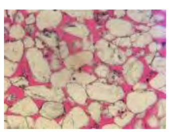
Emergent transport properties in nanopores: Isotopic fractionation

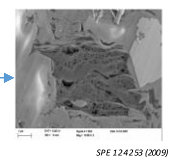




Zhou et al. (2018)

Conventional reservoir





Shale formation

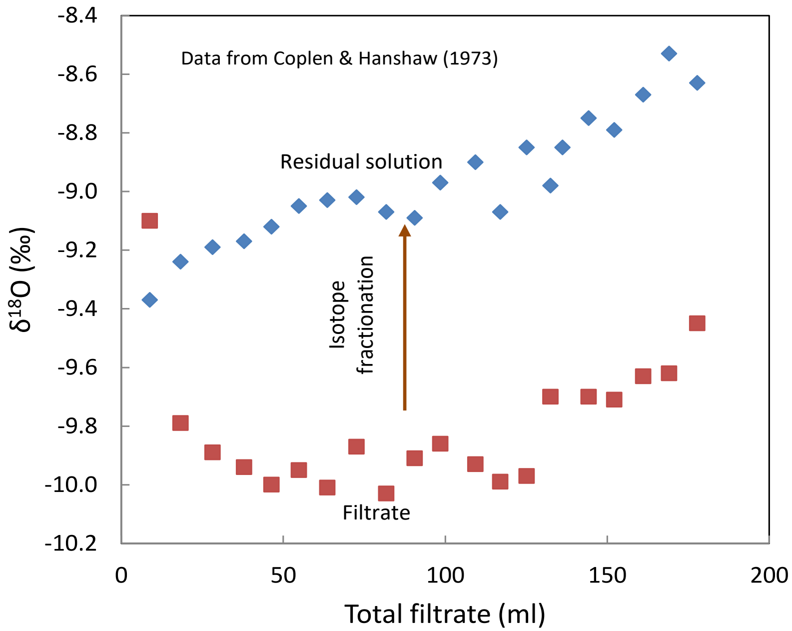
$$k_{app} = \frac{2r}{3RT}\left(\frac{8RT}{\pi M}\right)^{1/2} + \left[1 + \left(\frac{8\pi RT}{M}\right)^{1/2}\frac{\mu}{pr}\left(\frac{2}{\alpha} - 1\right)\right]\frac{cr^2}{8\mu}$$

M - Molecular weight

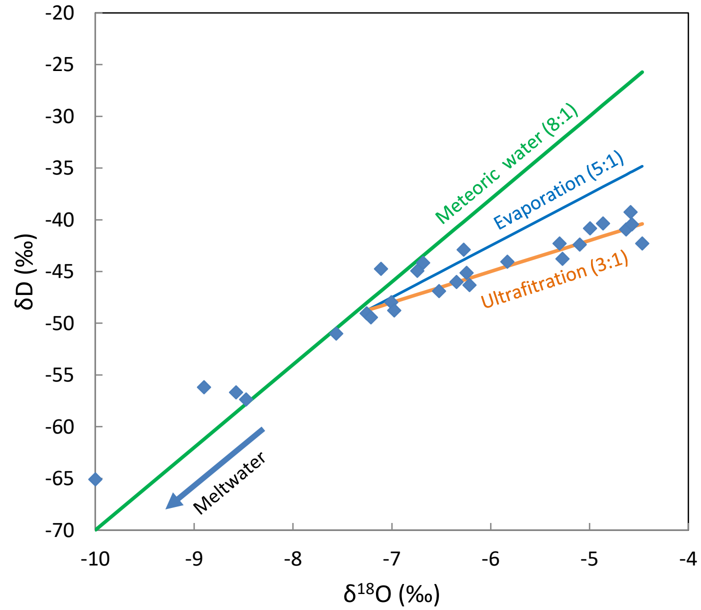
Mass dependent transport

Wang (2018)

Ultrafiltration in Nature



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



Waters extracted from Opallinus Clay at Benken (Switzerland) (Wang, 2018)

The nanometer-scale mass transfer in shale matrix has important ramifications to large-scale flow and transport processes, leading to a set of isotopic signatures that may not be observed in a conventional reservoir or highly permeable groundwater aquifer system.

Concluding remarks

Emergent properties

- Novel mineral-fluid interface chemistry may emerge when the dimension of one of the phases is reduced to nanometers.

Texture matters!

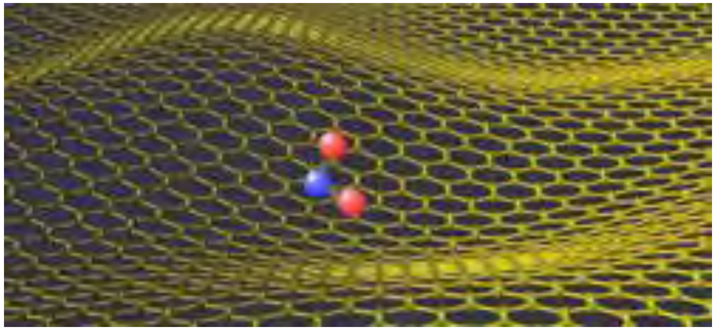
- Measurements on "isolated", unconfined surfaces may not be representative of actual geologic materials.

Perspectives

- Progress in nanoscience & technology
- Emergence of new properties (~40 identified in Wang 2014)

Geochemical implications

- New perspectives for understanding fundamental geochemical processes
  - Shale gas/oil
  - Nanofluidics and radionuclide transport in the subsurface
- Development of novel materials for environmental applications
  - New generation of buffer materials for waste isolation



Graphene sensor

(Hadlington, 2008)

Acknowledgments

Contributors:

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