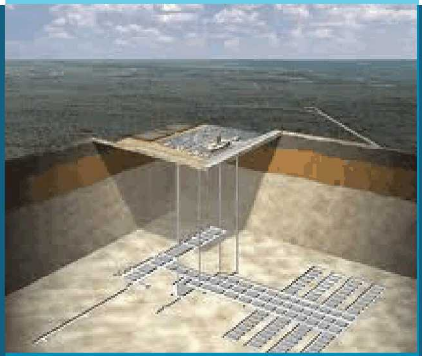
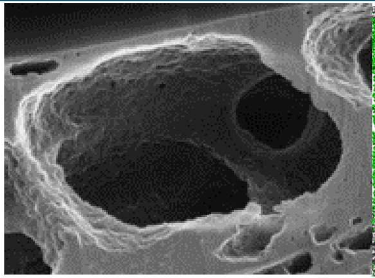
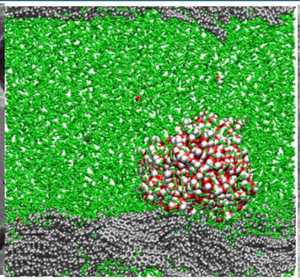
SAND2018-8681C

Understanding nanogeochemistry of radionuclide reaction and migration in subsurface environments







PRESENTED BY

Yifeng Wang

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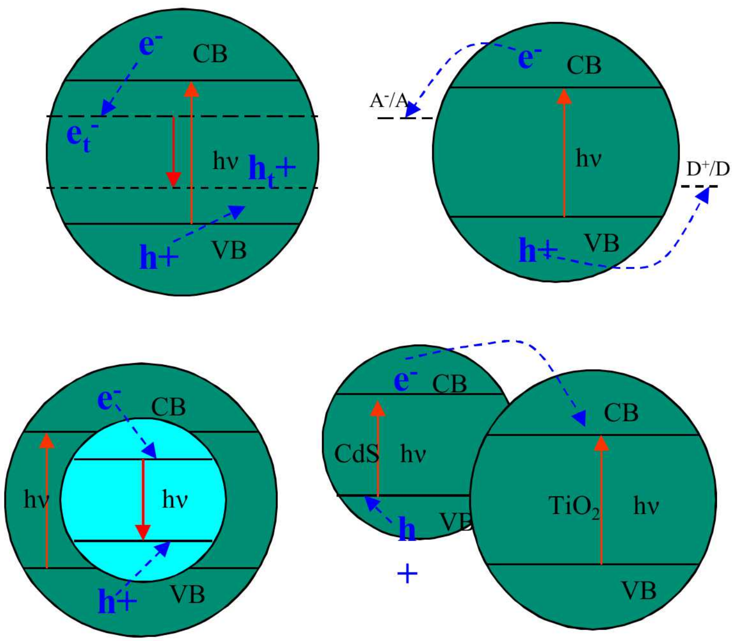
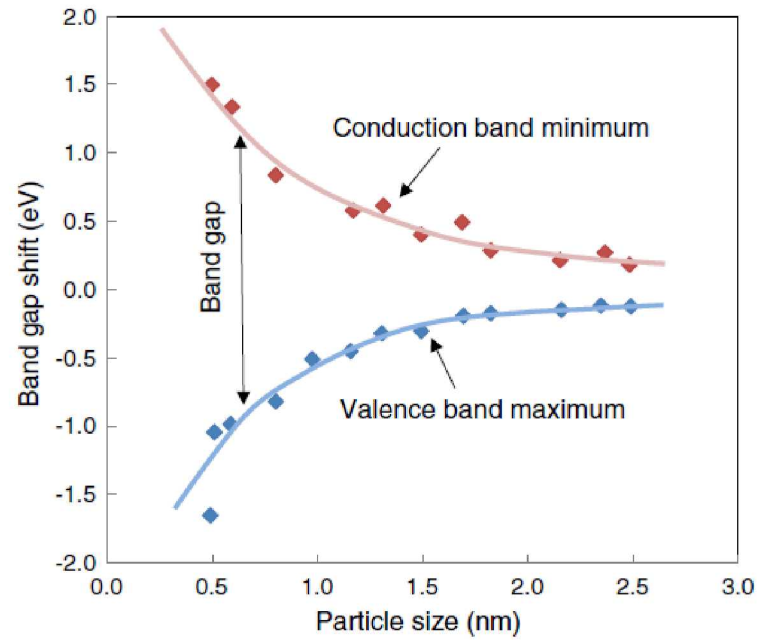
Nanoscience: Size-Dependent Material Properties

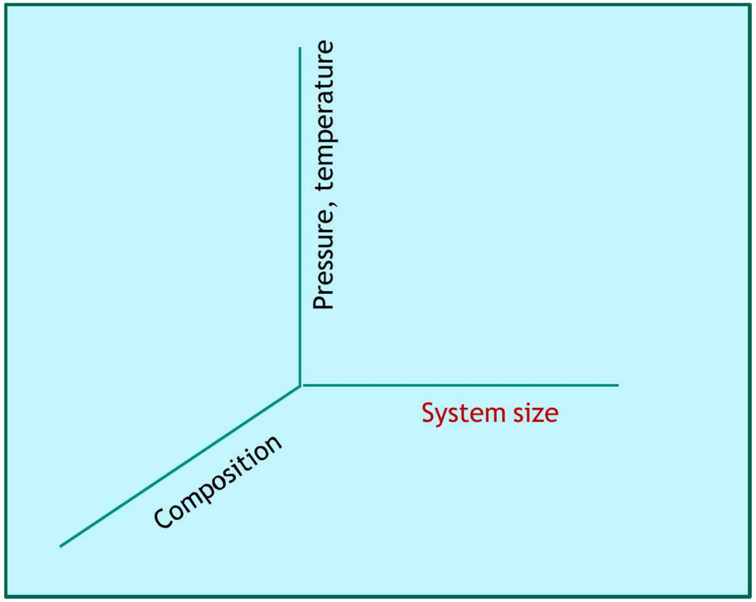


Photophysical/Photochemical Processes in Semiconductor Nanoparticles
(Roduner, 2006)



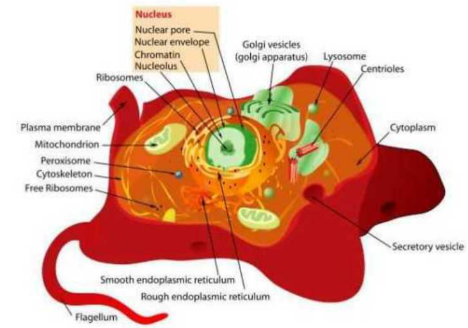
Size-dependent CdS band gap
(Lüning et al., 1999, Sold State Communication)

Nanogeochemistry

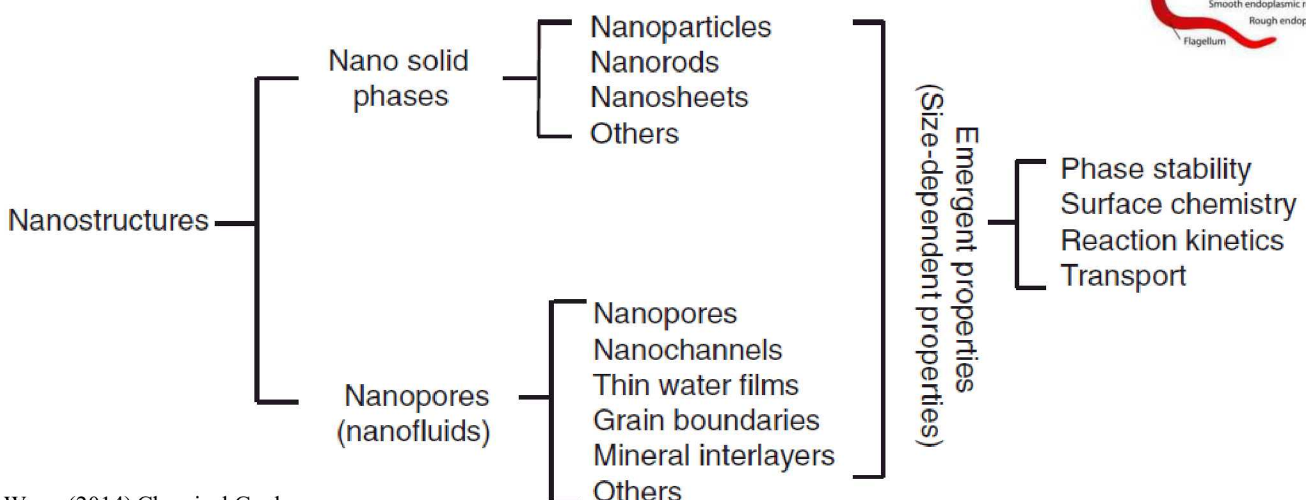


Nanogeochemistry: Understand emergent properties of geochemical systems under nano-scale structural constraints or organizations.

Rule of thumb: **<100 nm**

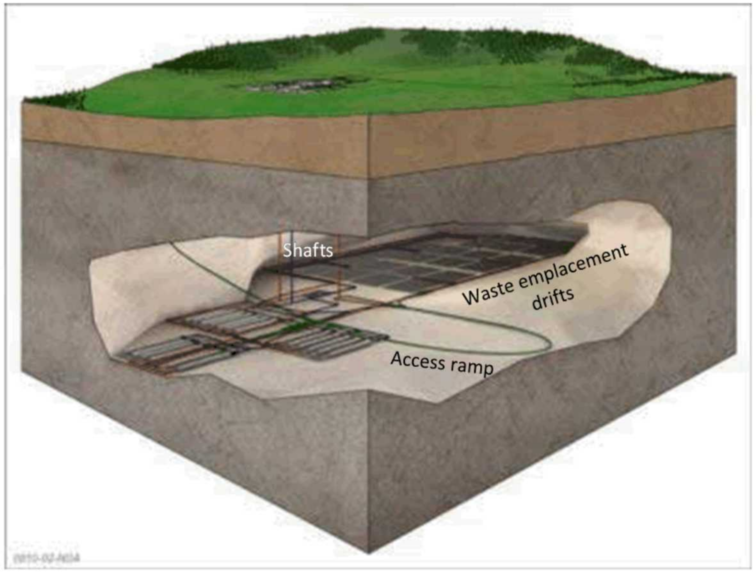


http://tamiport.hubpages.com/hub/Cell-Biology-Differences-Between-Prokaryotic-and-Eukaryotic-Cells#slide2150310

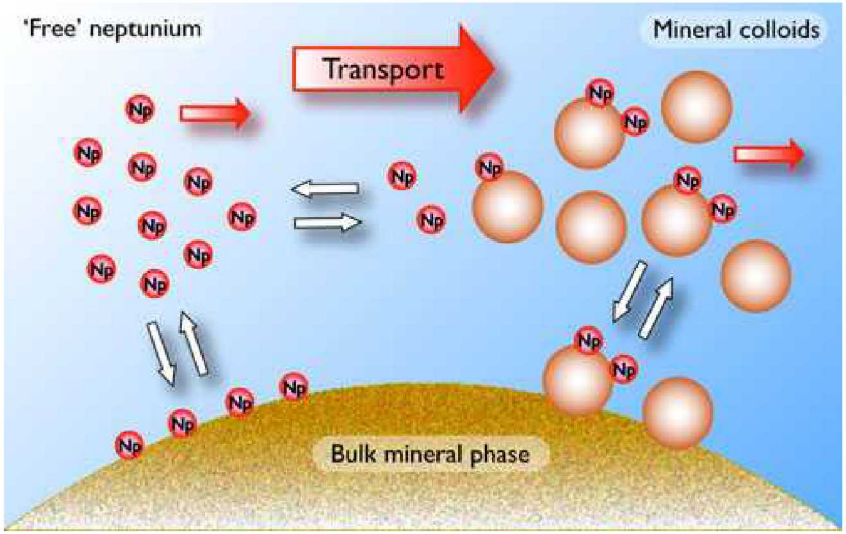


Wang (2014) Chemical Geology

Colloid-facilitated radionuclide transport



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

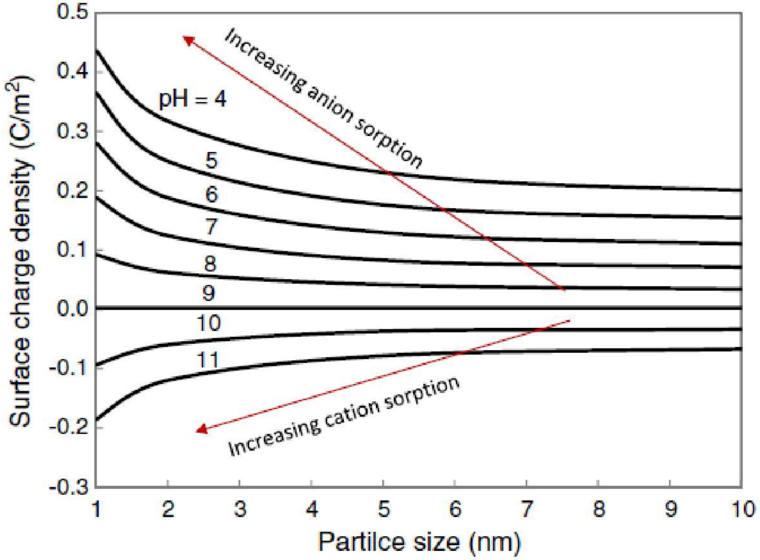


https://eesa.lbl.gov/radioactive-contamination-over-geologic-time/

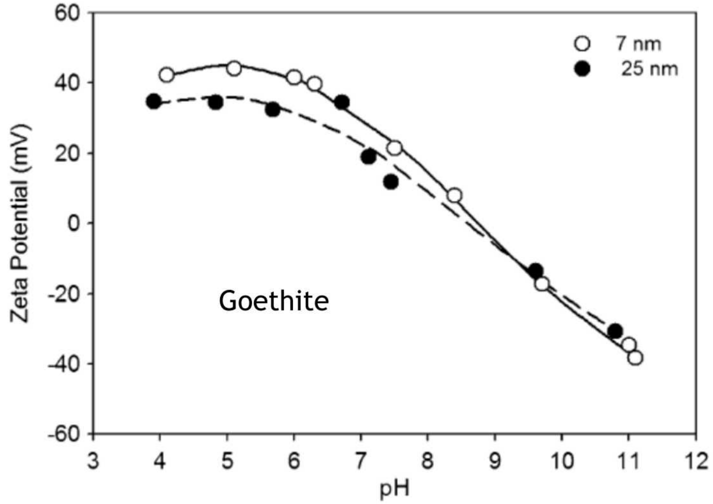
Key radionuclides:
Pu-239, Th-230, Am-241 – Strong interaction (colloids)
U-238, Np-237 – Moderate interaction
I-129, Tc-99 – Weak interaction (anions)

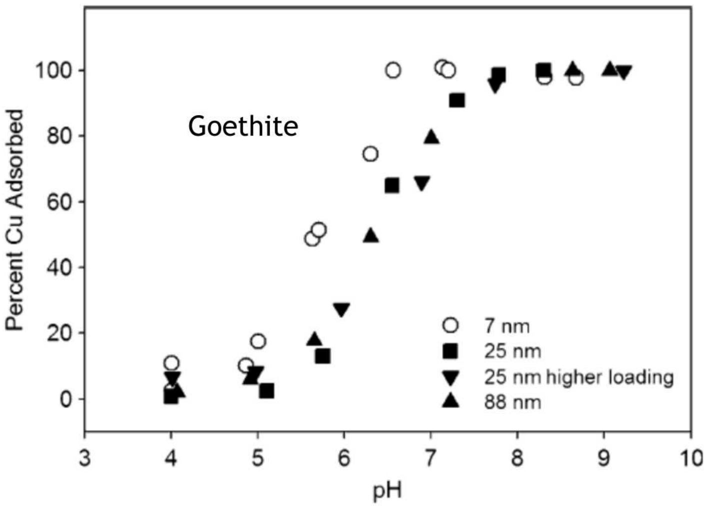
Colloids: ~1 - 1000 nm
Nanoparticles: ~1 - 100 nm

Surface charge and sorption capability of nanoparticles



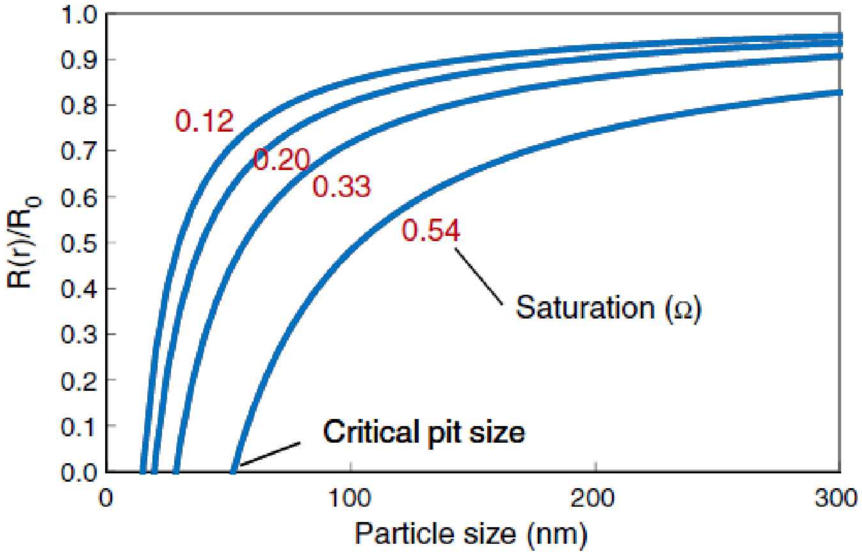
Surface charge density predicted by Monte-Carlo simulations for goethite nanoparticles (Abbas et al., 2008)

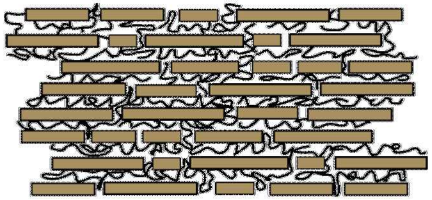


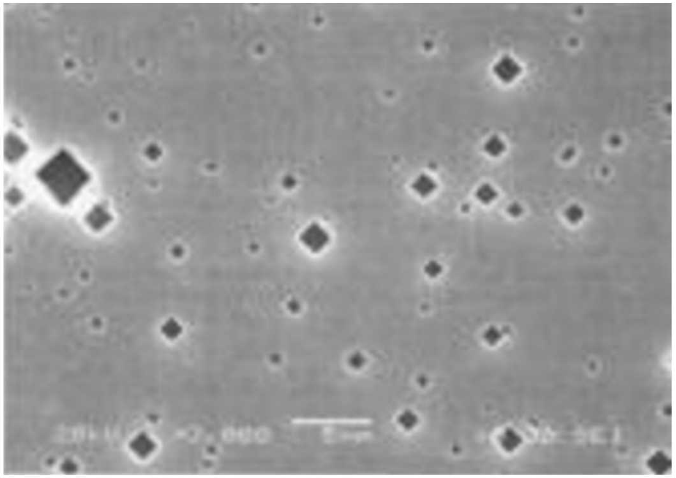


Madden et al., 2006, GCA

Self-inhibiting mechanism for nanoparticle dissolution





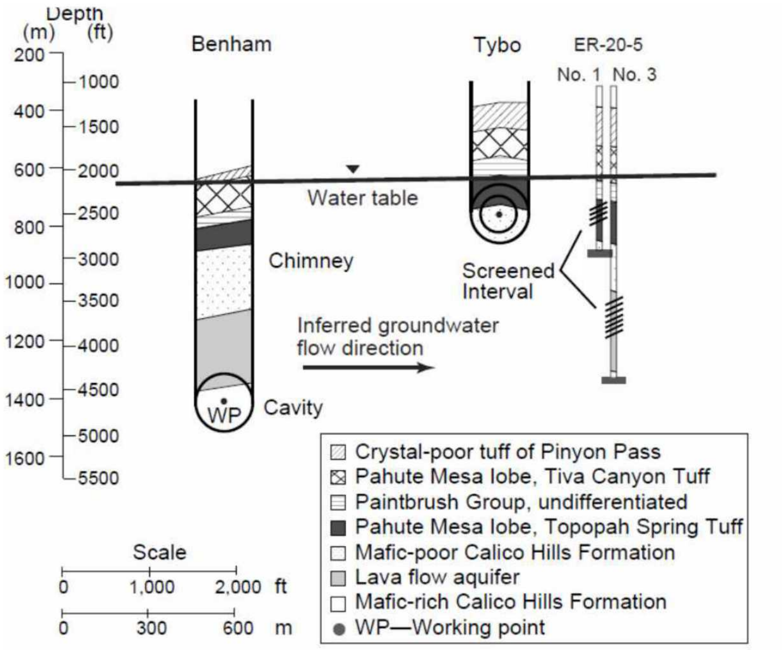


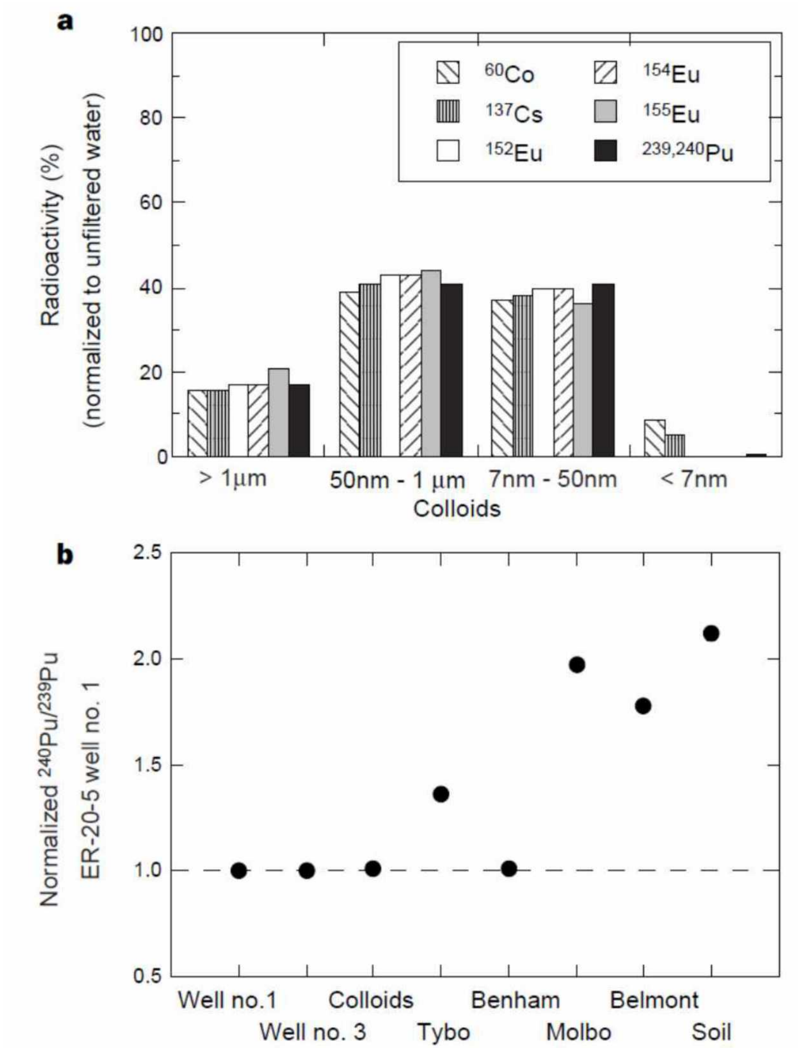
http://jes.ecsdl.org/content/150/9/B433/F1.large.jpg

Self-inhibiting mechanism (Tang et al., 2004)

- Resistance to dissolution
- Persistence of true colloids

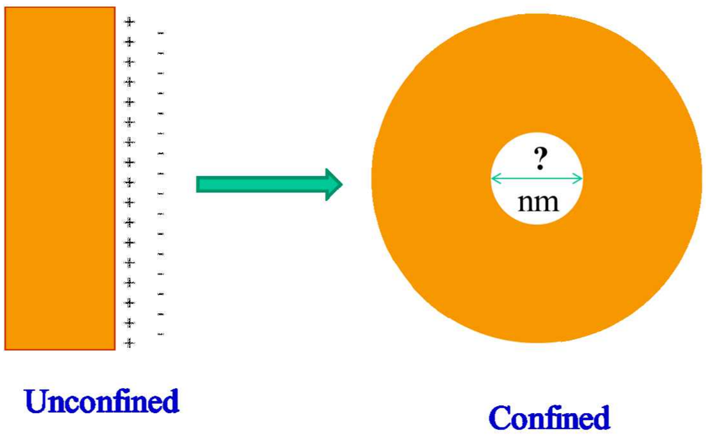
Long distance colloid-facilitated transport?

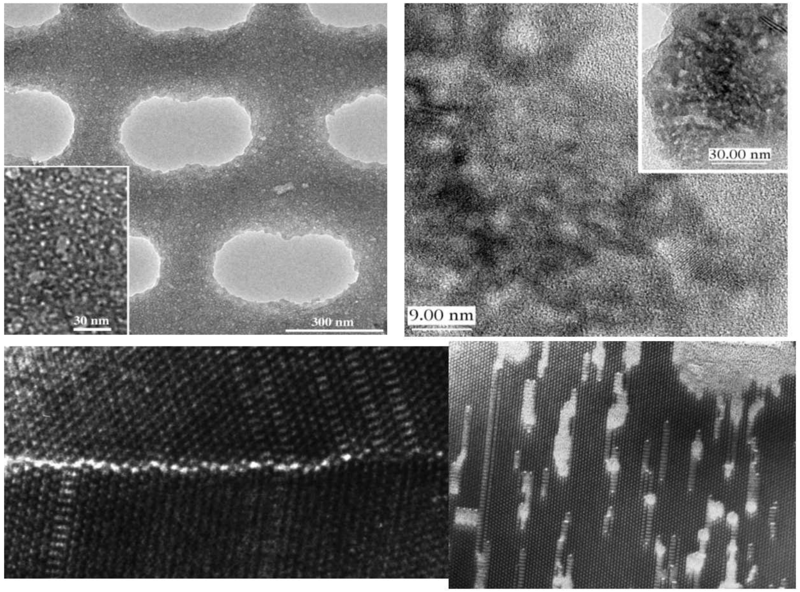




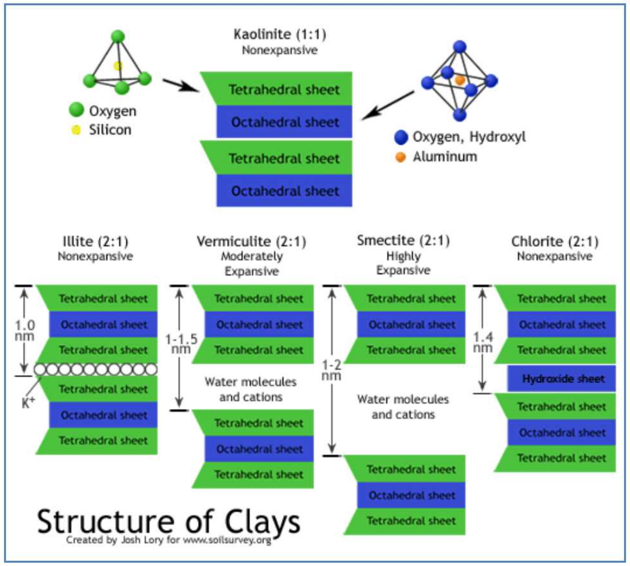
Kersting et al. (1999) Nature

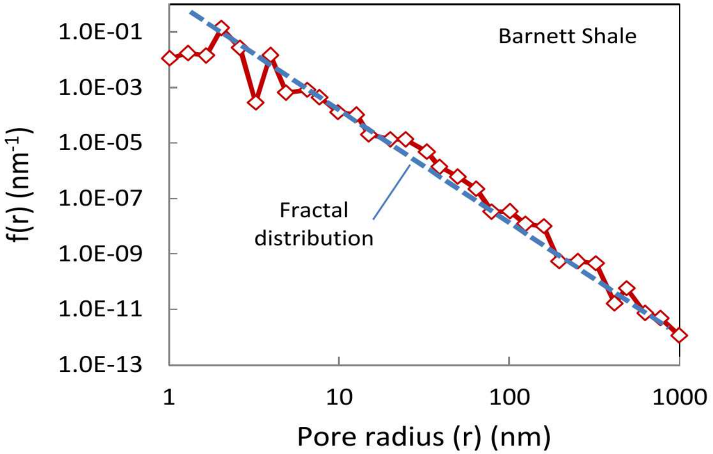
Effects of Nanopore Confinement





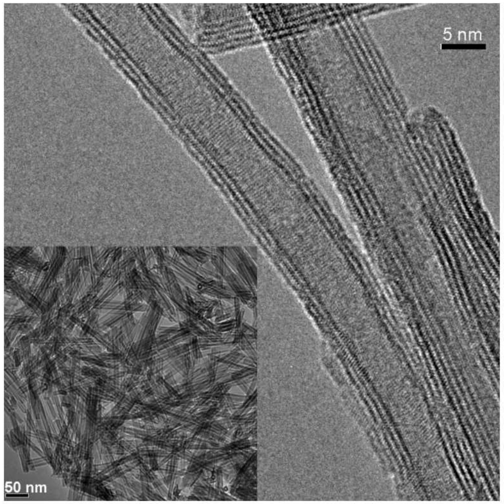
Wang et al., 2003, Geology

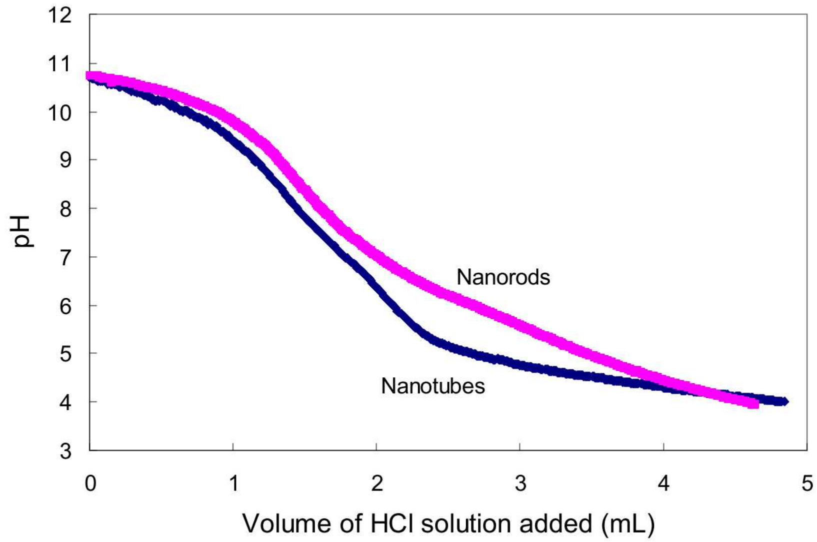


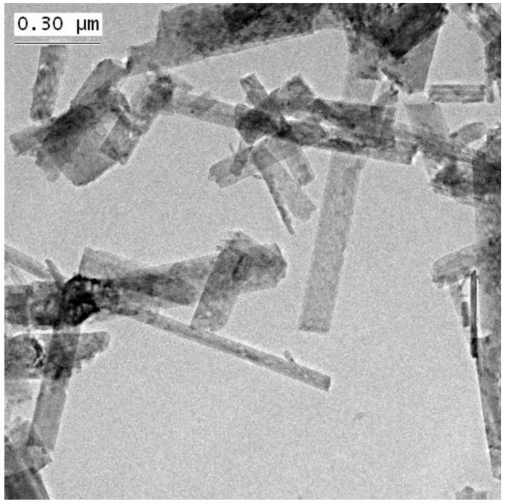


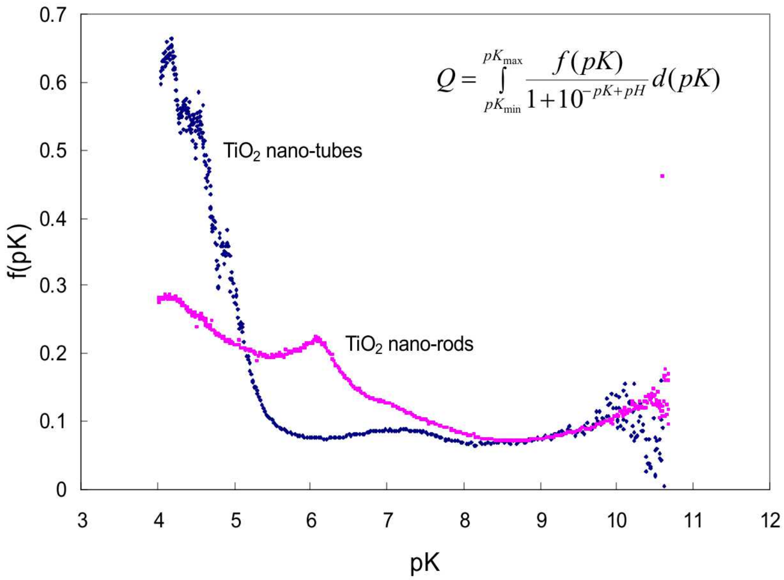
Clarkson et al. (2012)

Model Systems for Studying Nanopore Confinement



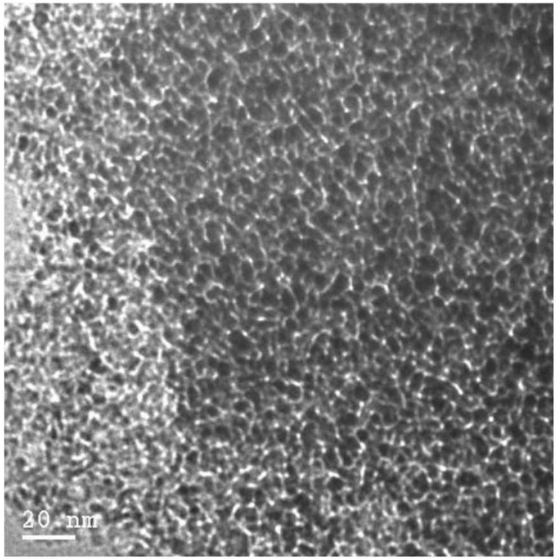


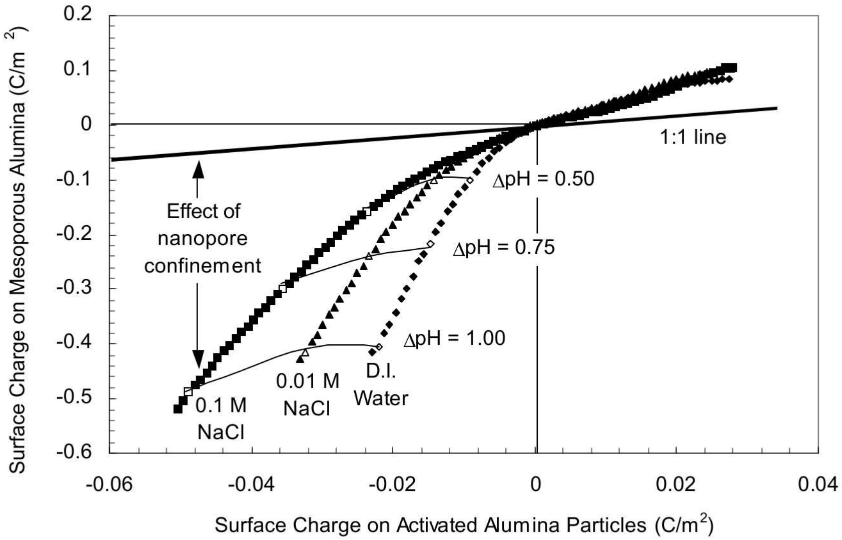


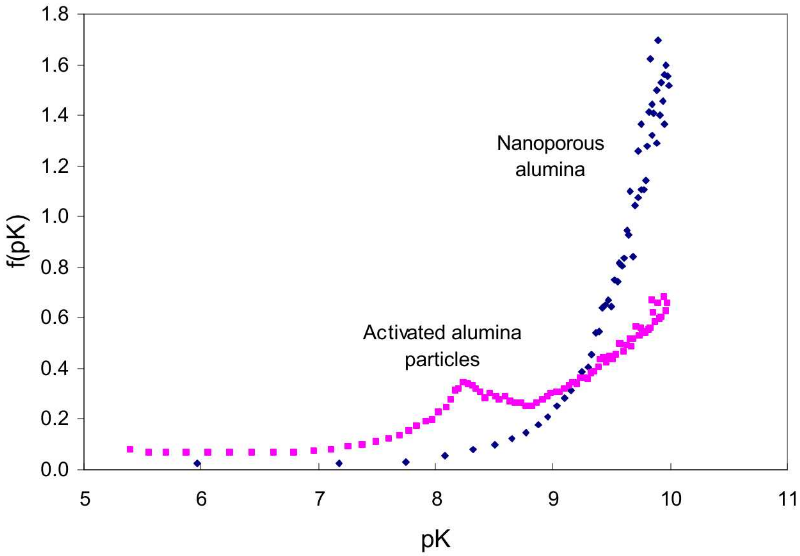


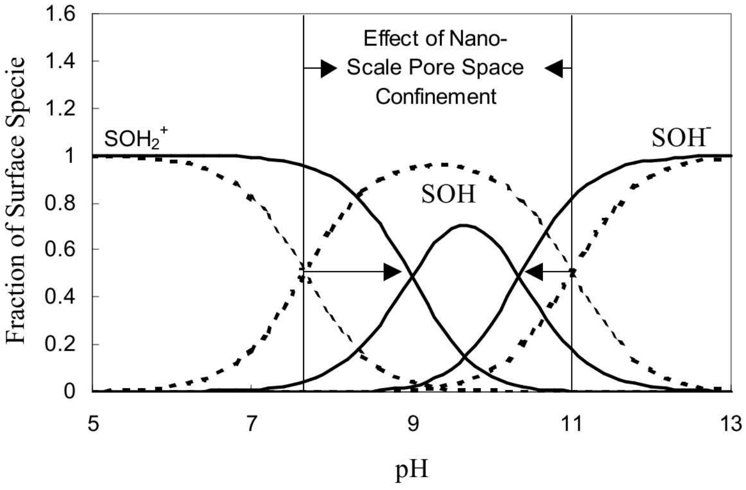
Wang et al. (2008)

Model Systems for Studying Nanopore Confinement (cont.)



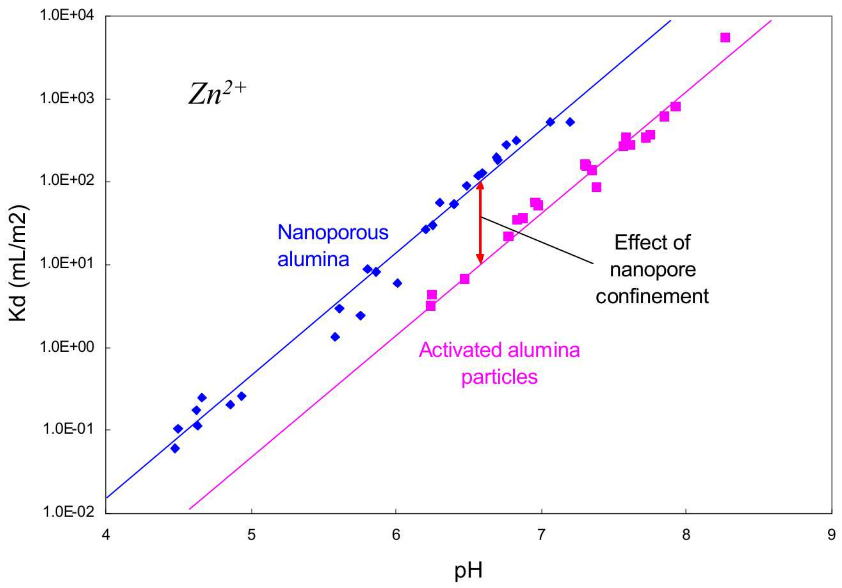


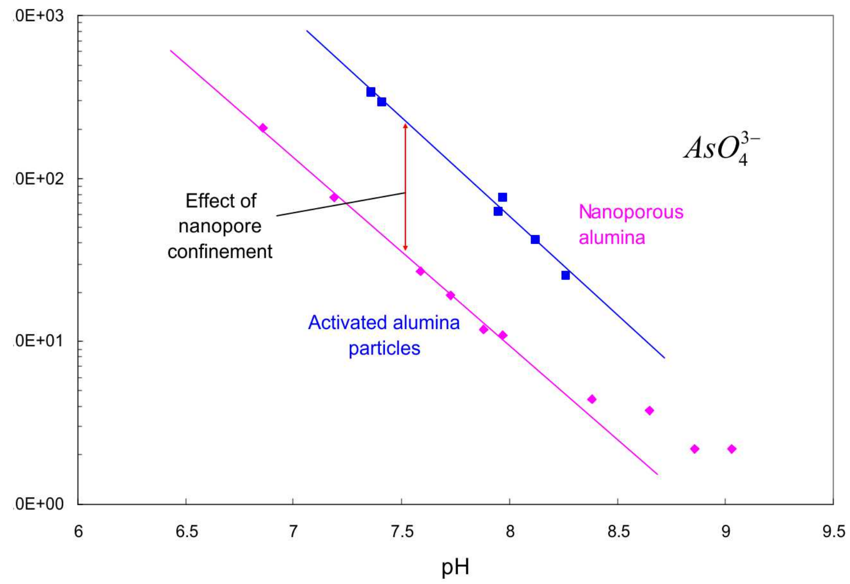




Wang et al., 2002, JCIS; 2003, Geology

Nanoconfinement and Ion Sorption

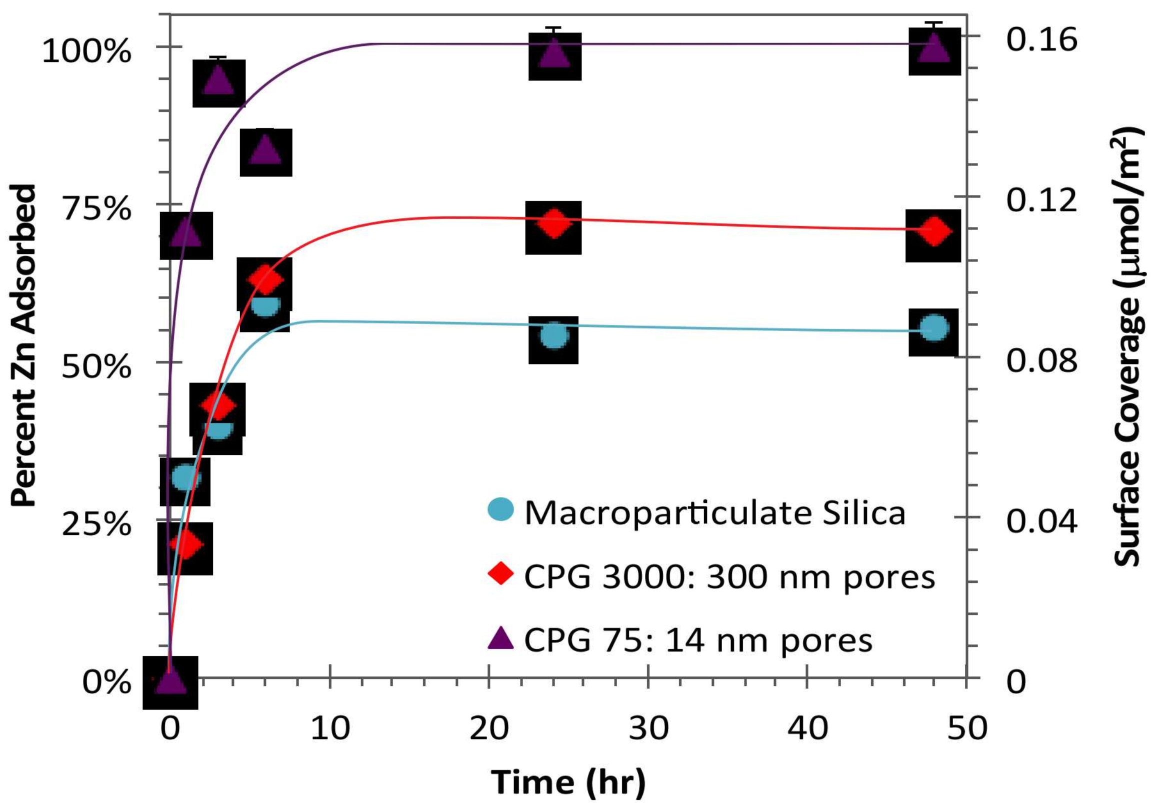




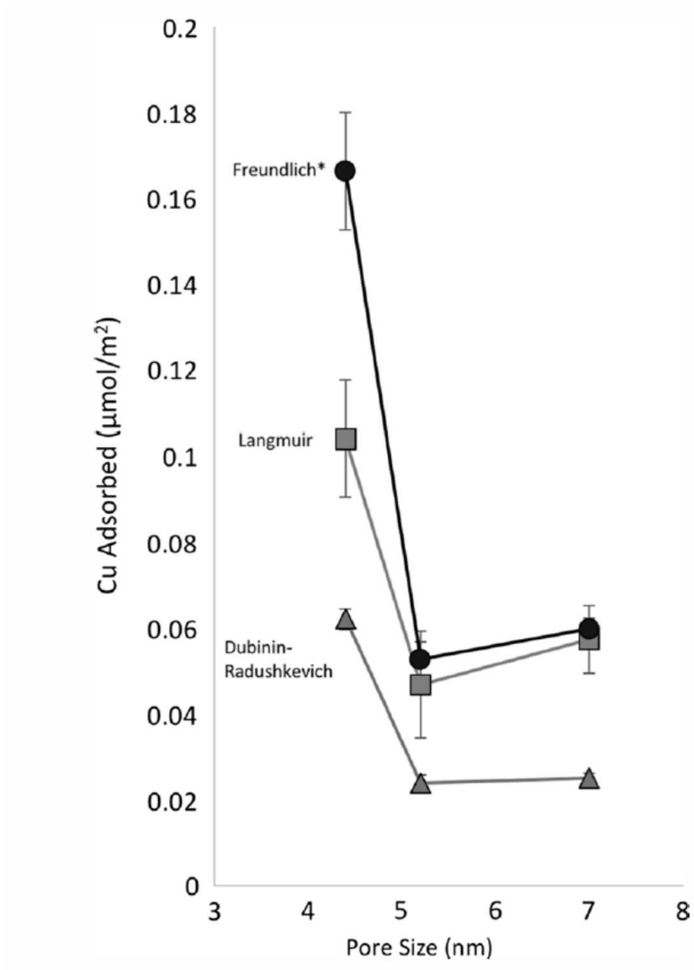
Nanopore confinement enhances ion sorption onto a solid-water interface for both cations and anions.

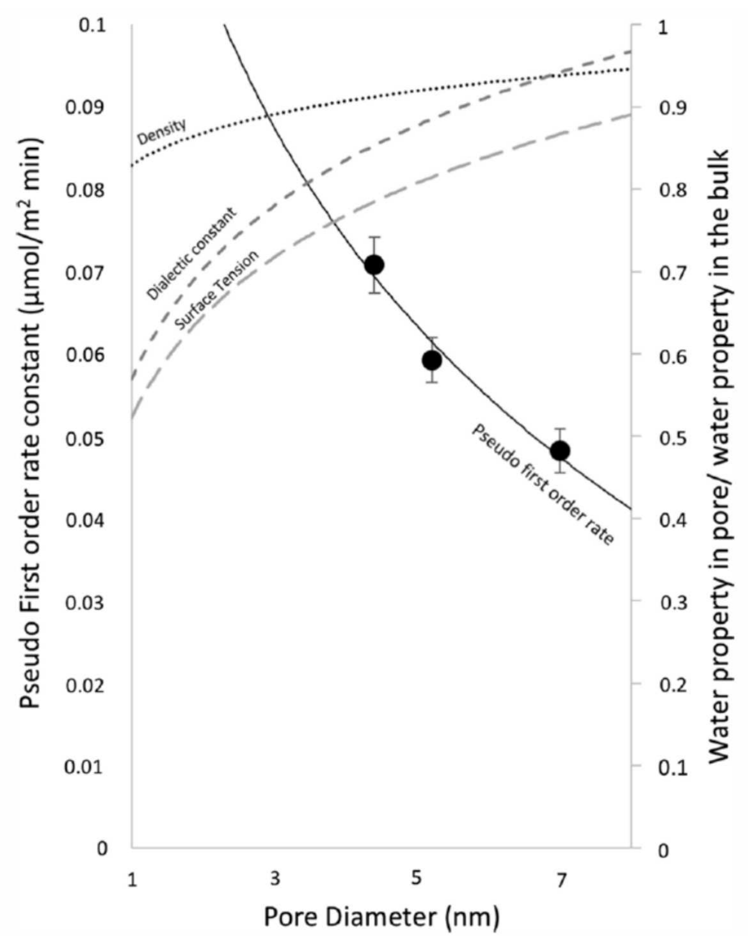
Wang et al., 2003, Mat. Res. Soc. Symp. Proc.; 2003, Geology

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

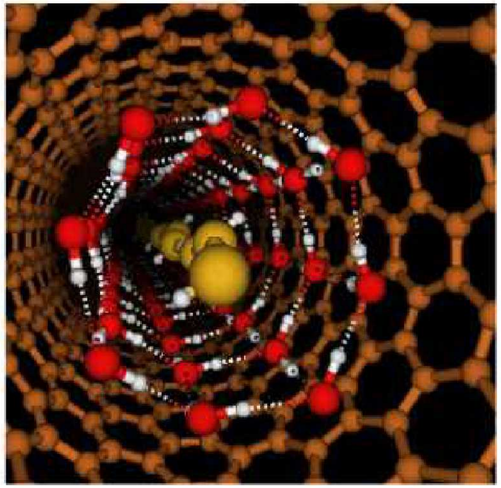


Cu(II) sorption onto mesoporous silica (Knight et al., 2018)

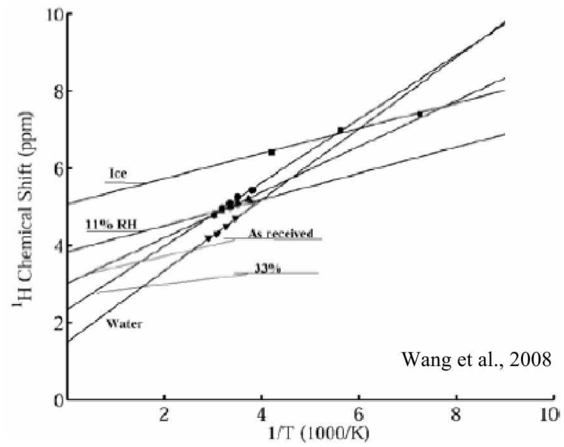


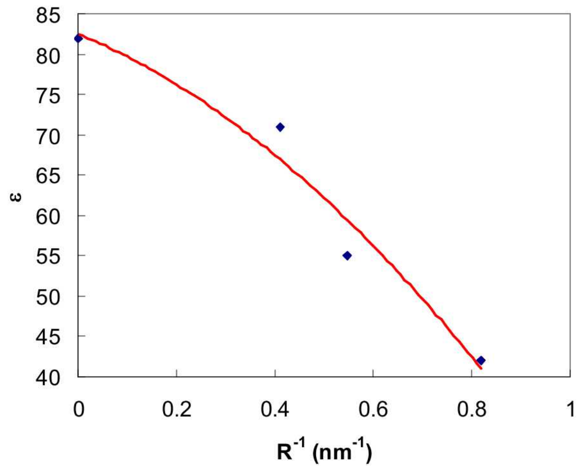


Effect of Nanopore Confinement on Water



Kolesnikov et al., 2004





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

Postulations:

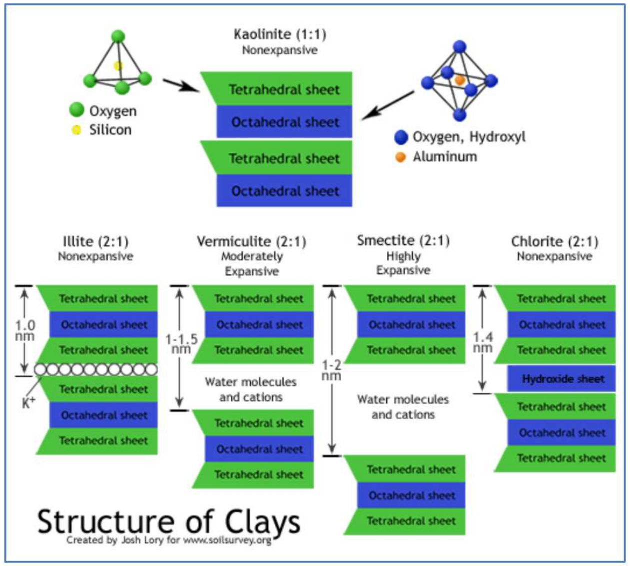
Water molecules in nanopores are more restrained.

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

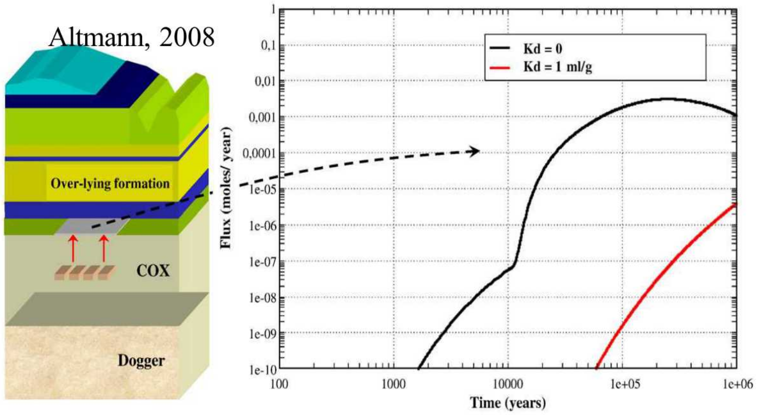
$M(H_2O)_n^{z+} = M^{z+} + nH_2O$ inner sphere

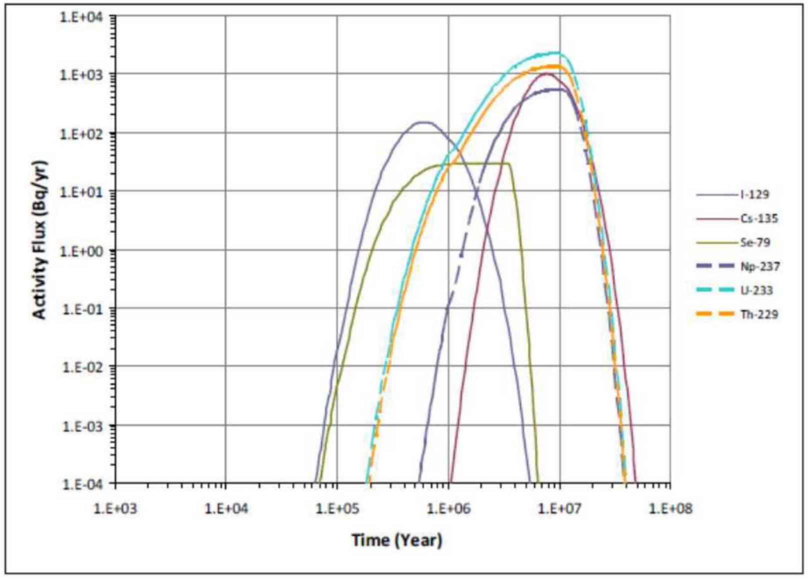
$Na^+ + Cl^- = NaCl^0$ ion pairing

Can an anion such as iodide get into interlayers of clay materials?



Clay Mineral	Column K_D Value (mL/g)	Batch K_D Value (mL/g)	Ref.
Opalinus (Illite)	0.008-0.02		Van Loon et al., 2003
Montmorillonite	0.57		Sato et al., 1992
Callovo-Oxfordian (Interstratified illite/smectite)		0.15-0.37	Bazer-Bachi et al., 2006
Illite		27.7	Kaplan et al., 2000
Montmorillonite		-0.33	Kaplan et al., 2000





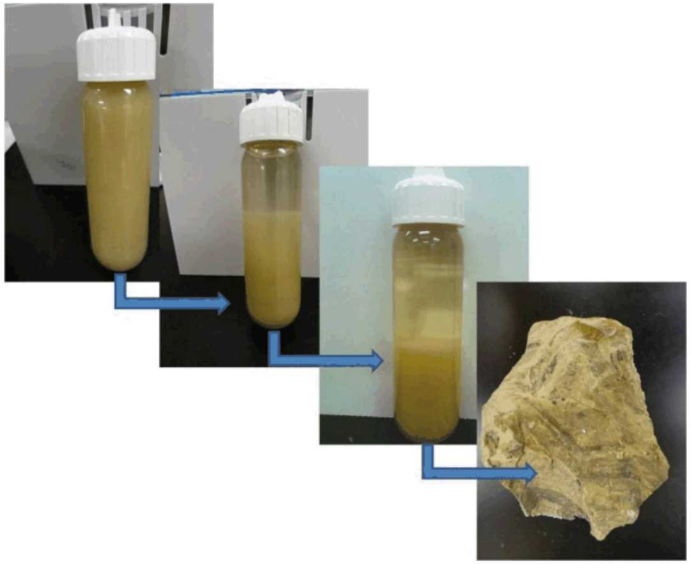
Generic clay repository

Structure-function study of clay materials

7 clays under consideration:

All clays obtained from the clay bank repository (Purdue Univ.)

- Kaolinite
- Ripidolite
- Illite
- Illite/Smectite
- Montmorillonite
- Palygorskite
- Sepiolite



Miller et al. (2015)

Sorption experiments:

- **N_2 BET (external surface)**
- **Methylene Blue (MB) (total surface including interlayer)**
  - Na-exchanged clays
  - Variable amounts of MB were added until clay surface was saturated
- **$BaCl_2$ Exchange (total surface including interlayer)**
  - Excess of barium displaces native cations
  - Measure native cation release
- **Iodide**
  - Solid:Liquid ratio: 100g/L
  - No specific pH control; 'natural' pH of clay
  - Seven day reaction time

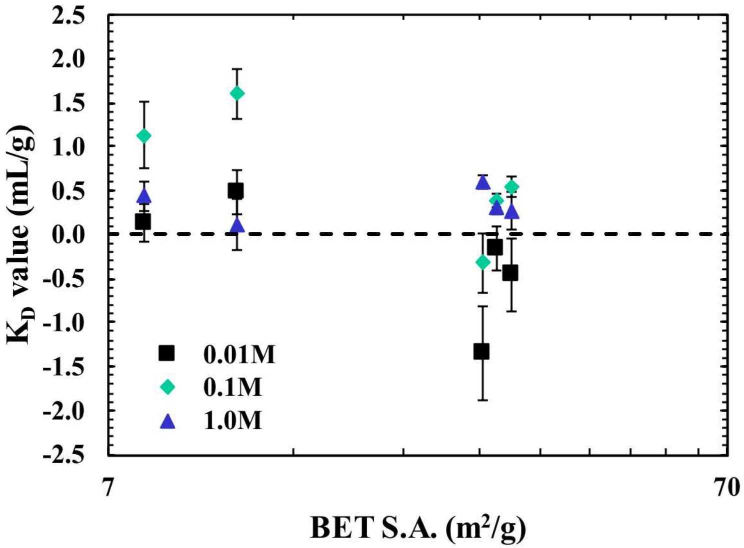
Concentration (M)	NaCl	NaBr	KCl
1.0	X		
0.1	X	X	X
0.01	X		

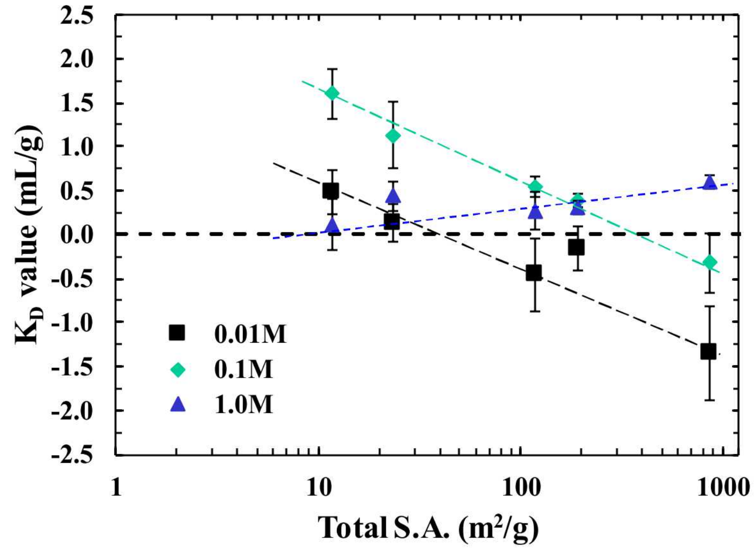
Iodide uptake is dependent on ionic composition of swamping electrolyte.

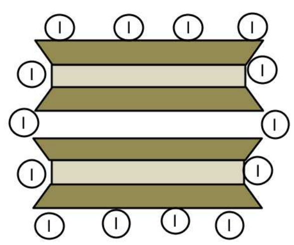
			CEC meq/100g	K_D [mL/g] (Std. Dev.)		
				NaCl	NaBr	KCl
Layered	Kaolinite		4.61	1.61 (0.28)	0.02 (0.63)	-0.01 (0.22)
Layered	Ripidolite		6.03	1.13 (0.38)	-0.16 (0.72)	-0.31 (0.17)
Layered	Illite		27.61	0.54 (0.12)	0.13 (0.002)	-0.50 (0.24)
Layered	Illite.Smectite		30.39	0.38 (0.08)	-0.01 (0.11)	-0.49 (0.11)
Layered	Montmorillonite		151.92	-0.32 (0.35)	-0.58 (0.07)	-1.69 (0.90)
Fibrous	Sepiolite		8.98	0.01 (0.28)	0.79 (0.14)	0.11 (0.30)
Fibrous	Palygorskite		29.22	0.24 (0.30)	1.26 (0.05)	0.99 (0.17)

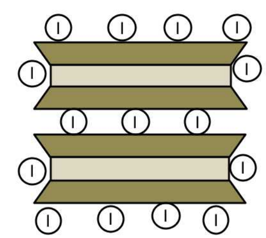
All electrolytes at 0.1M

K_D values trend with total surface area, suggesting interactions with negatively charged surfaces.

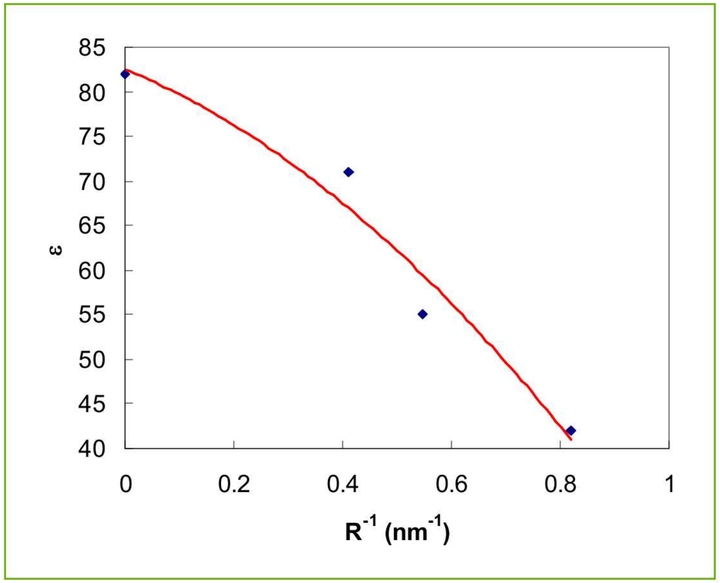




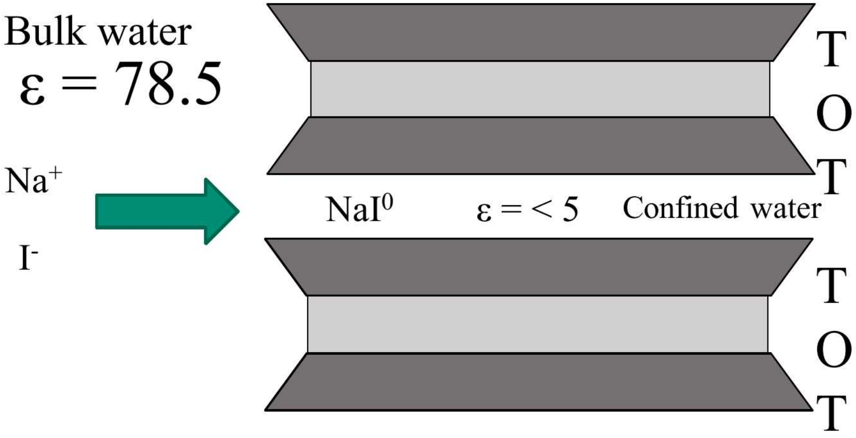




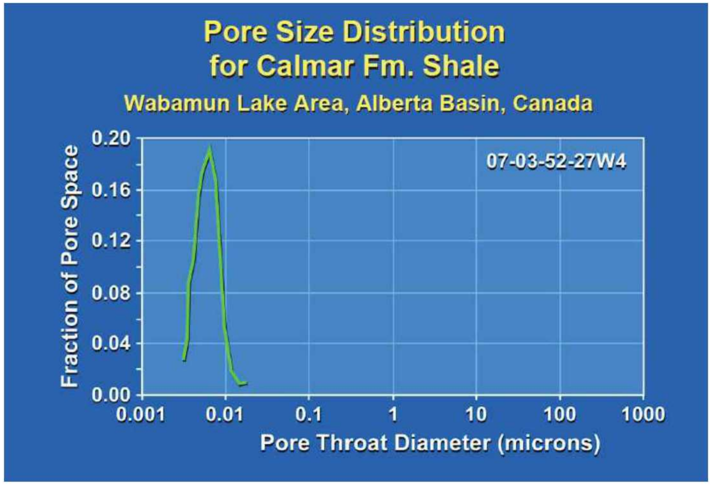
Data is consistent with ion pair formation caused by reduced dielectric constant of confined water.



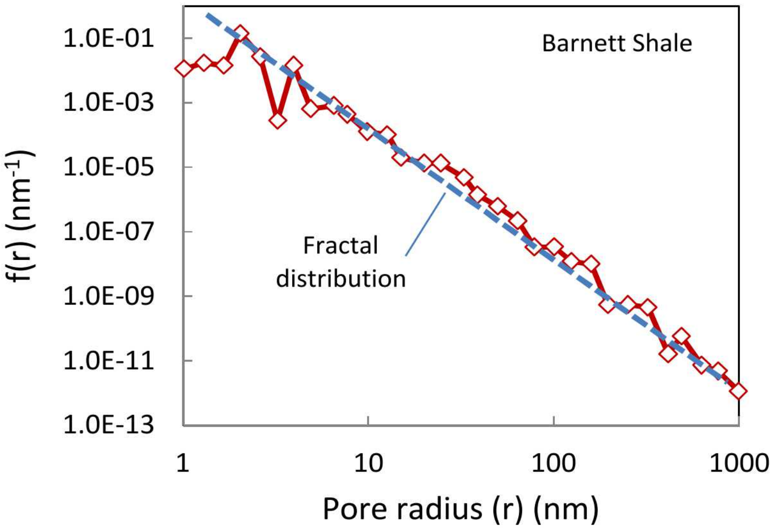
Senapati & Chandra, 2001, J. Phys. Chem.



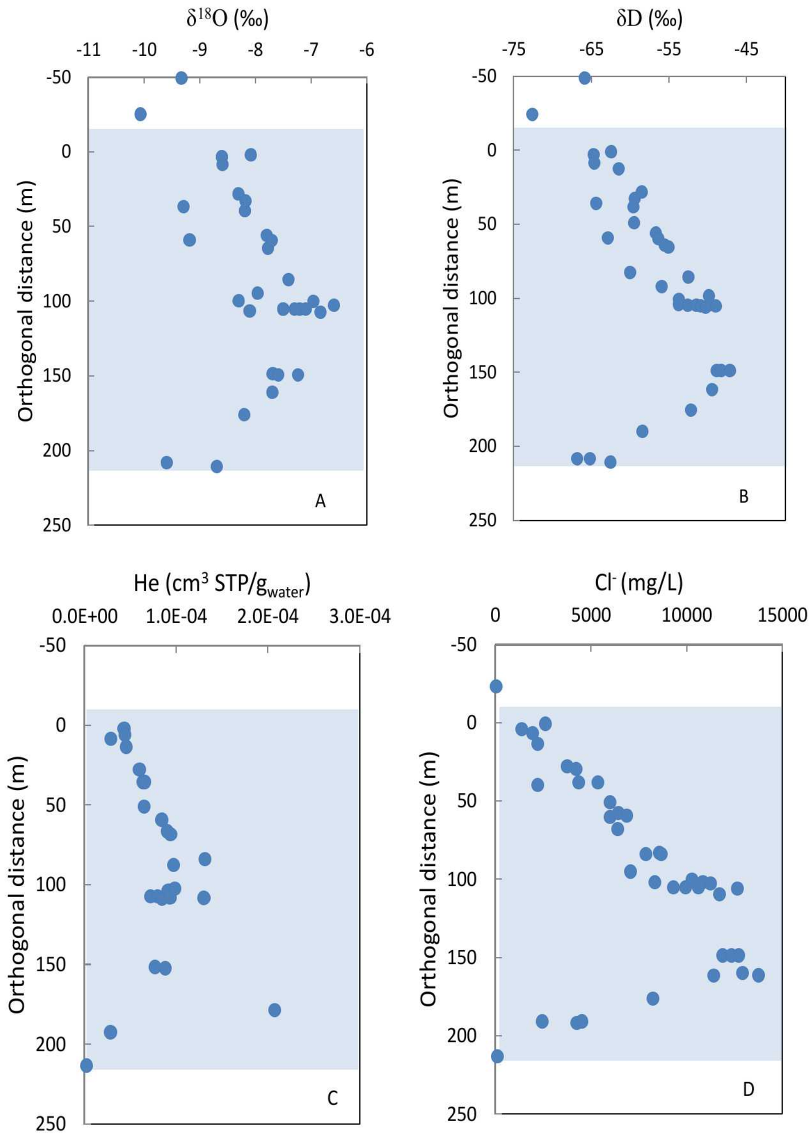
Shale as a nanocomposite material



Bachu & Bennion (2006)



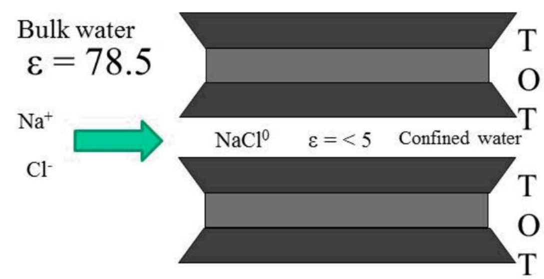
Clarkson et al. (2012)



Tracer measurements at Mont Terri site (Switzerland)

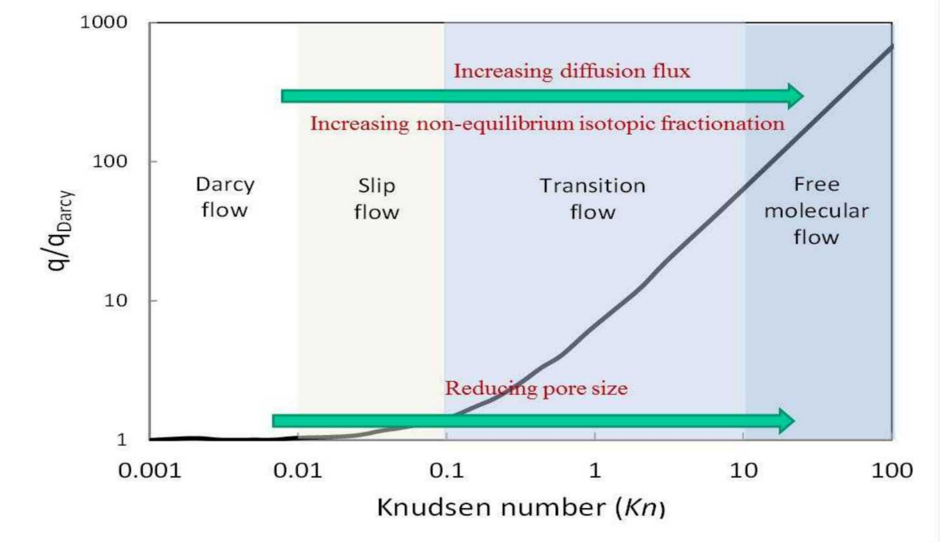
Mazurek et al. (2011)

- Due to nanoconfinement, anions and cations tend to pair up to form neutral species, which are much easier to diffuse through nanopores than dissociated anions and cations themselves.
- A shale formation, previously thought to be semi-permeable, may be "leaky" due to the effect of nanopore confinement, though the leakage rate could be small.

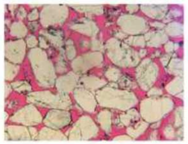


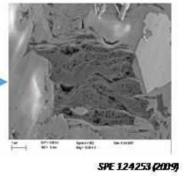
Miller et al. (2015)

Emergent transport properties in nanopores: Isotopic fractionation



Conventional reservoir





Shale formation

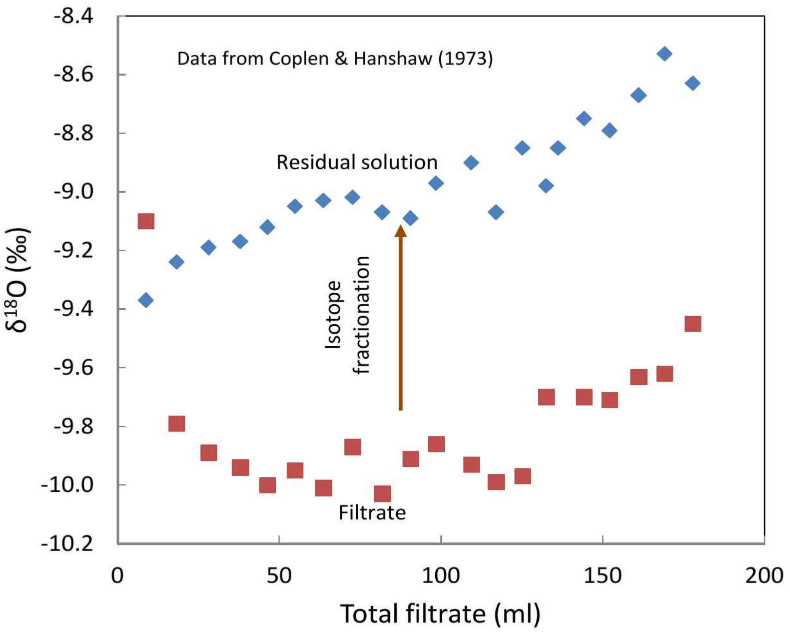
$$k_{app} = \frac{2r}{3RT}\left(\frac{8RT}{\pi M}\right)^{1/2} + \left[1 + \left(\frac{8\pi RT}{M}\right)^{1/2}\frac{\mu}{pr}\left(\frac{2}{\alpha} - 1\right)\right]\frac{cr^2}{8\mu}$$

M - Molecular weight

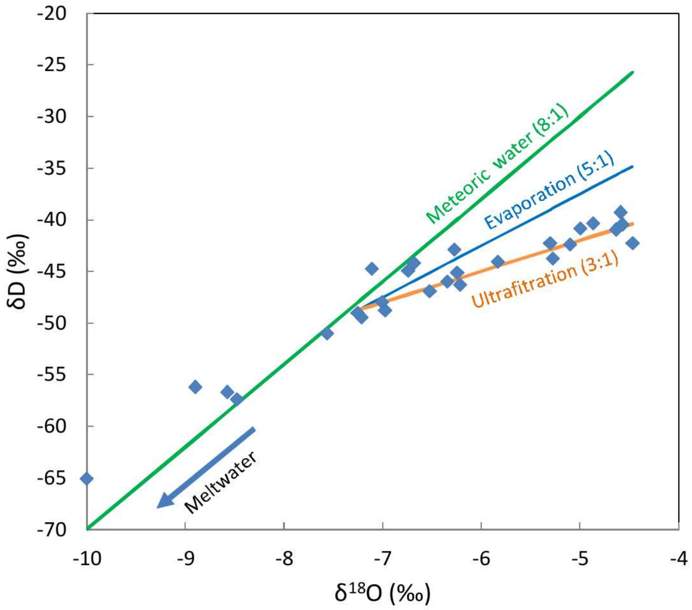
Mass dependent transport

Wang (2018)

Ultrafiltration in Nature



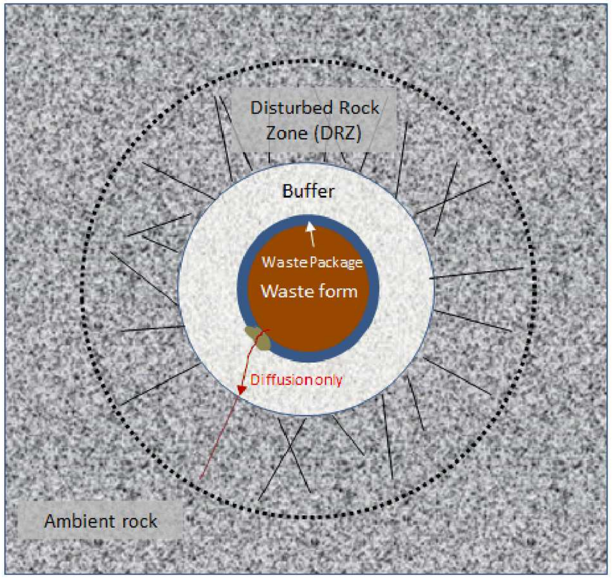
Isotope fractionation of water by ultrafiltration across a compacted clay membrane (Coplen and Hanshaw, 1973)

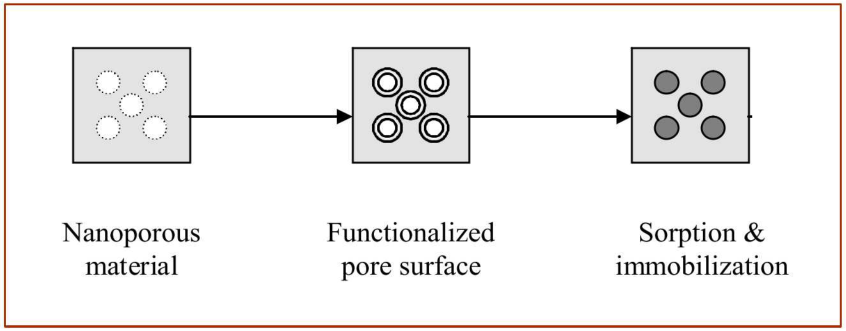


Waters extracted from Opallinus Clay at Benken (Switzerland) (Wang, 2018)

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.

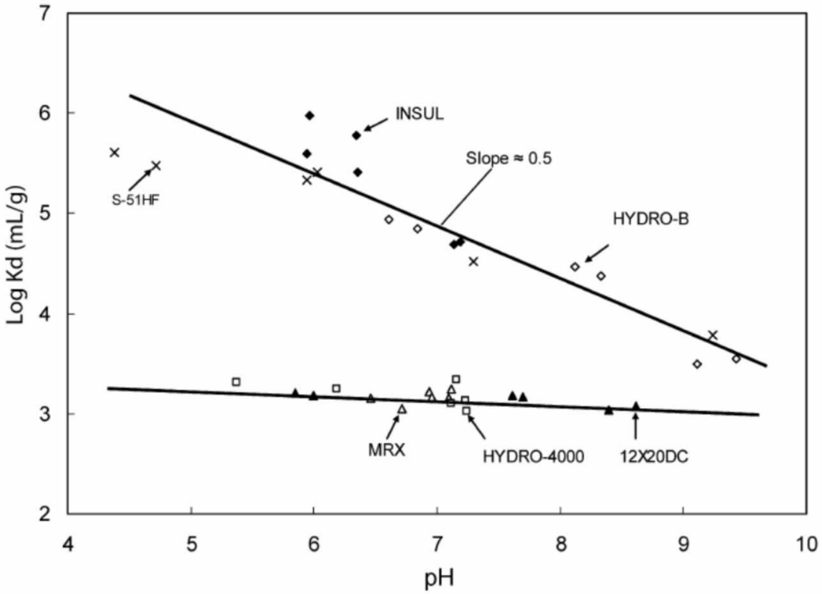
Exploit nanogeochemistry concept for subsurface engineering applications





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



TcO_4^- uptake by activated carbon

Wang et al. (2007)

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!

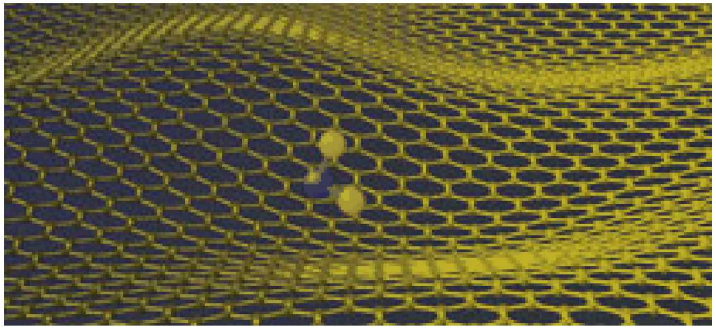
- Measurements on "isolated", unconfined surfaces may not be representative of actual geologic materials.

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

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