SAND2015-3647C

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

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May 11, 2015, Los Alamos National Laboratory

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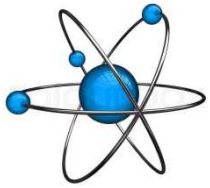
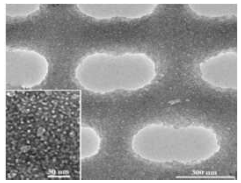
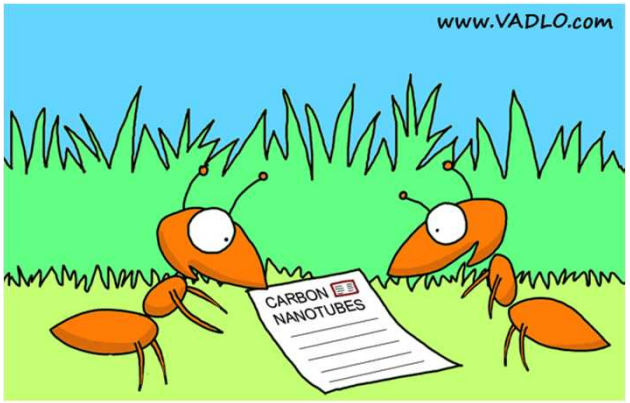
Nanoscales

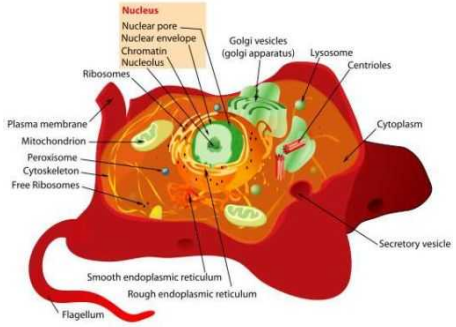

Angstrom (10^{-10} m)	Nanometer (10^{-9} m)	Micron (10^{-6} m)	Millimeter (10^{-3} m)	Meter (m)	Kilometer (10^{3} m)	1000 kilometers (10^{3} m)



"Finally, we can drink Coke with a straw."

Why so important?

- Emergent properties
- Key linkage between micro to macro (Miller & Wang et al., 2012, ES&T)



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

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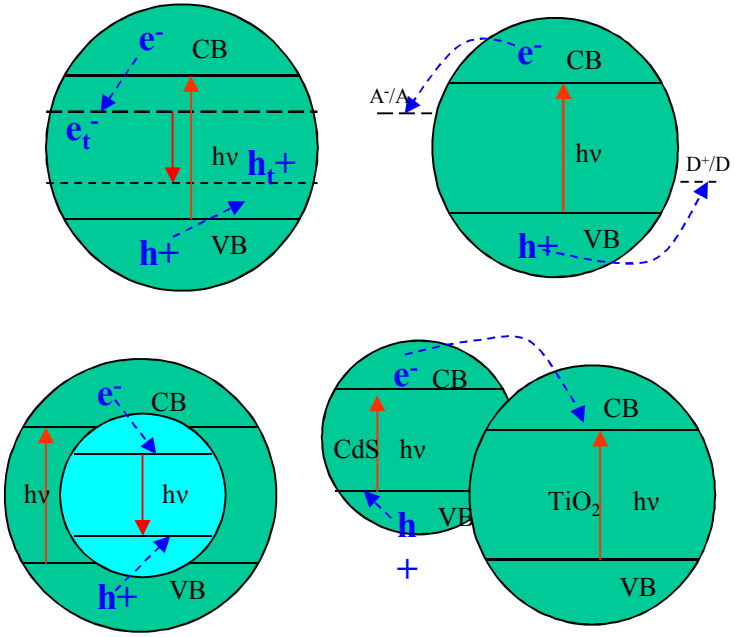
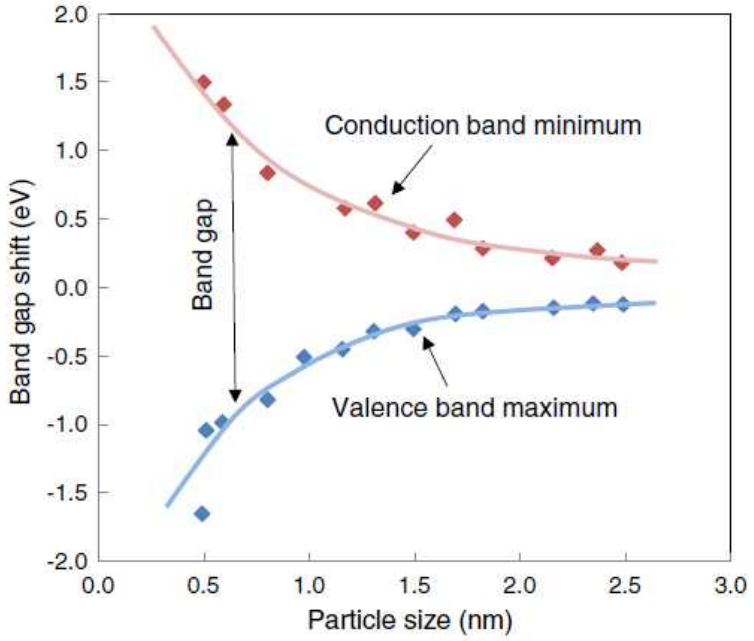
Size-Dependent Material Properties



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



Size-dependent CdS band gap

(Lüning et al., 1999, Sold State Communication)

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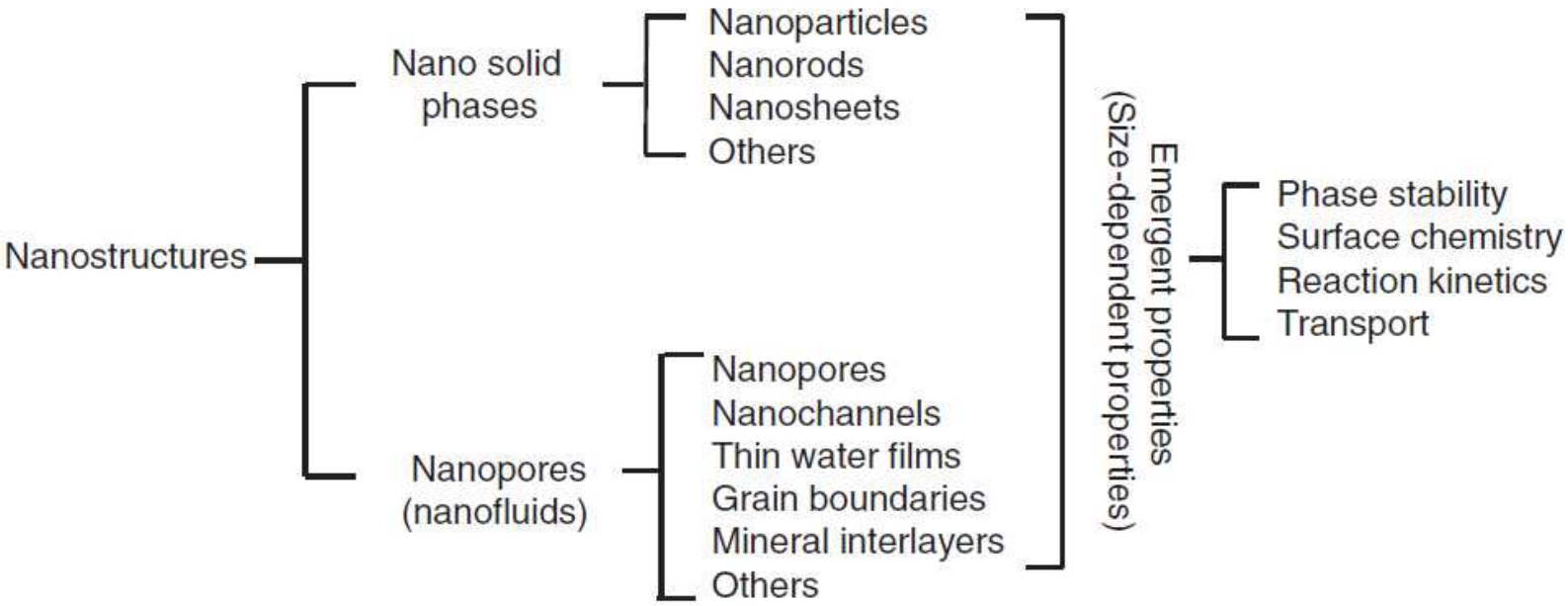
Systematics of Nanogeochemistry



Wang (2014) Chemical Geology

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

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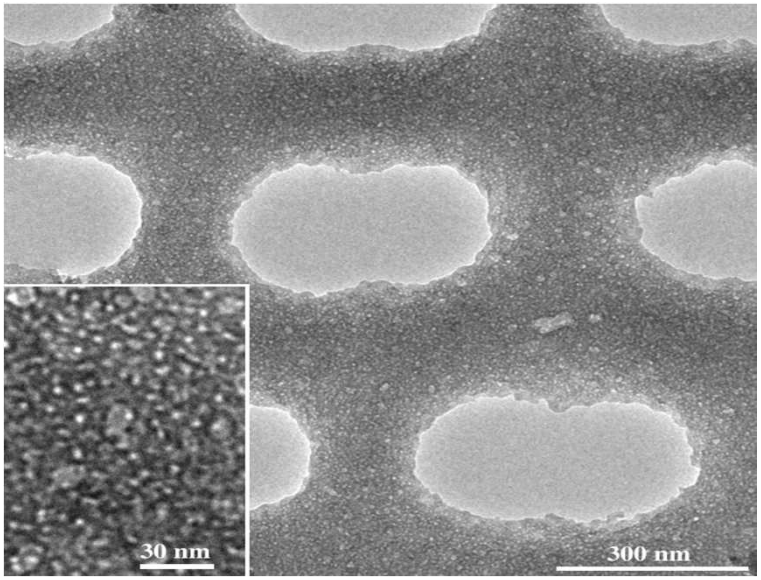
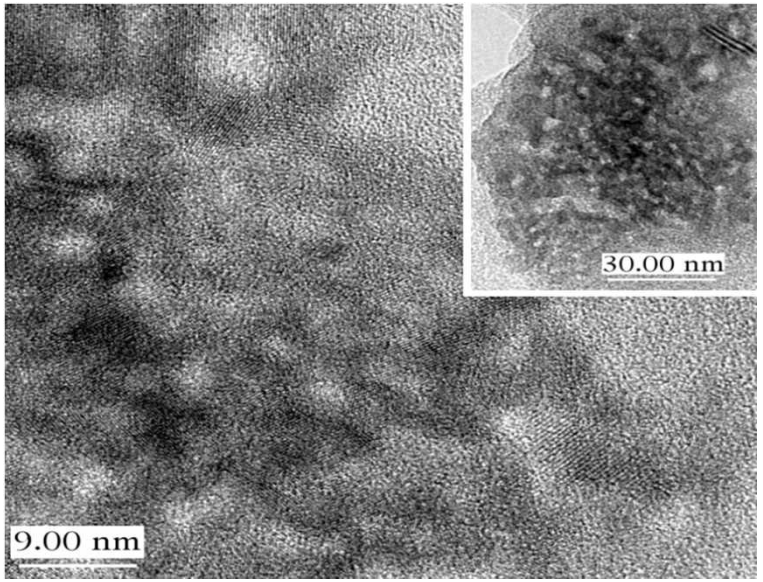
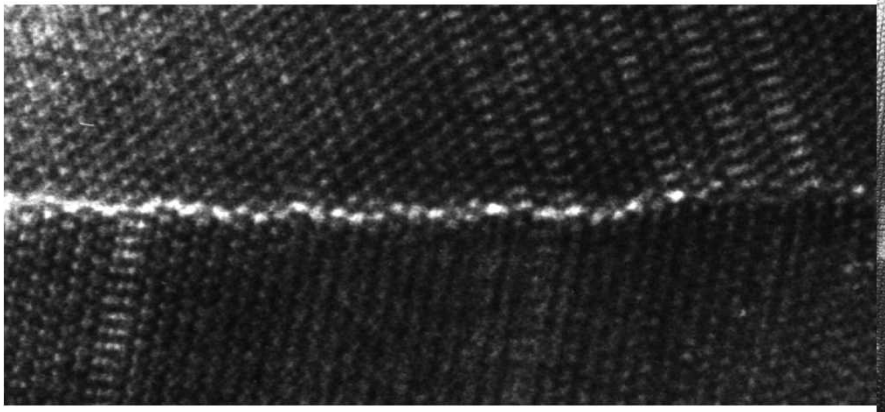
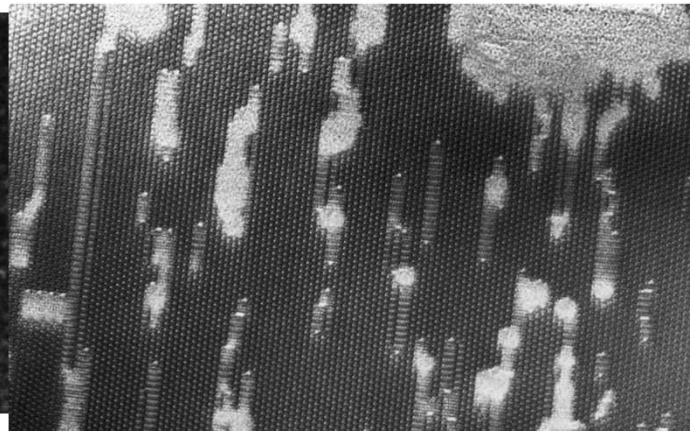
Nanostructures in Geologic Materials









Wang et al., 2003, Geology

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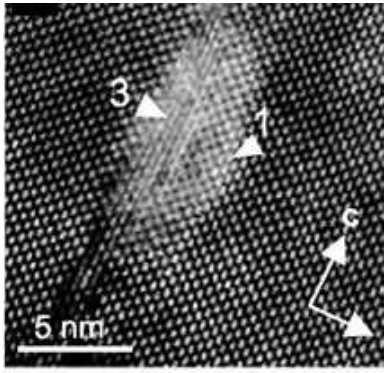
Nano solid phases: Occurrence and geochemical implications

- 96% Fe in Atlantic associated with colloid fractions.
- Ferrihydrite nanoparticles as a main colloidal Fe phase in the Rio Negro (Brazil)

http://blueattraction.com/?attachment_id=137



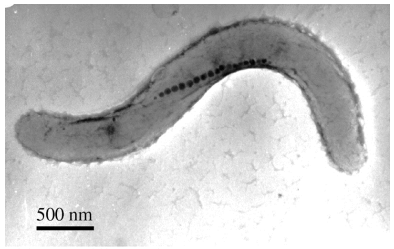
http://what-when-how.com/wp-content/uploads/2011/03/tmp1C128_thumb.jpg

http://geology1403.blogspot.com/p/travels.html

Ultrafine grains (80 m^2/g) in fault gouge accounting for >50% energy consumed in earthquake

Carlin type of gold deposits: invisible gold – gold nanoparticles

Biogenic nanoparticles – a mechanism to reduce the toxicity of a heavy metal



http://rsif.royalsocietypublishing.org/content/5/26/977

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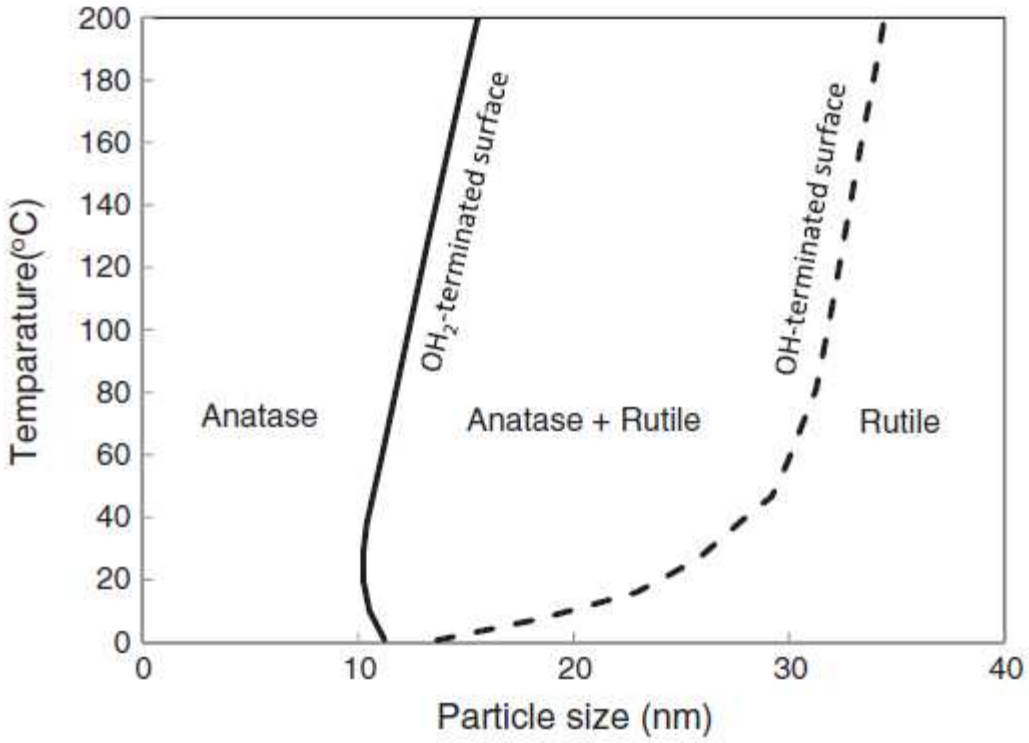
Emergent properties of nano solid phases: Phase stability



$$\Delta p = \frac{2\gamma}{r}$$

As the dimension of a solid phase is reduced to nanometers, the surface tension term becomes significant.

$$dG = -SdT + VdP + \sum \mu_i dn_i + \sum \gamma_j dA_j$$

Barnard & Xu (2008)

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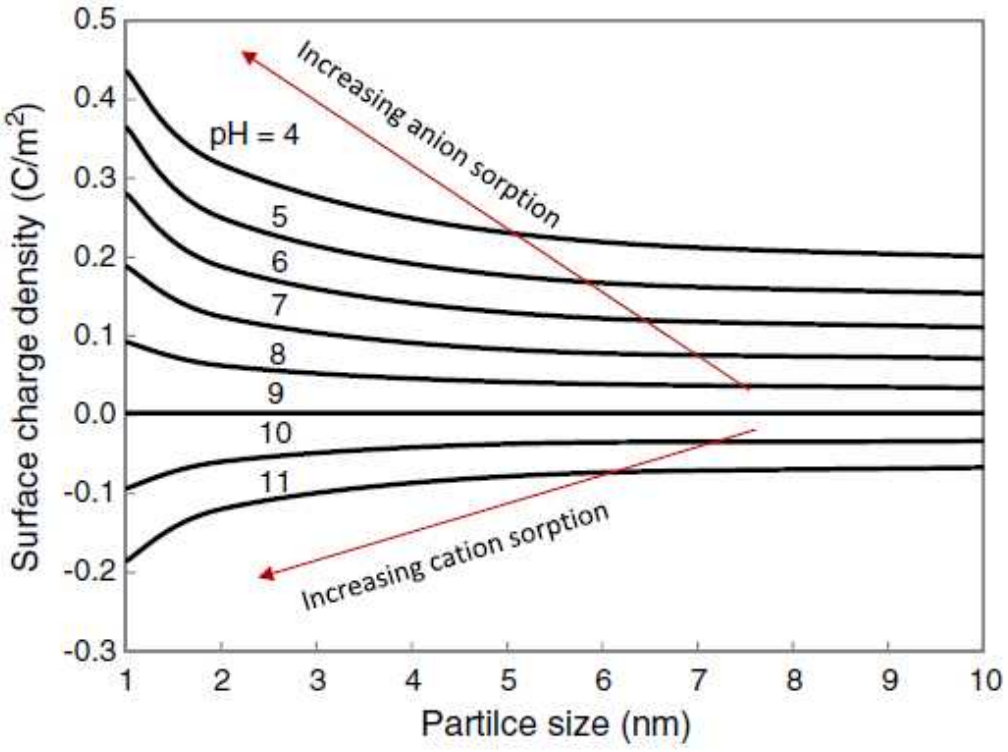
Surface charge density predicted by Monte-Carlo simulations for goethite nanoparticles (Abbas et al., 2008)



The prediction seems supported by a limited experimental observations:

- Higher zeta potential on finer hematite particles (Madden et al., 2006)
- Metal adsorption affinity increases with reducing particle size (Zeng et al., 2009)

Implications to colloid-facilitated transport

- Size-dependent trace metal partitioning
- Matrix diffusion vs. filtration

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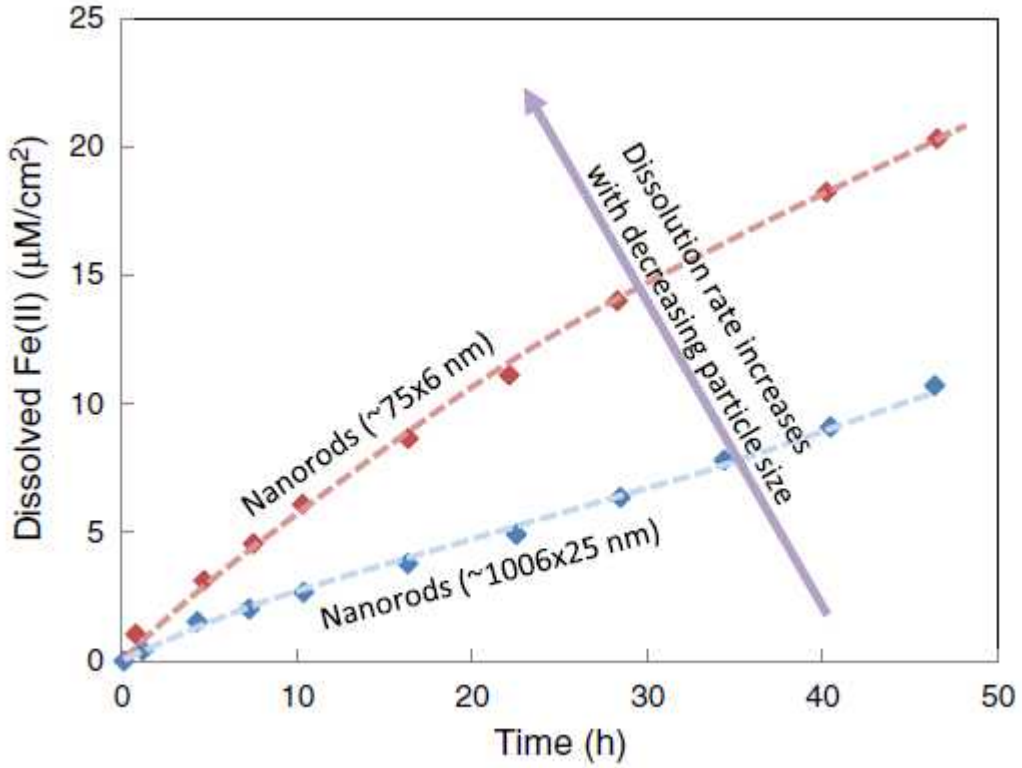
Dissolution kinetics under far-from-equilibrium conditions



Dissolution of α-FeOOH nanorods in the solution of 0,01 HNO_3 under simulated solar light (Rubasinghedge et al., 2010)

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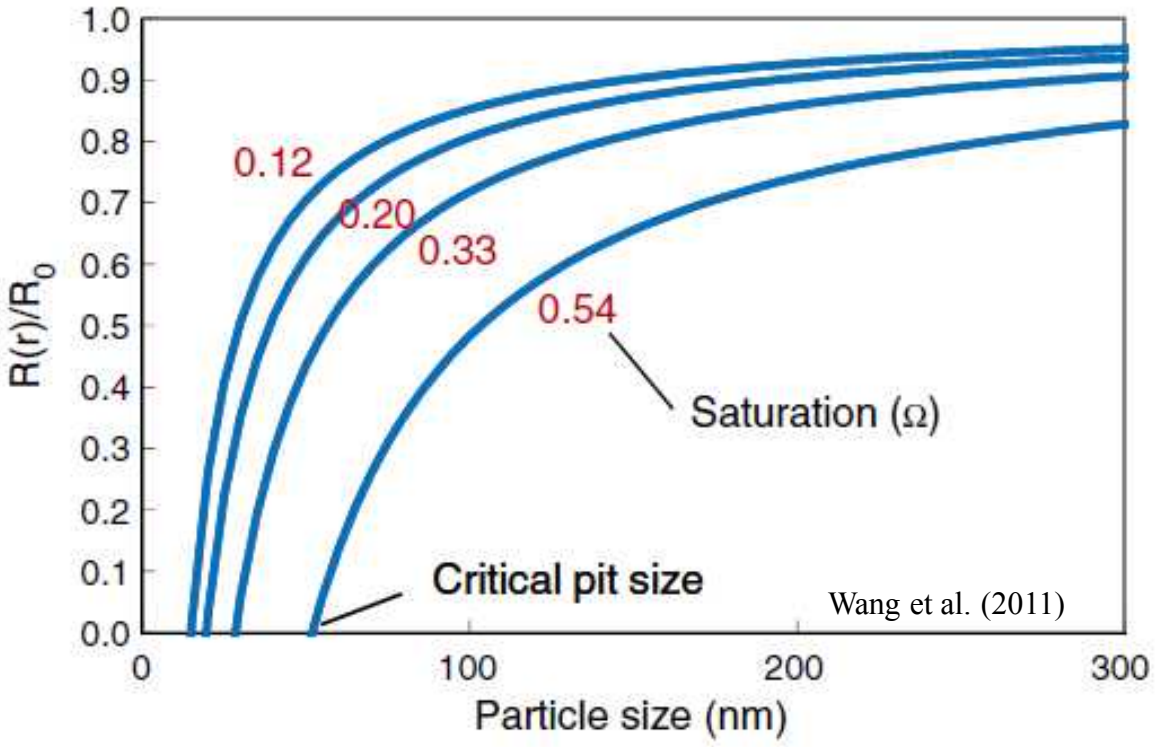
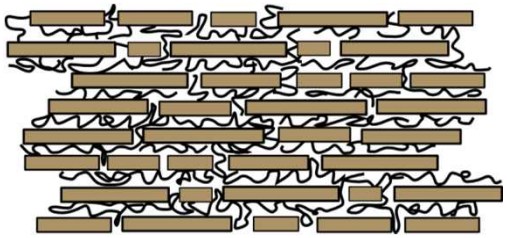
Dissolution kinetics under near-equilibrium conditions



Wang et al. (2011)



http://en.wikipedia.org/wiki/Nacre

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

- Colloid stability
- Resistance to demineralization

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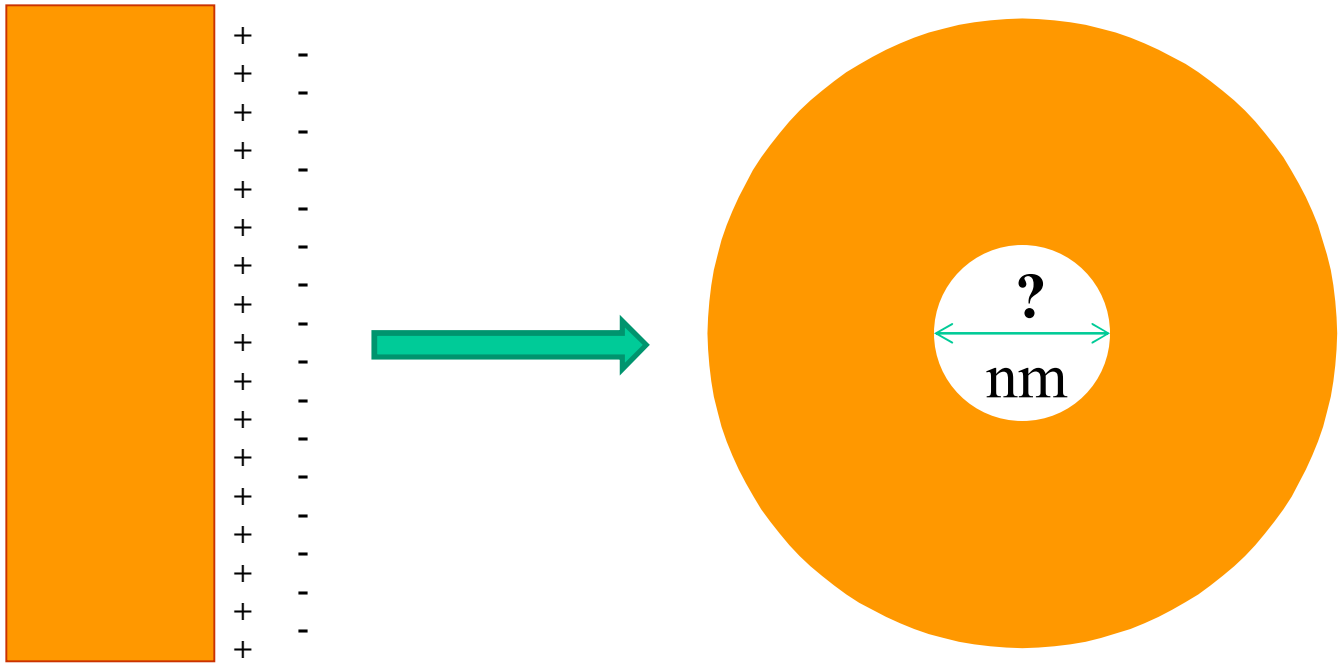
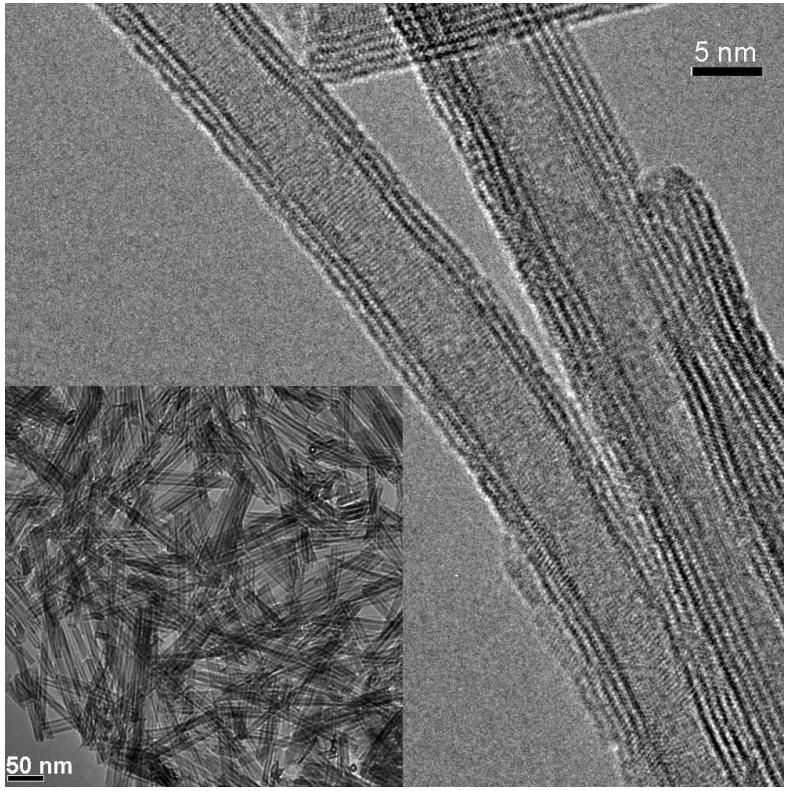
Confined vs. Unconfined Surface

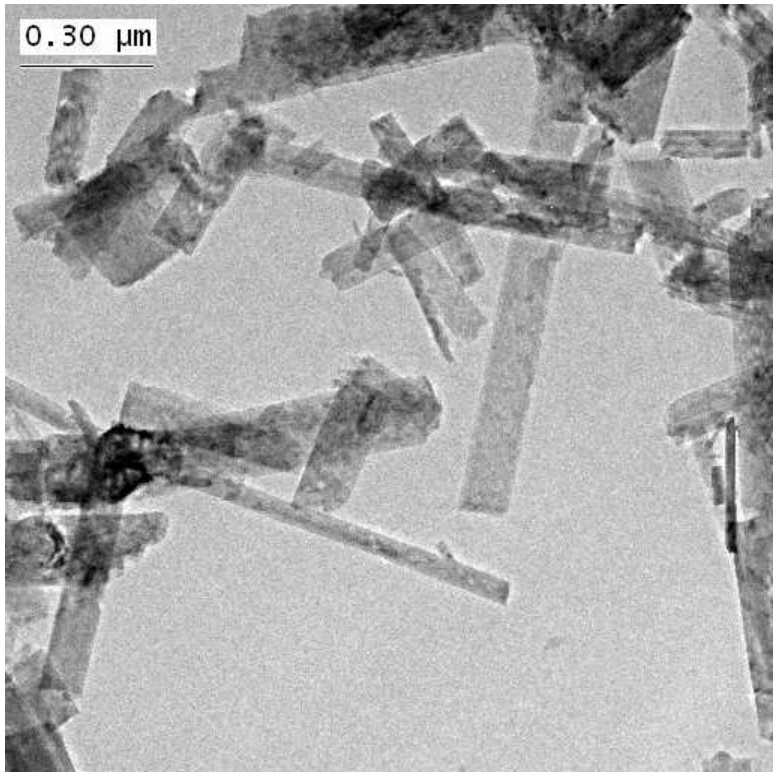


Unconfined

Confined

Synthesis of TiO_2 Nanotubes and nanorods





Wang et al. (2008)

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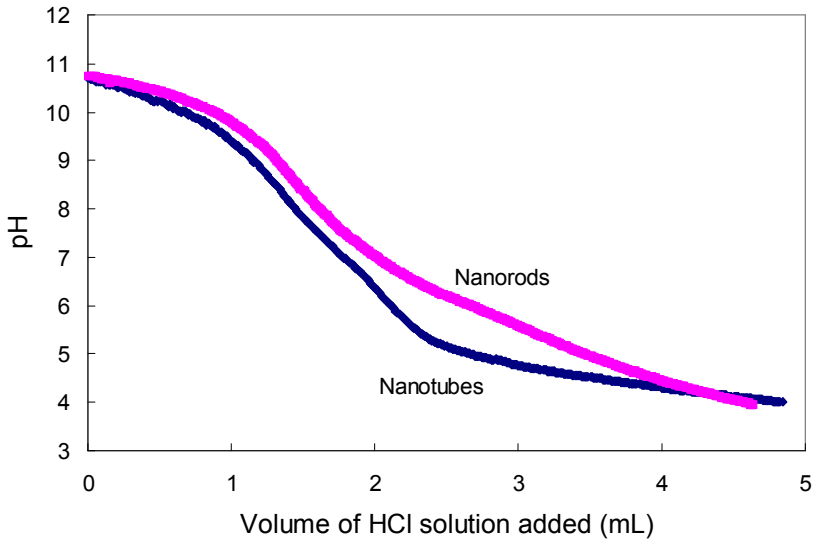
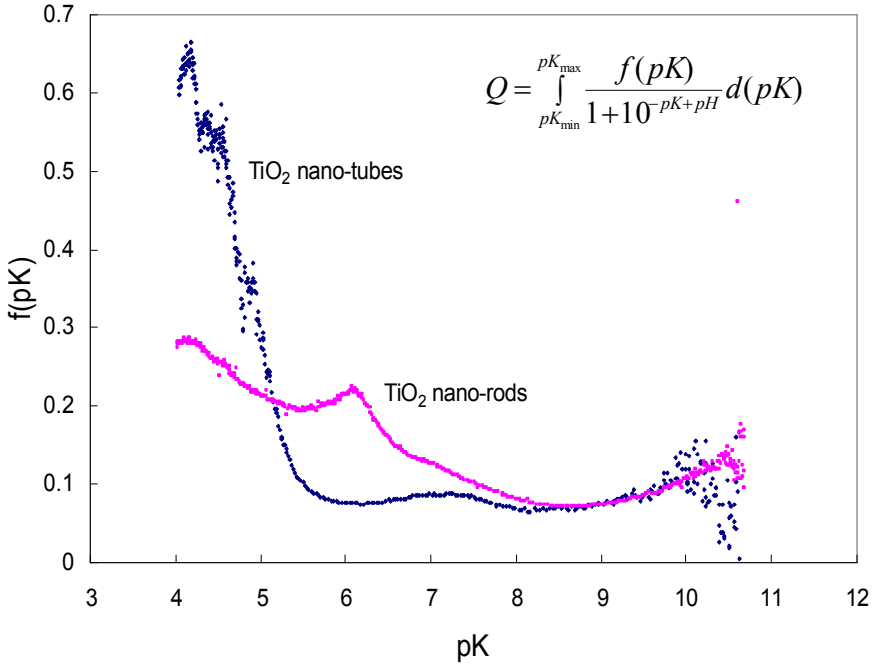
Distribution of Acidity Constant





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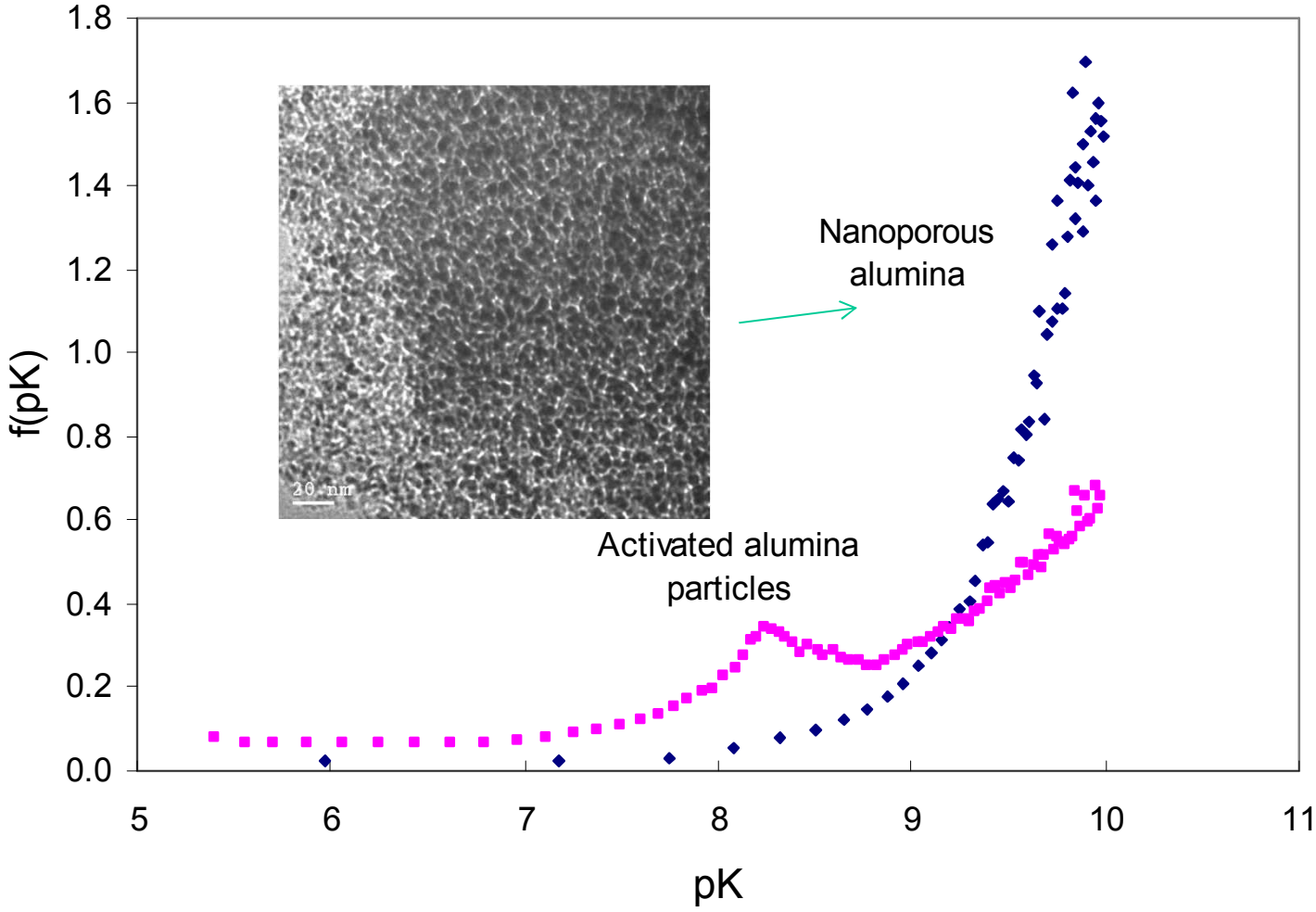
Distribution of Acidity Constant



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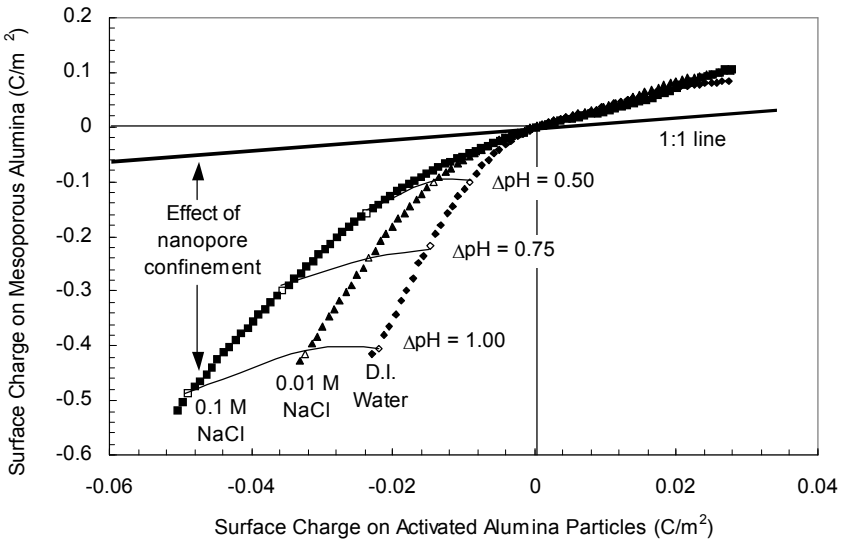
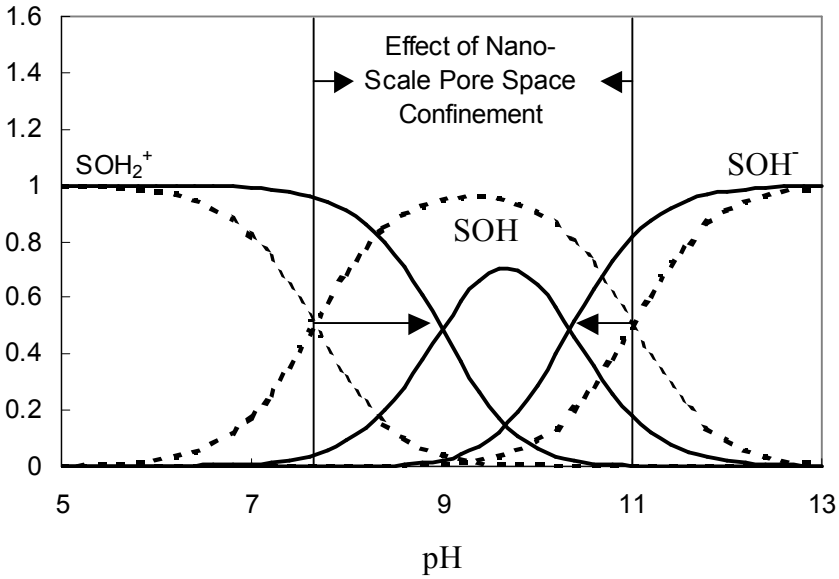
Effect of Nanopore Confinement on Surface Chemistry





Nanoporous alumina has a higher surface charge density, which is less sensitive to ionic strength changes.

Nanopore confinement causes a solid-water interface to be more either positively or negatively charged.

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

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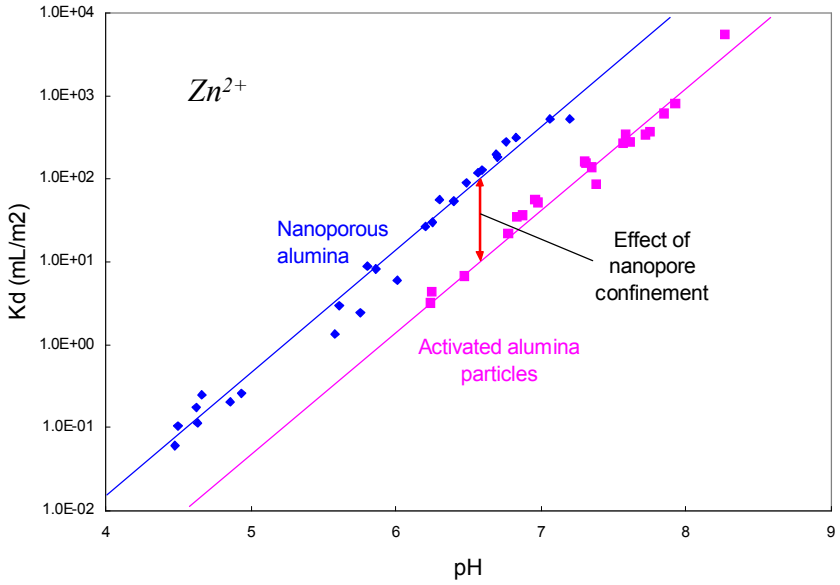
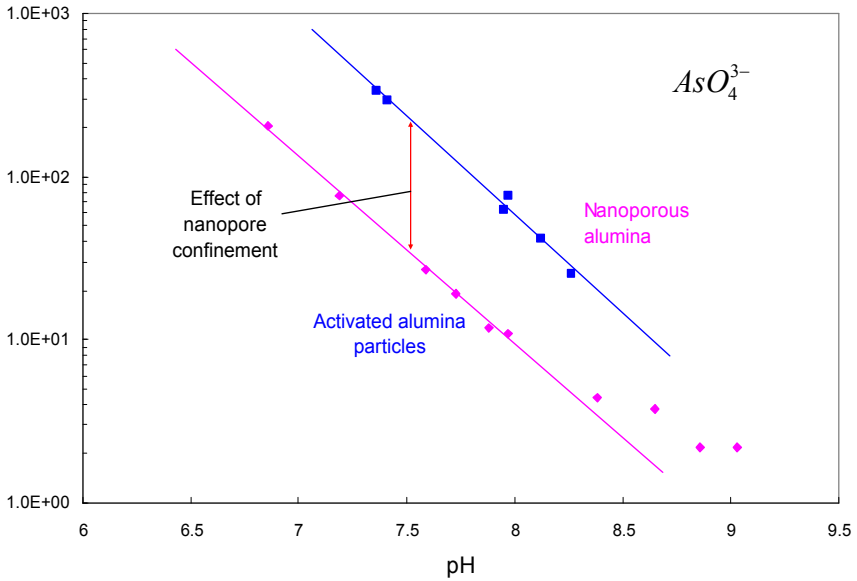
Nanopore Confinement and Ion Sorption





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

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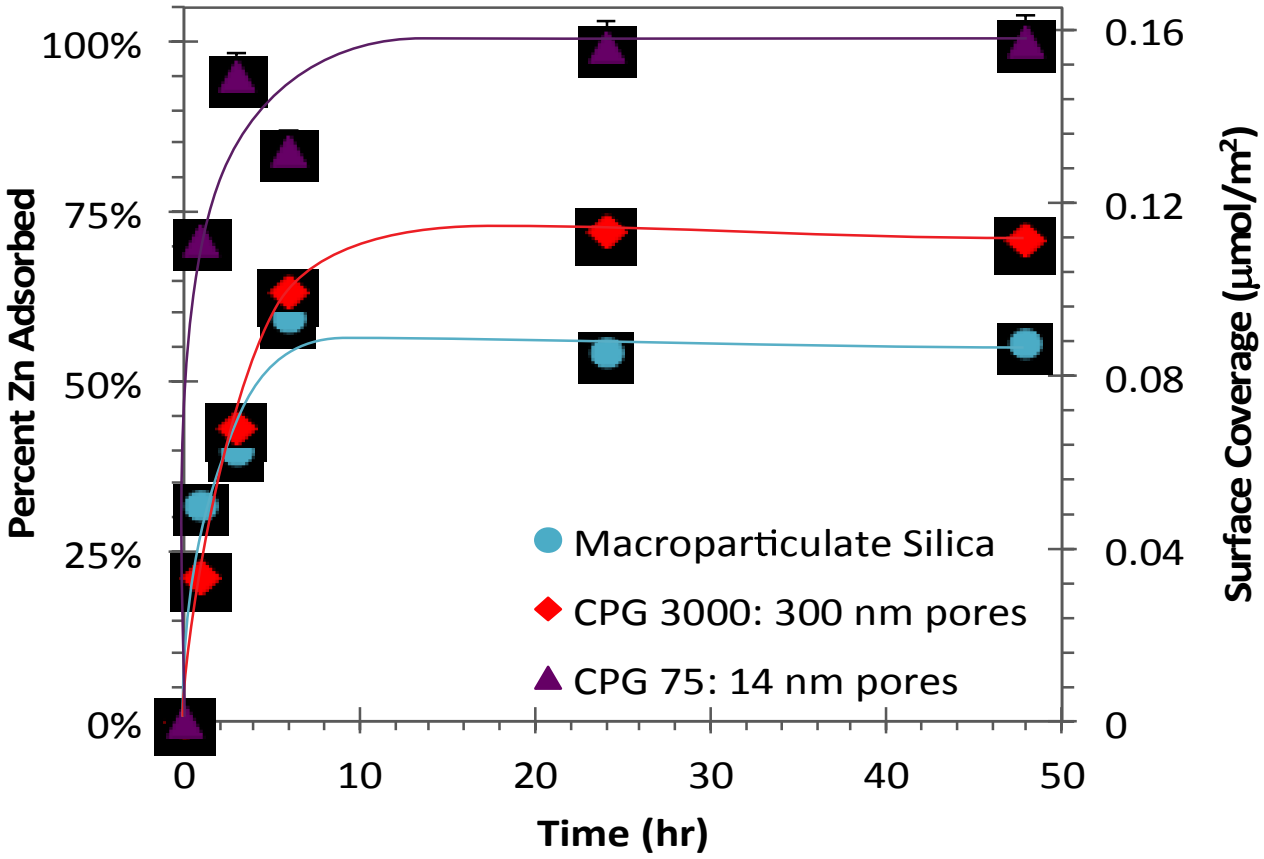
Zn Adsorption Capacity



Nelson et al. (2014)

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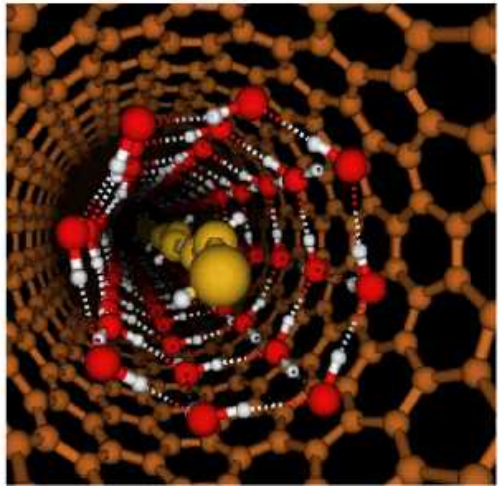
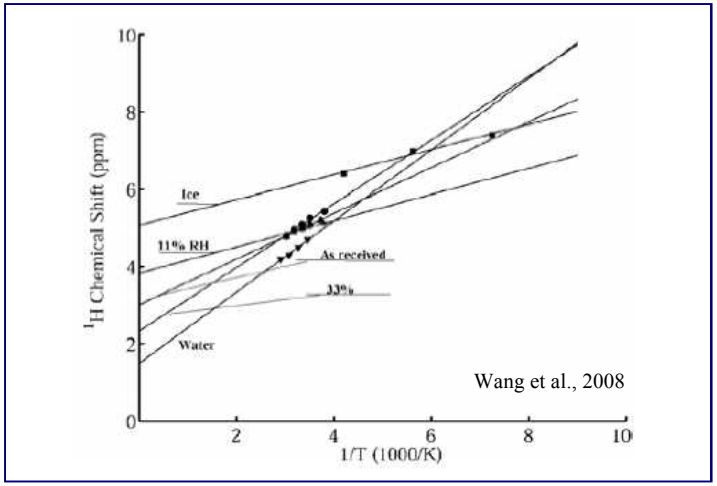
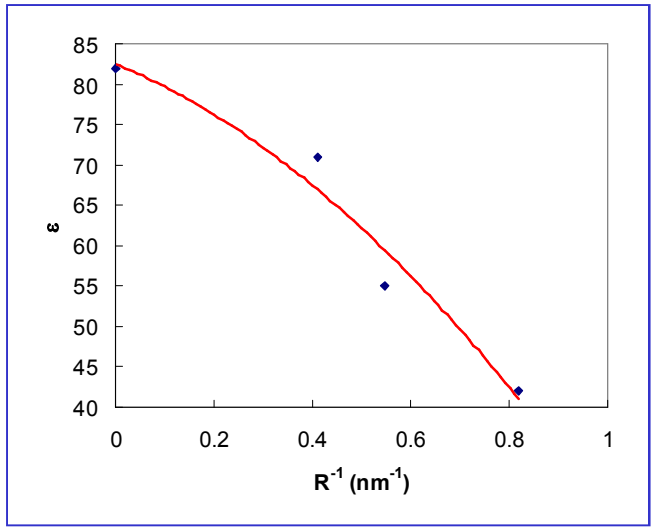
Effect of Nanopore Confinement on Water



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

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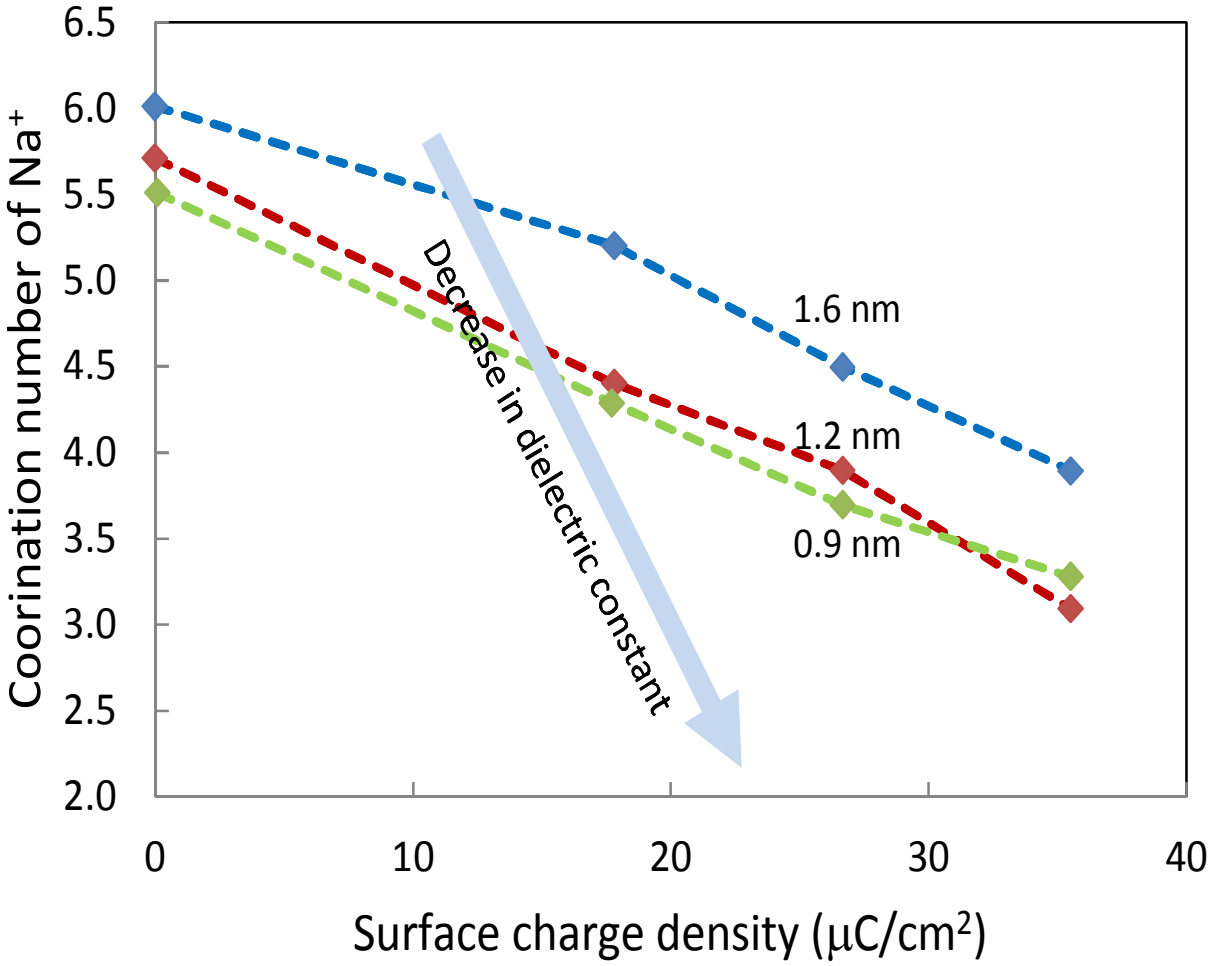
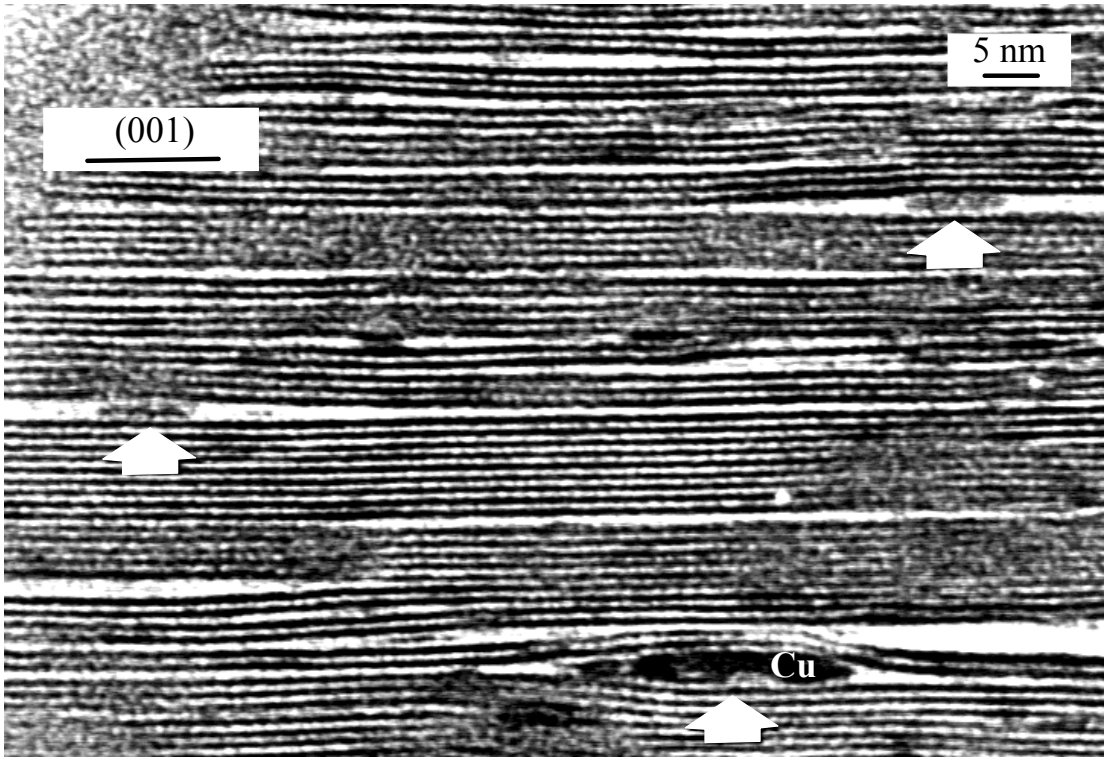
Molecular Dynamics Simulation of NaCl in confinement



Kalluri et al. (2011).

Preferential Enrichment of Trace metals



TEM image of highly weathered illite containing nano-scale Cu inclusions, indicating preferential enrichment of heavy metal in nano-scale pores.

Wang et al., 2003, Geology

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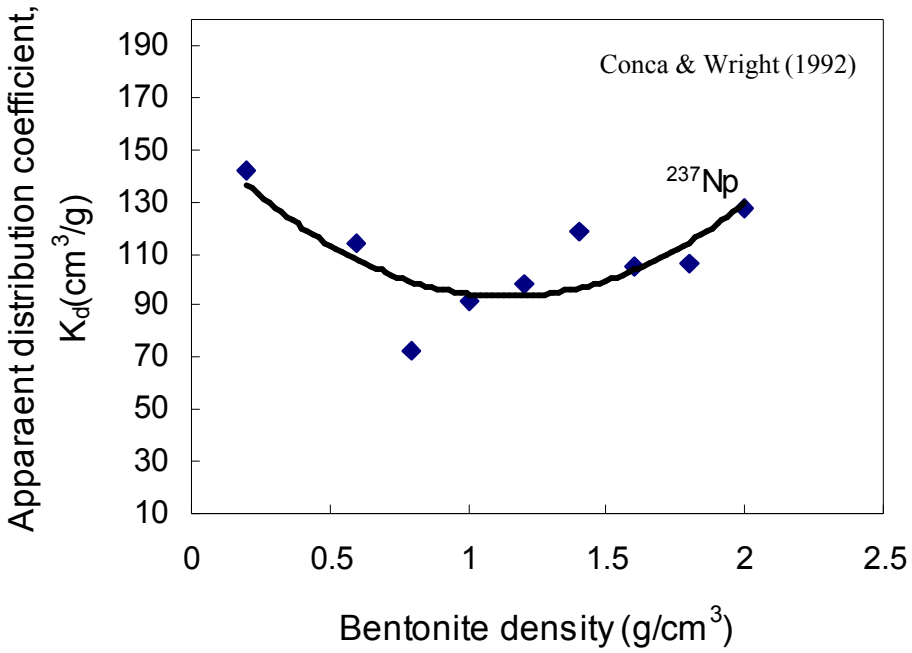
Effect of compaction Radionuclide uptake by clays



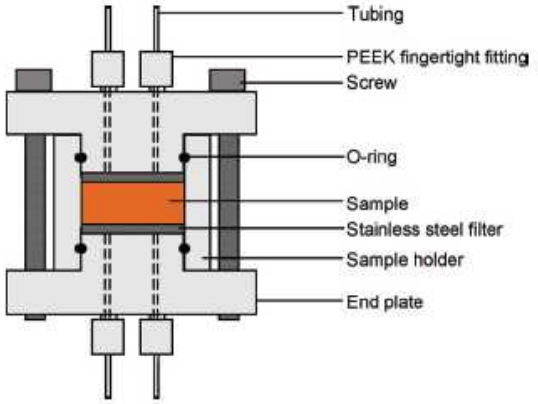


FIGURE 1. Cross-section picture of the diffusion cell used for the sorption measurements on compacted bentonite.

TABLE 4. R_d, K_e and ΔG_{ex} Values for Sorption of Cs^+ on Compacted Bentonite for Different Bulk Dry Densities (ρ_b)[a]

ρ_b [kg m^{-3}]	1300	1600	1900
[Na^+] [M]	0.183	0.207	0.254
R_d [dm^3 kg^{-1}]	69.0 ± 2.0	109 ± 4	620 ± 4
K_e	21.6	38.6	269
ΔG_{ex} [kJ mol^{-1}]	−7.6	−9.1	−13.9

[a] R_d was calculated by eq (1), K_e was calculated by eq (5) and ΔG_{ex} is defined by eq (6).

Hydration energy: $\Delta G_{s,M^{n+}} = \omega_{M^{n+}}(1/\varepsilon - 1)$

$$K_e = \frac{[X-Cs][Na^+]}{[X-Na][Cs^+]}$$

Van Loon & Glaus (2008)

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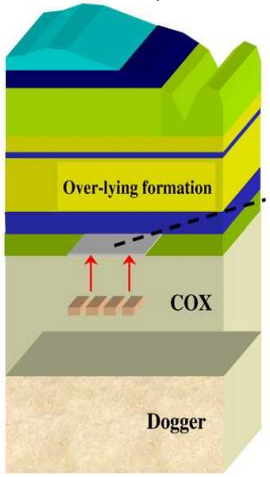
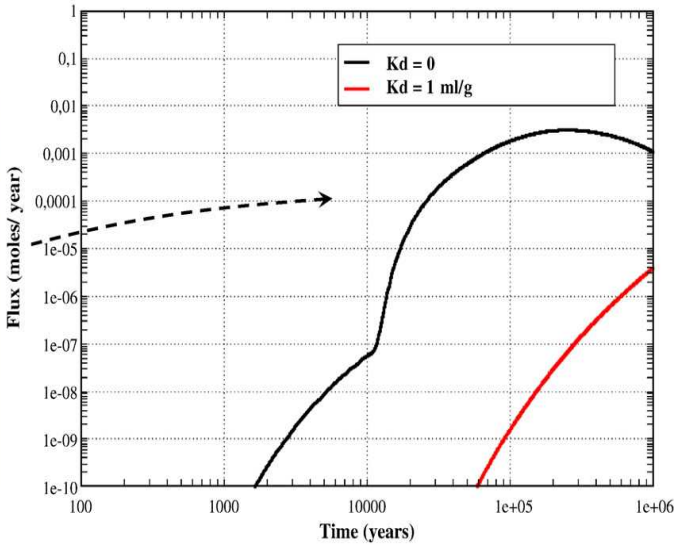
Retention of Iodide by Clays

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

Altmann, 2008





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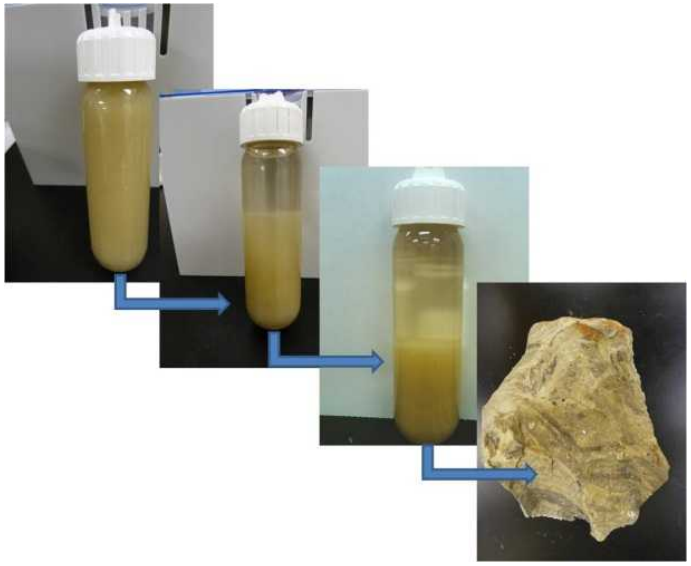
Batch sorption experiments were used to characterize clay sorption site & cation exchange capacity (CEC)

7 clays under consideration: All clays obtained from the clay bank repository (Purdue Univ.)

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



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		

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Surface area was separated between total, interior, and exterior surface areas.

	MB CEC (meq/100 g)	$BaCl_2$ CEC (meq/100 g)	BET S.A. (m^2/g)	MB S.A. (m^2/g)	Internal S.A. (m^2/g)
Kaolinite	1.50	4.61	11.31	11.76	0.45
Ripidolite	3.00	6.03	8.02	23.49	15.47
Illite	14.98	27.61	31.46	117.21	85.76
Illite.Smectite	24.69	30.39	29.82	193.23	163.41
Montmorillonite	109.53	151.92	28.29	857.17	828.88
Sepiolite	17.41	8.98	201.43	136.27	-65.16
Palygorskite	39.96	29.22	141.52	625.45	483.93

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)
	Ripidolite	6.03	1.13 (0.38)	-0.16 (0.72)	-0.31 (0.17)
	Illite	27.61	0.54 (0.12)	0.13 (0.002)	-0.50 (0.24)
	Illite.Smectite	30.39	0.38 (0.08)	-0.01 (0.11)	-0.49 (0.11)
	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)
	Palygorskite	29.22	0.24 (0.30)	1.26 (0.05)	0.99 (0.17)

All electrolytes at 0.1M

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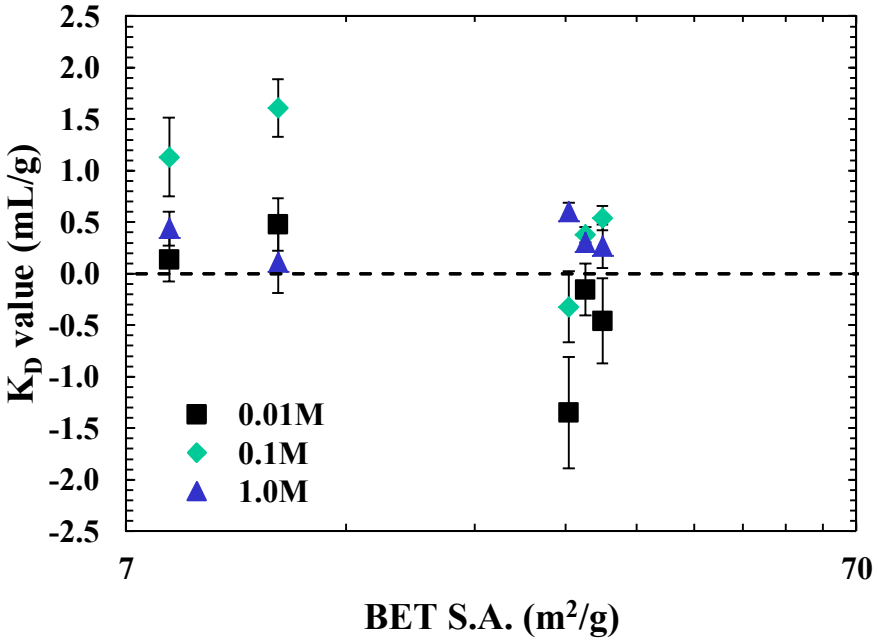
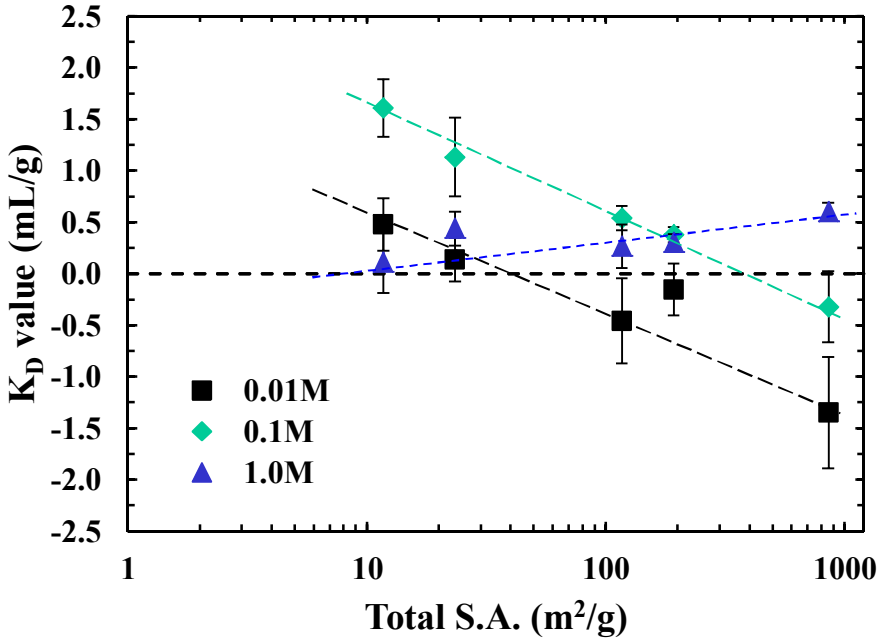
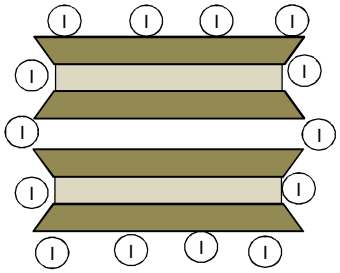
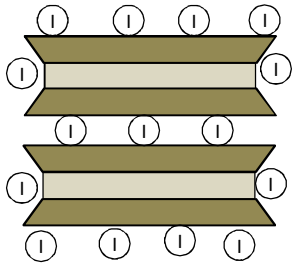
K_D values trend with total surface area, suggesting interactions with negatively charged surfaces.









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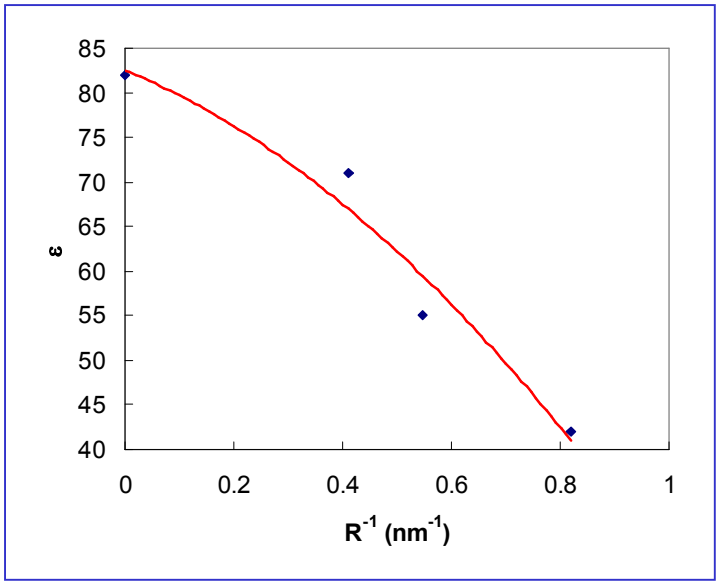
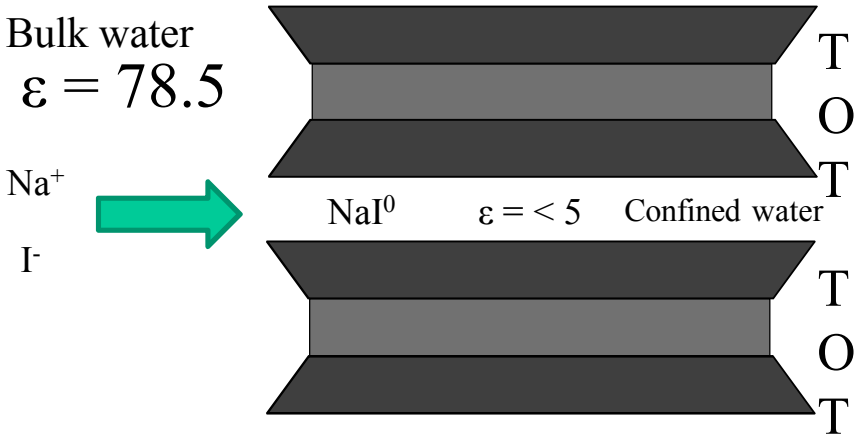
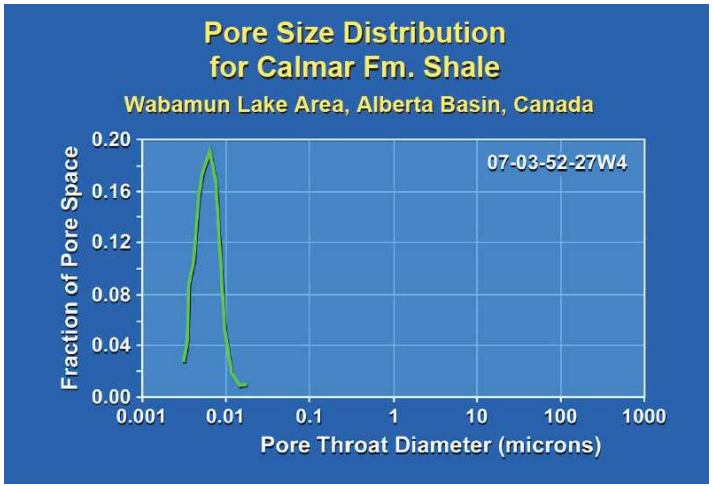
Data is consistent with ion pair formation caused by reduced dielectric constant of confined water



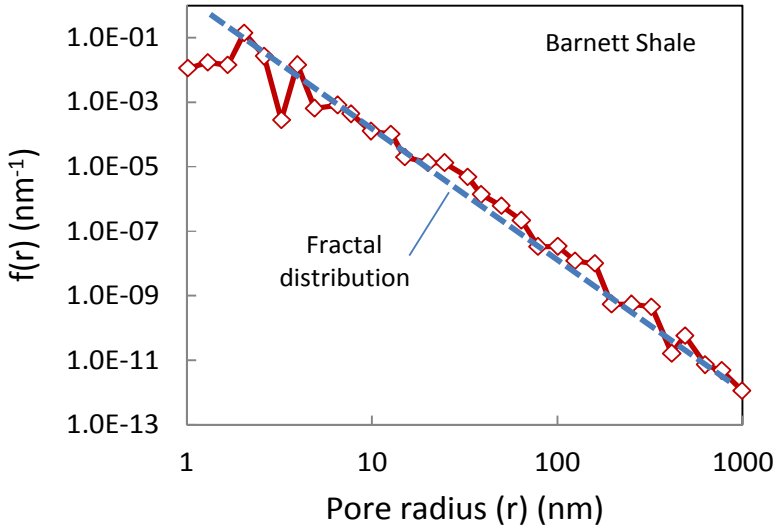


Senapati & Chandra, 2001, J. Phys. Chem.

Shale as a nanocomposite material



Bachu & Bennion (2006)



Clarkson et al. (2012)

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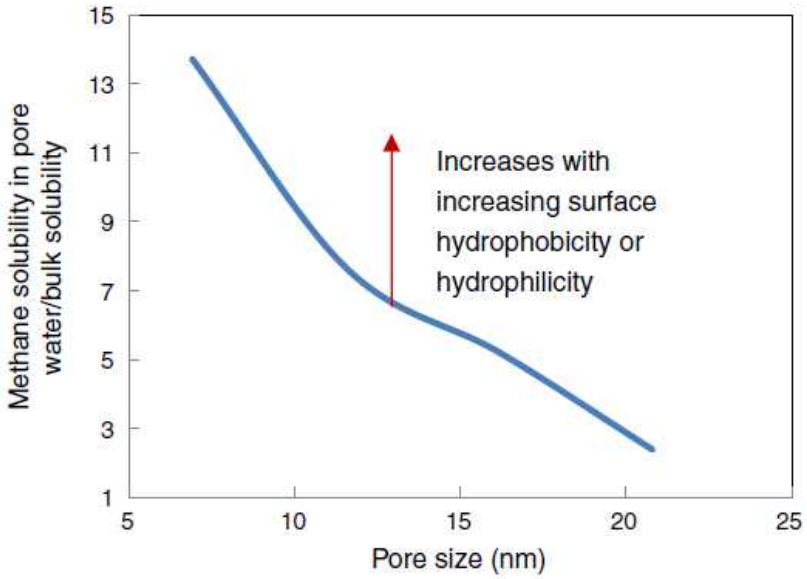
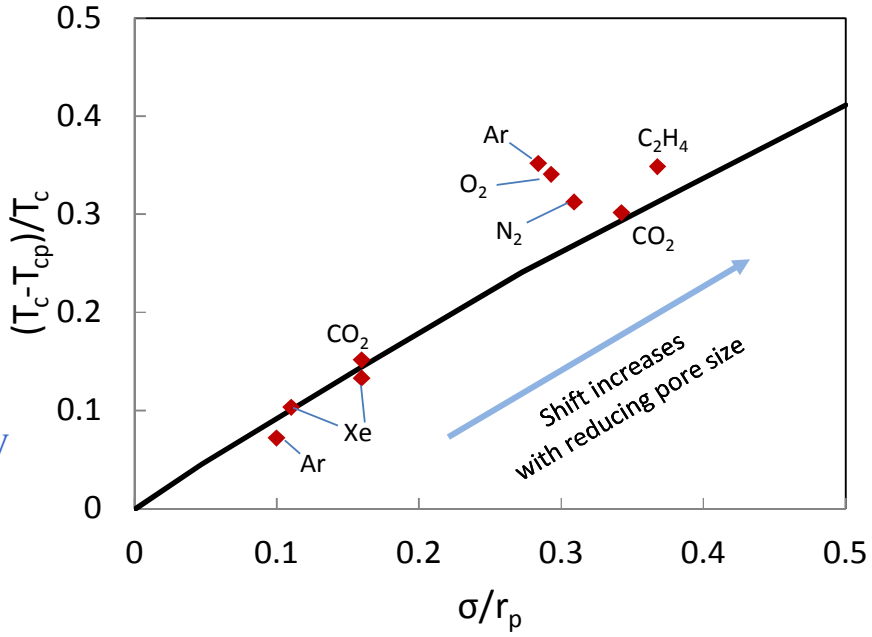
Thermodynamics of gas in nanopores

Solubility of methane in pore water as a function of ore size and pore surface chemistry (Diaz-Campos et al., 2009)





Shift of critical temperature of fluid as a function of pore size (Zarragoicoechea & Kuz, 2004)

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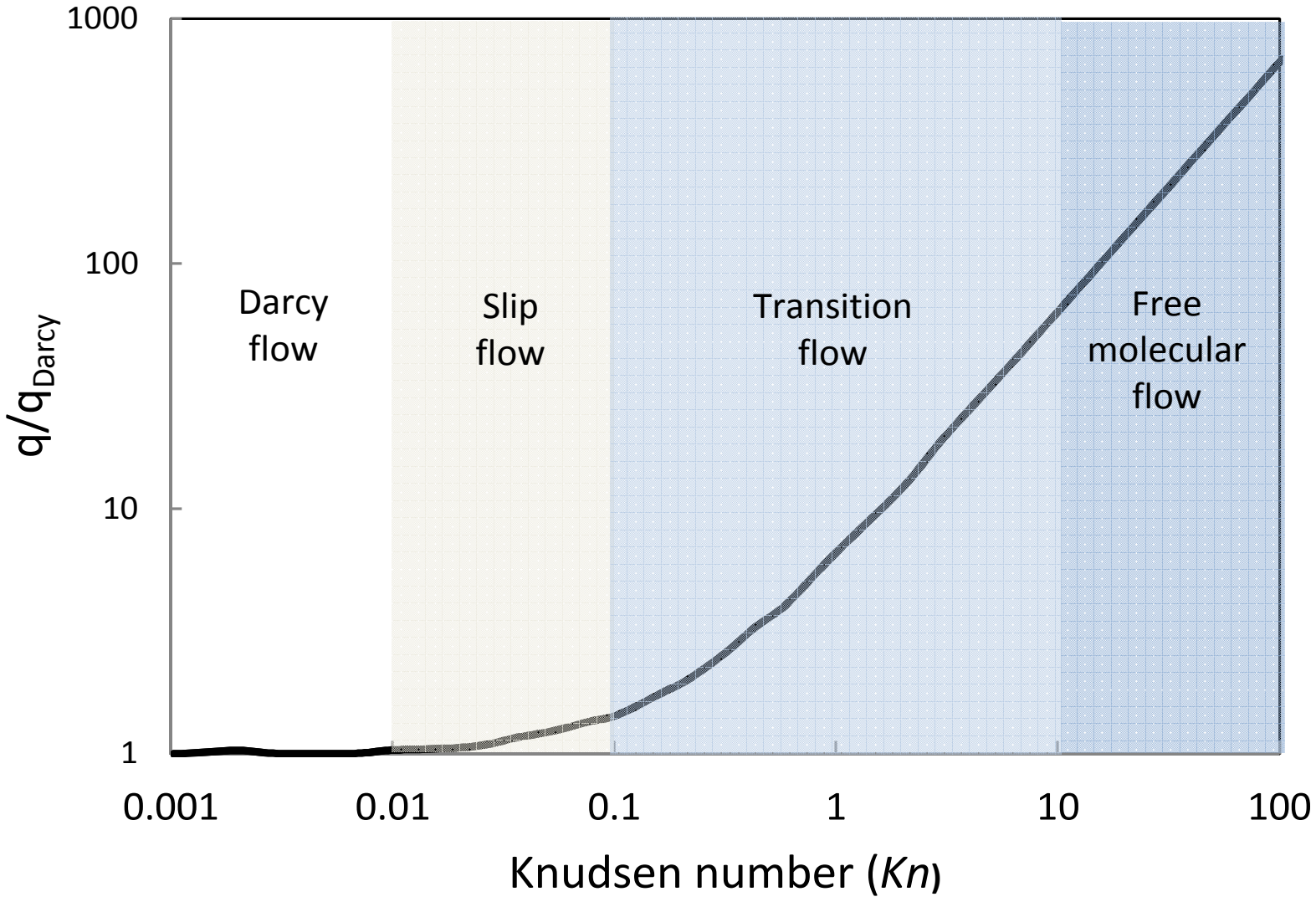

Ziarani and Aguilera (2012)

Kn = Mean free path of molecules/characteristic length of flow system

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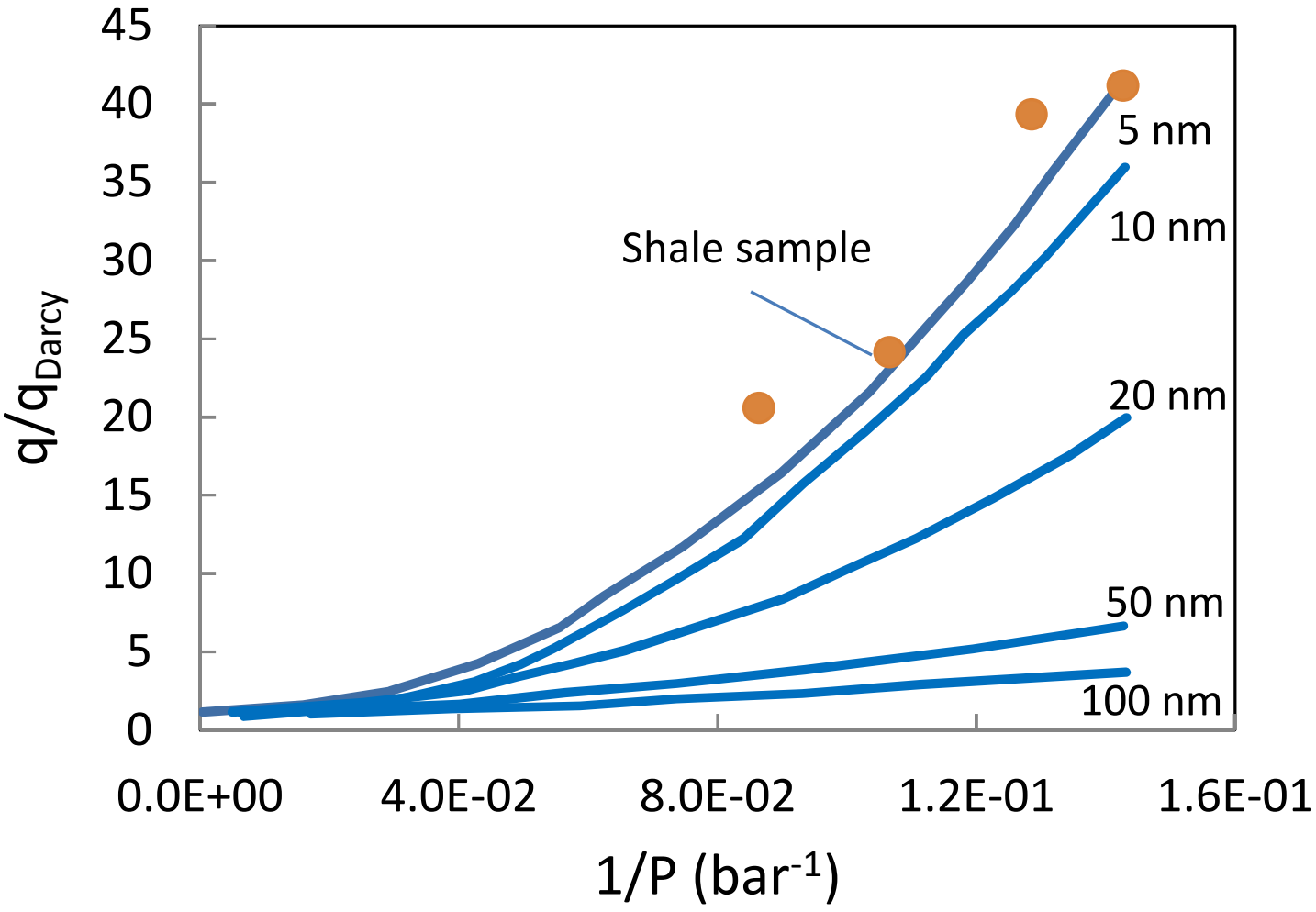

Fathi et al. (2012)

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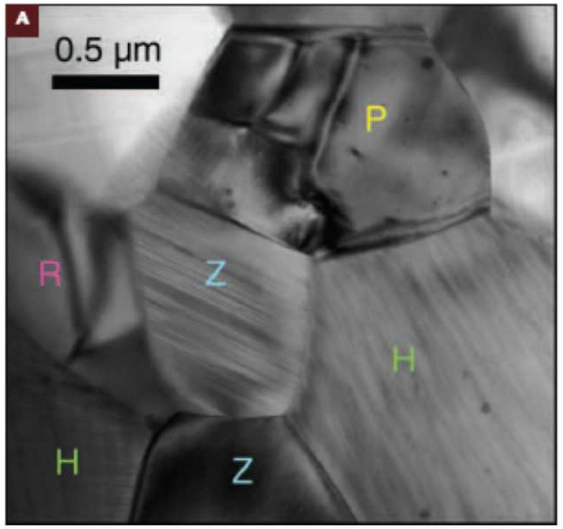
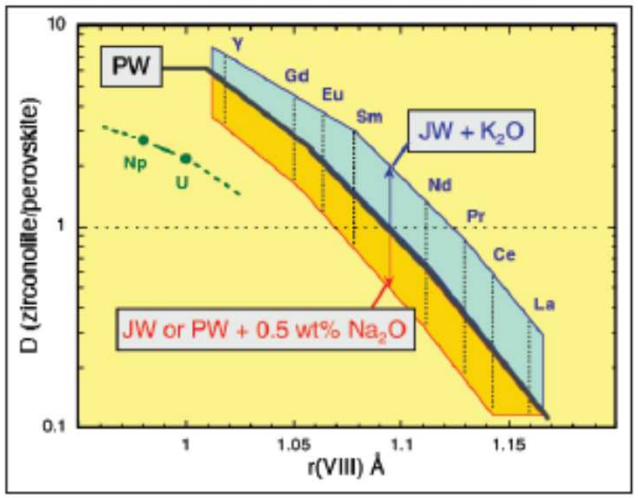
Limitations of Existing Waste Forms





Lumpkin, 2006

- Immobilization Mechanism
  - Incorporation of radionuclides (RNs) into mineral structure sites
- Limited ability to accommodate different radionuclides
- Limited waste loading factors
- Dilemma in Durability
  - Soluble RN vs. durable WF
    - Changing stability of hosting minerals
  - Dissolution kinetics vs. long term (1 My)
    - Metal/alloy for Tc
- Thermodynamically stable waste forms?

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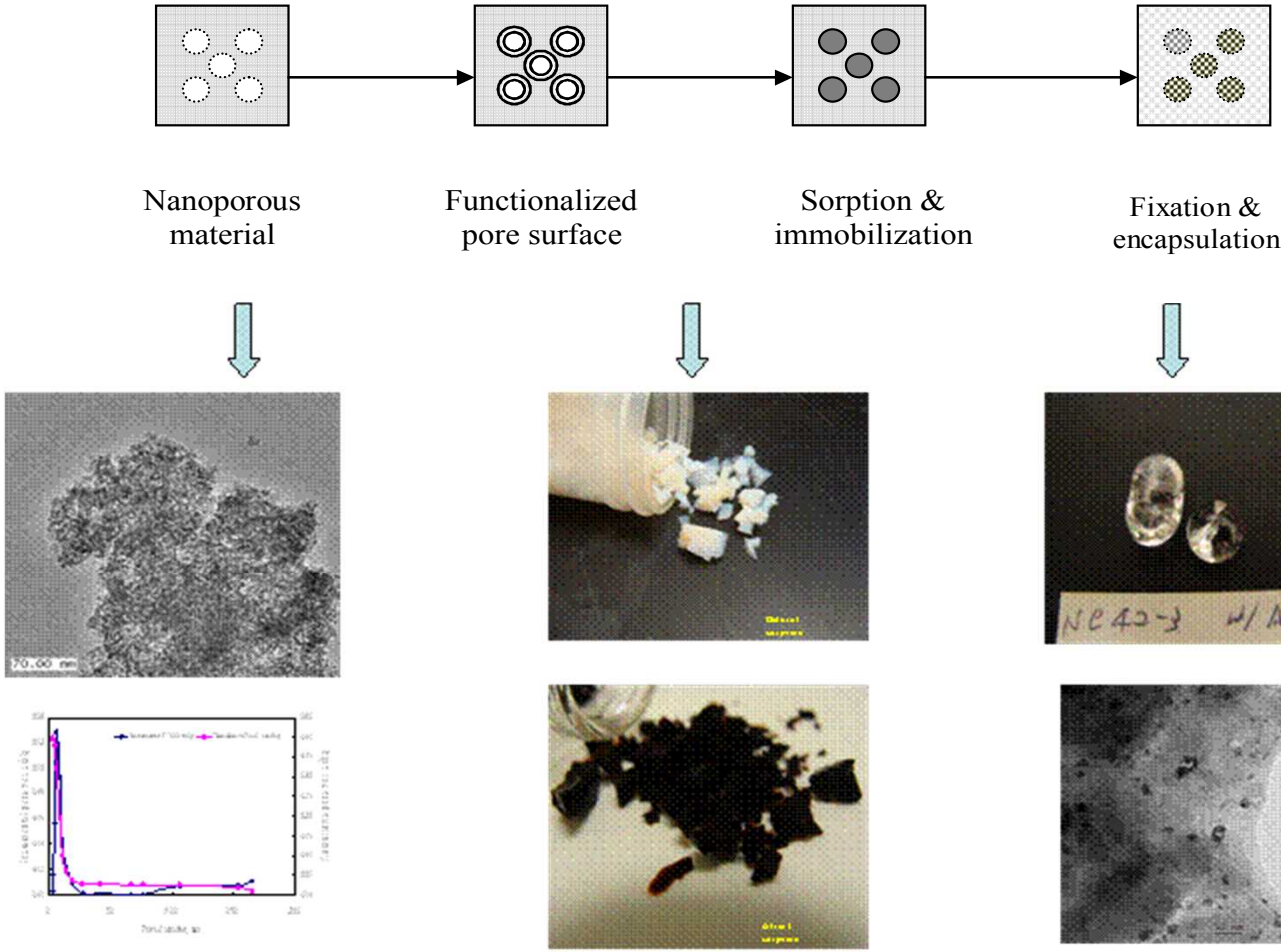
Development of New Generation of Waste Forms: Nano-immobilization & Nano-encapsulation



Wang et al., 2011

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Nanopore Structures & Radionuclide Retention

Material	I sorption (ppm)	% of I lost during fixation	% of I lost during vitrification
Particles	98	~100%	~100%
Activated particles	8700	45	65
Nanoporous material	25000	~ 0	~ 0

- Nanoporous structures not only enhance I sorption but also help to retain I during the fixation and encapsulation.
- Silver is not needed either for iodine retention!

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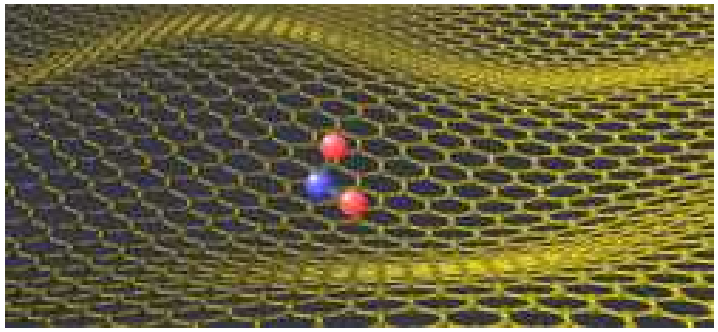
Concluding Remarks

- Size-dependent 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 through cooperative processes
- Geochemical implications
  - New perspectives for understanding fundamental geochemical processes
  - Development of novel materials for environmental applications



Graphene sensor

(Hadlington, 2008)

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Acknowledgments

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