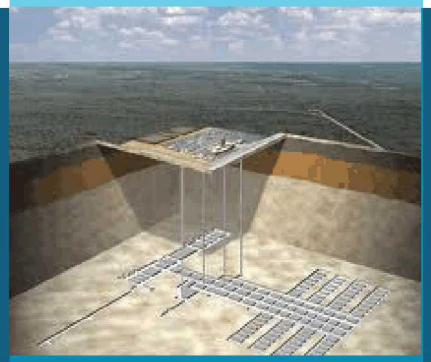
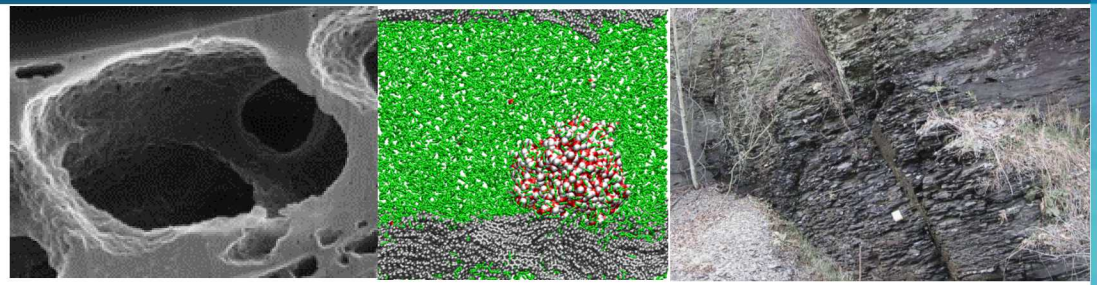
SAND2019-3084C

Nanogeochemistry of radionuclide reaction and migration in subsurface environments



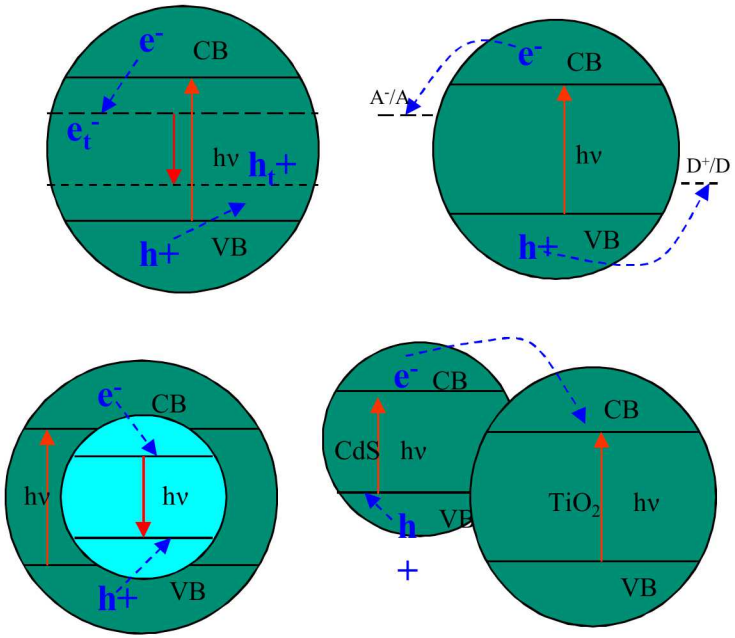


PRESENTED BY

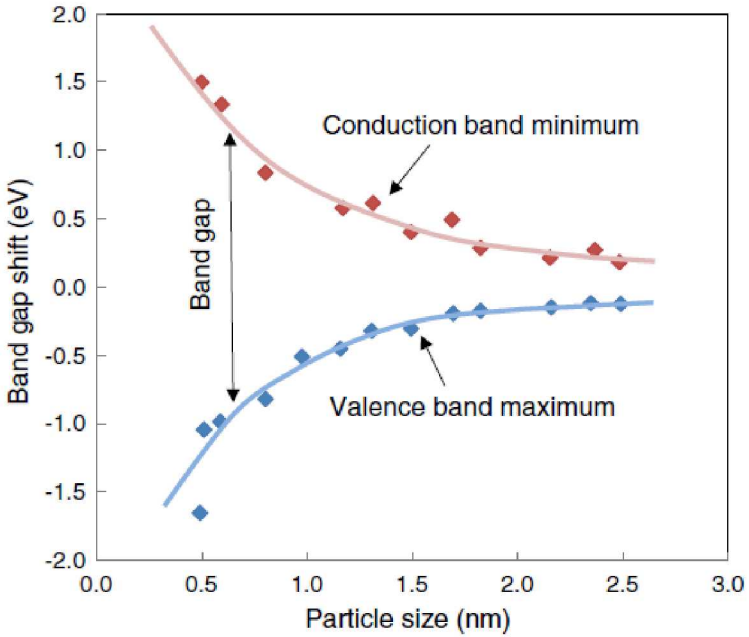
Yifeng Wang

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Nanoscience: Size-Dependent Material Properties

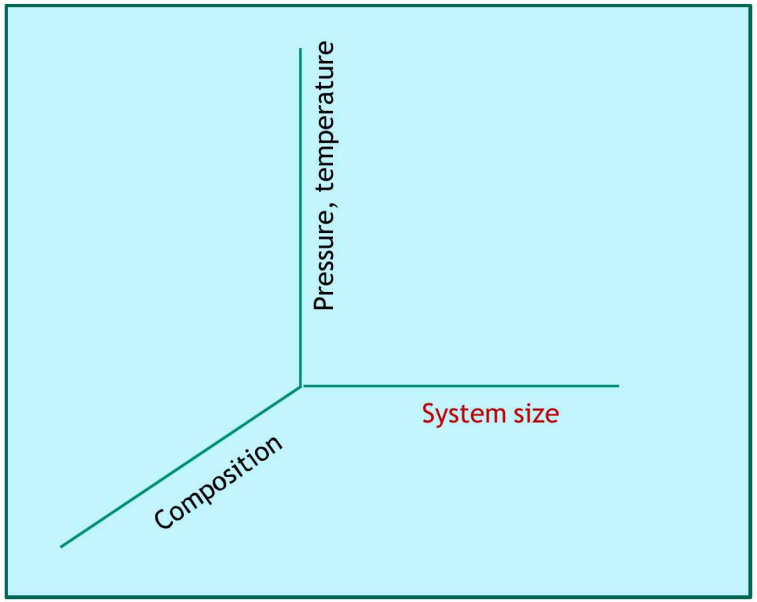


Photophysical/Photochemical Processes in Semiconductor Nanoparticles
(Roduner, 2006)



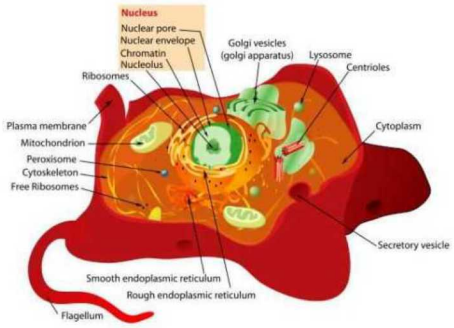
Size-dependent CdS band gap
(Lüning et al., 1999, Sold State Communication)

Nanogeochemistry



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

Rule of thumb: <100 nm

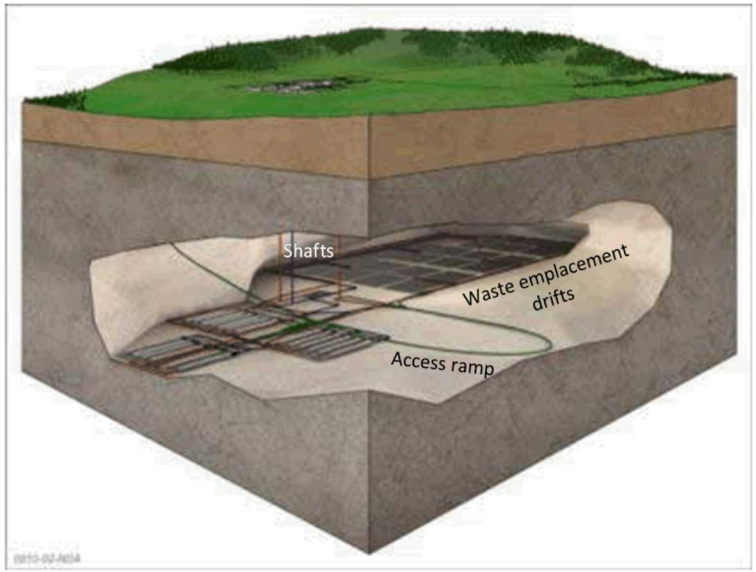


http://tamiport.hubpages.com/hub/Cell-Biology-Differences-Between-Prokaryotic-and-Eukaryotic-Cells#slide2150310

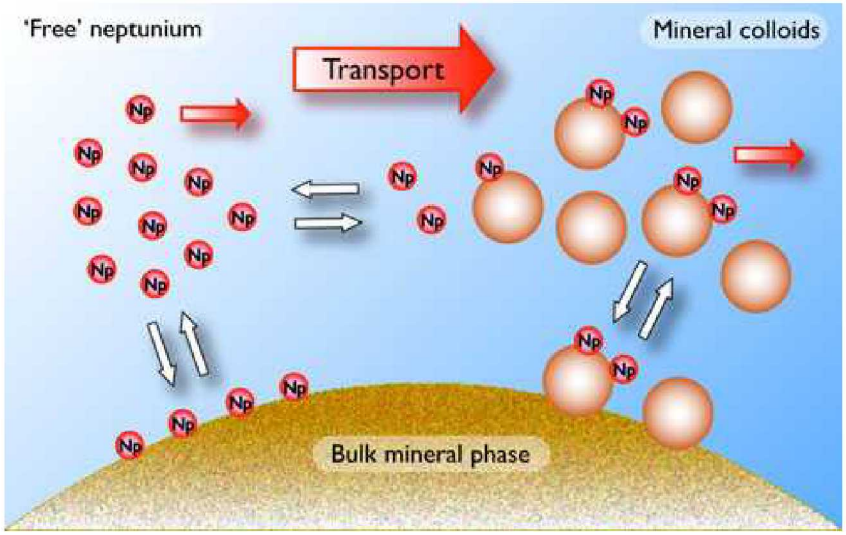
- Nanostructures
  - Nano solid phases
    - Nanoparticles
    - Nanorods
    - Nanosheets
    - Others
  - Nanopores (nanofluids)
    - Nanopores
    - Nanochannels
    - Thin water films
    - Grain boundaries
    - Mineral interlayers
    - Others
- Emergent properties (Size-dependent properties)
  - Phase stability
  - Surface chemistry
  - Reaction kinetics
  - Transport

Wang (2014) Chemical Geology

Colloid-facilitated radionuclide transport



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

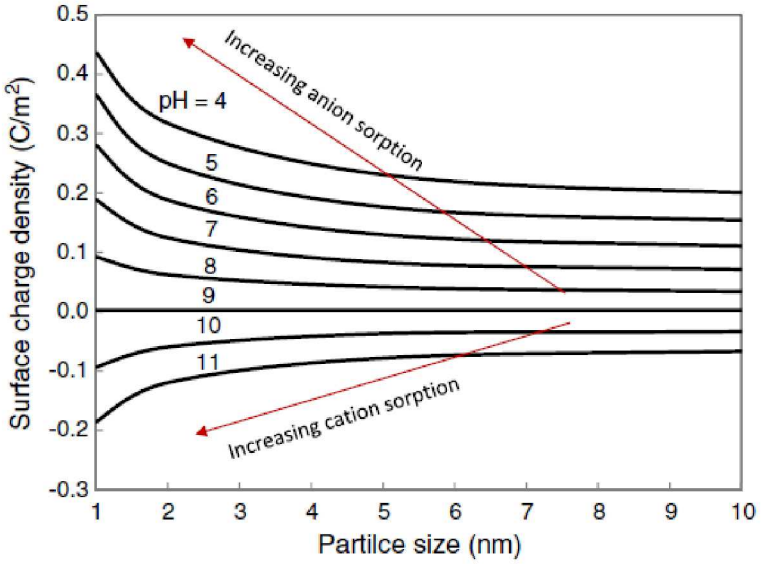


https://eesa.lbl.gov/radioactive-contamination-over-geologic-time/

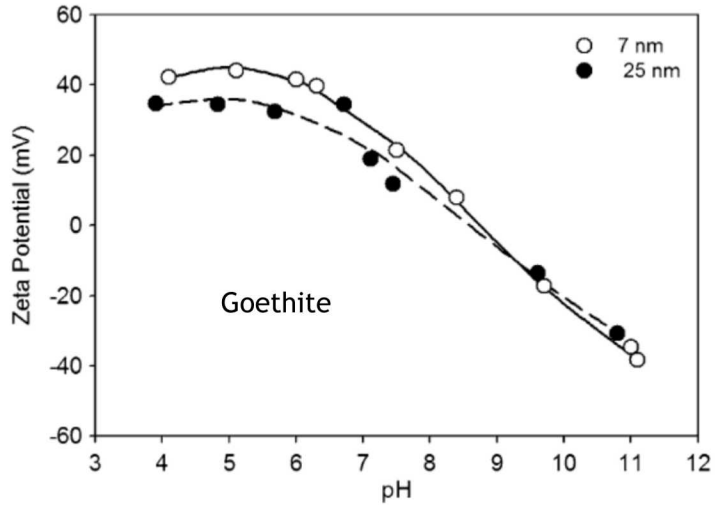
Key radionuclides:
Pu-239, Th-230, Am-241 – Strong interaction (colloids)
U-238, Np-237 – Moderate interaction
I-129, Tc-99 – Weak interaction (anions)

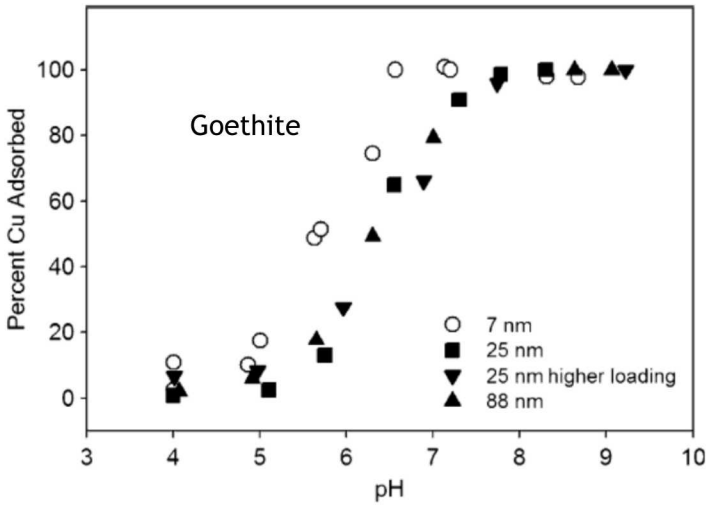
Colloids: ~1 - 1000 nm
Nanoparticles: ~1 - 100 nm

Surface charge and sorption capability of nanoparticles



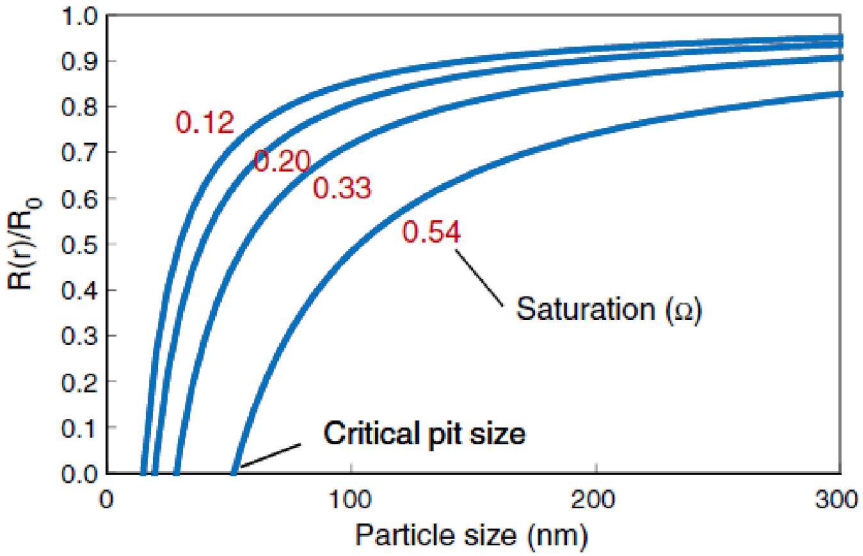
Surface charge density predicted by Monte-Carlo simulations for goethite nanoparticles (Abbas et al., 2008)

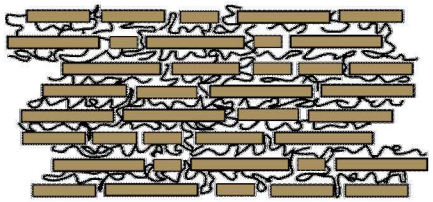


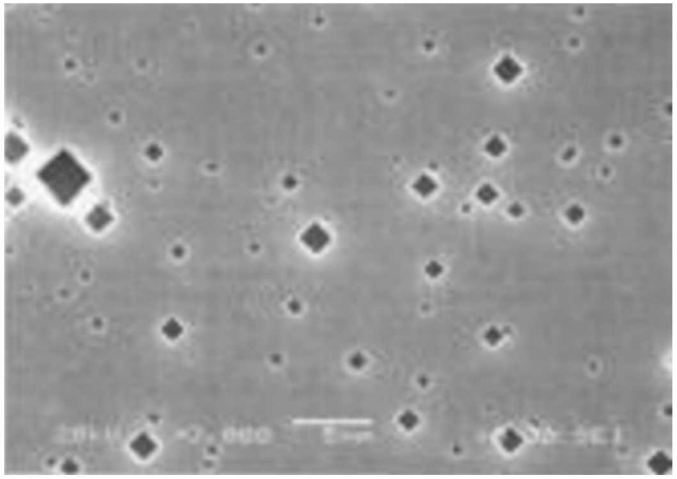


Madden et al., 2006, GCA

Self-inhibiting mechanism for nanoparticle dissolution



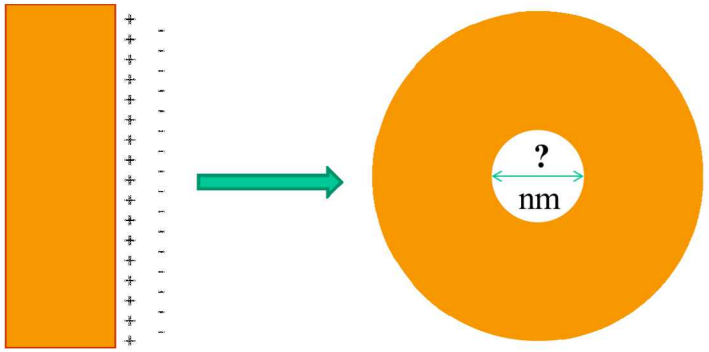


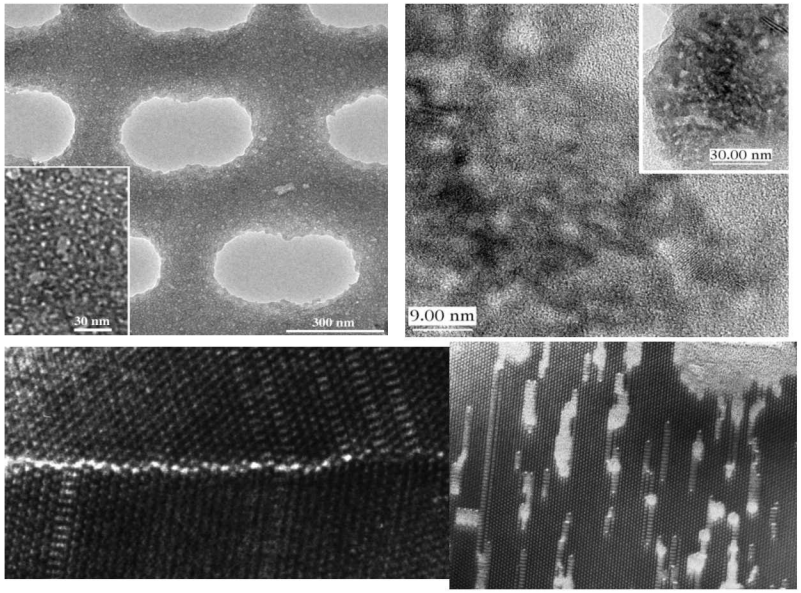


http://jes.ecsdl.org/content/150/9/B433/F1.large.jpg

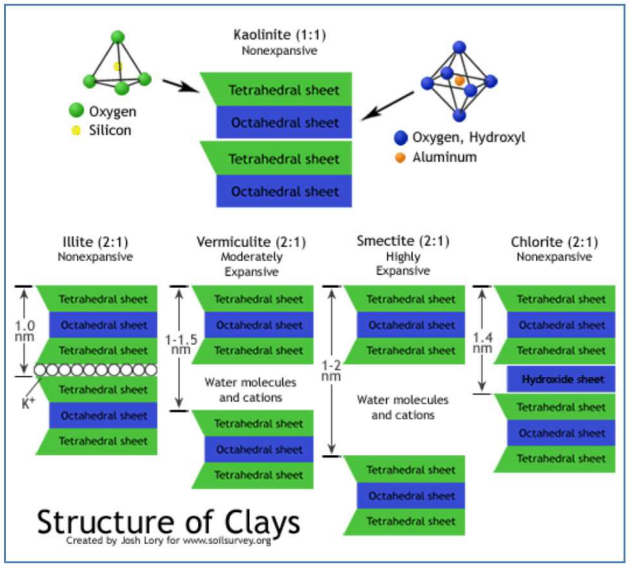
Self-inhibiting mechanism (Tang et al., 2004)
- Resistance to dissolution
- Persistence of true colloids

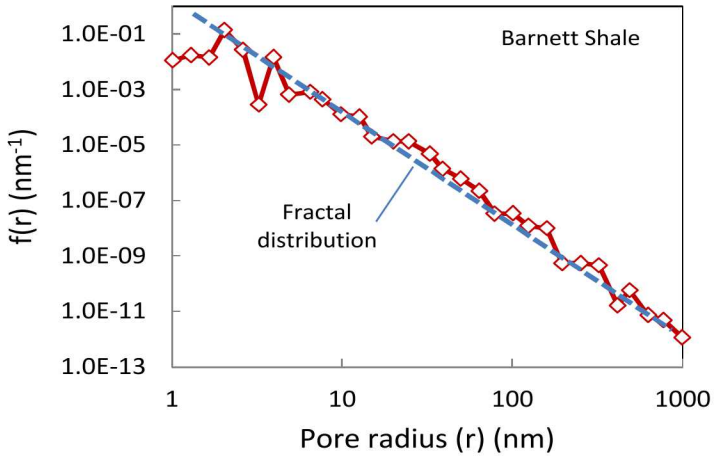
Effects of Nanopore Confinement





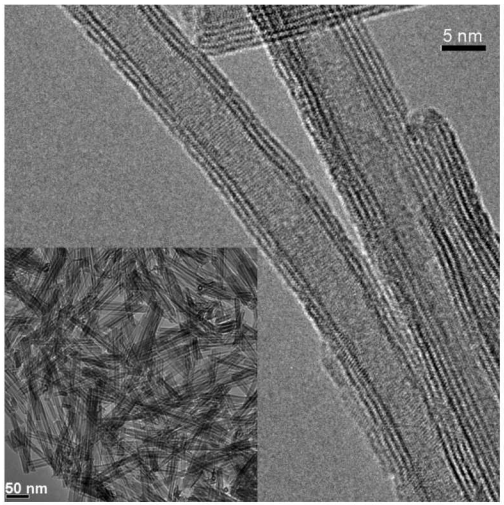
Wang et al., 2003, Geology

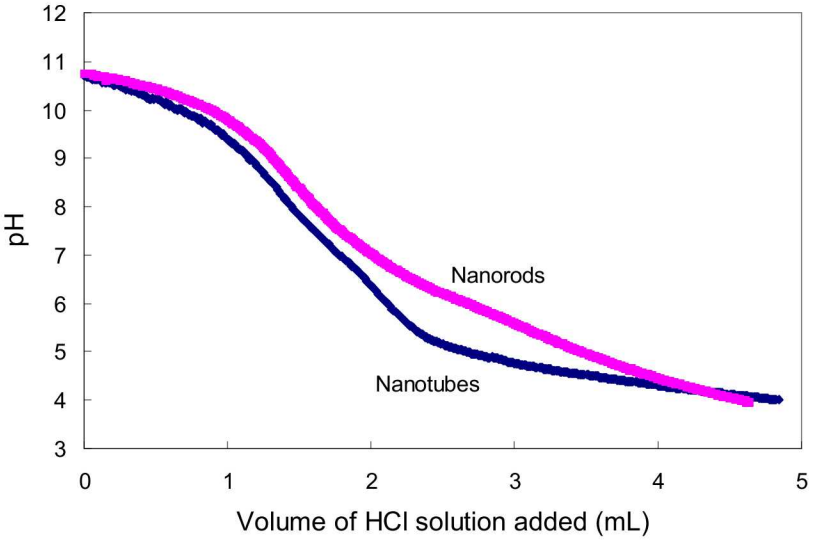


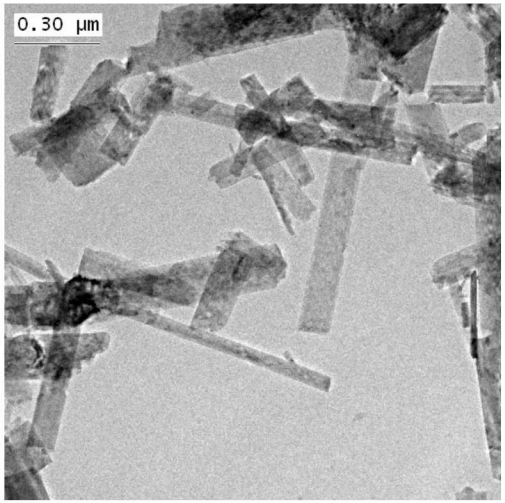


Clarkson et al. (2012)

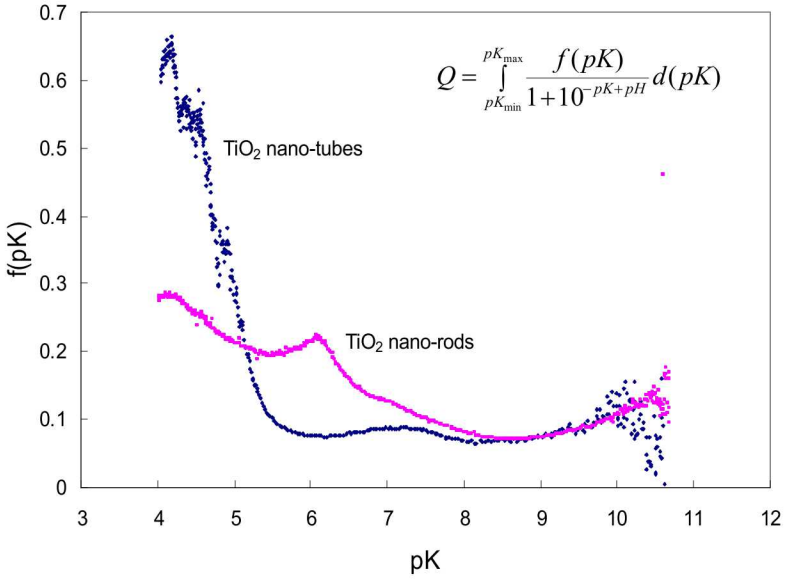
Model Systems for Studying Nanopore Confinement



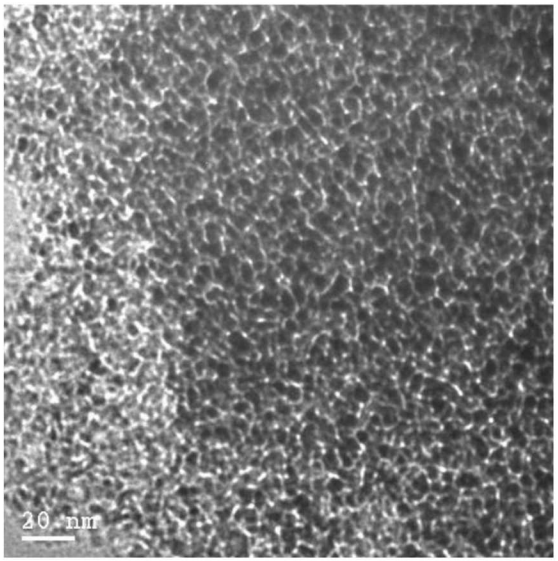


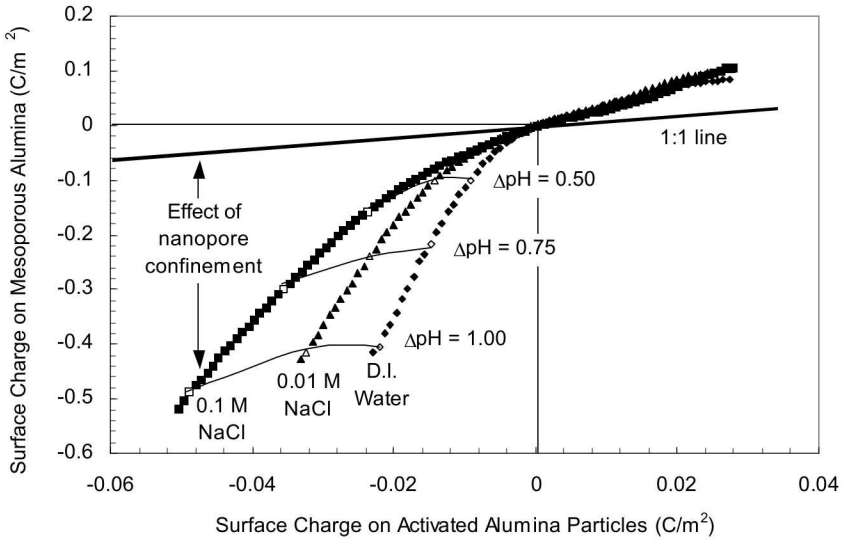


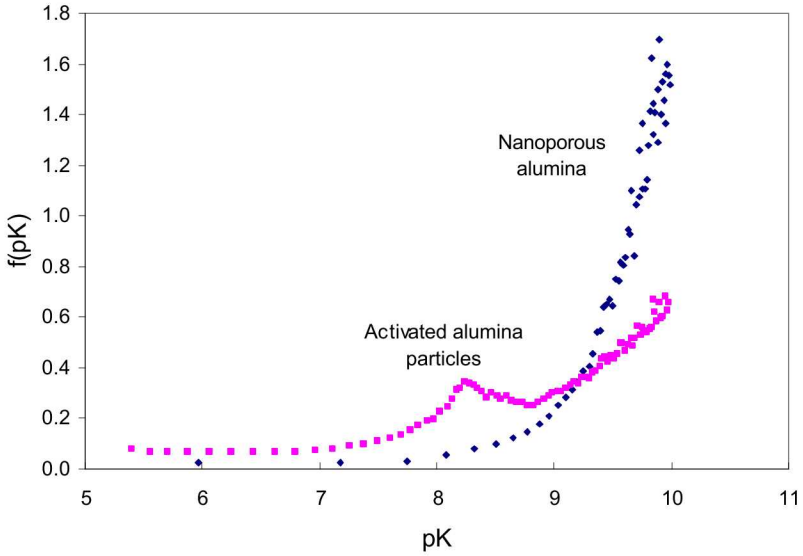
Wang et al. (2008)

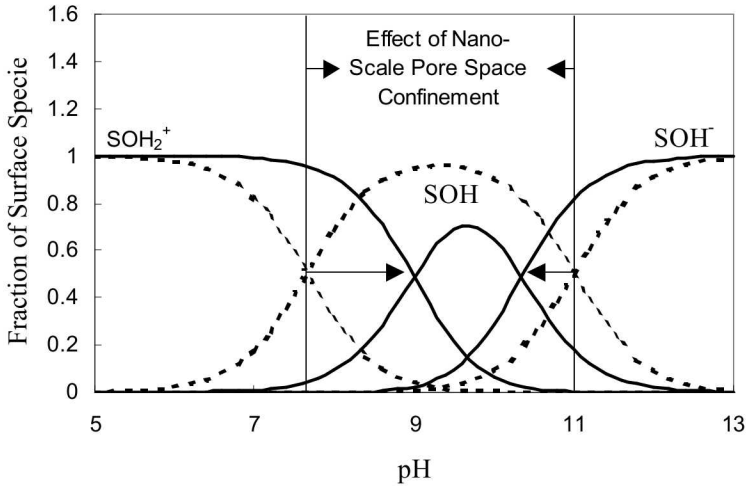


Model Systems for Studying Nanopore Confinement (cont.)



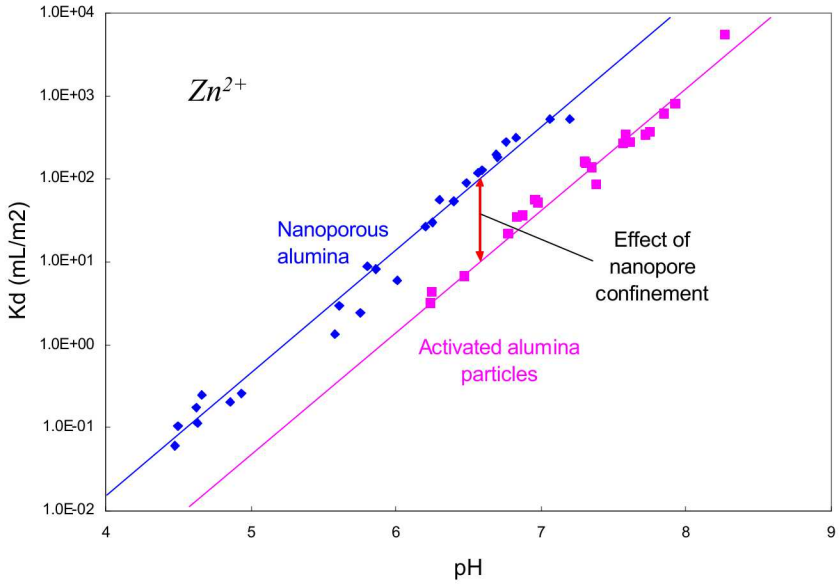


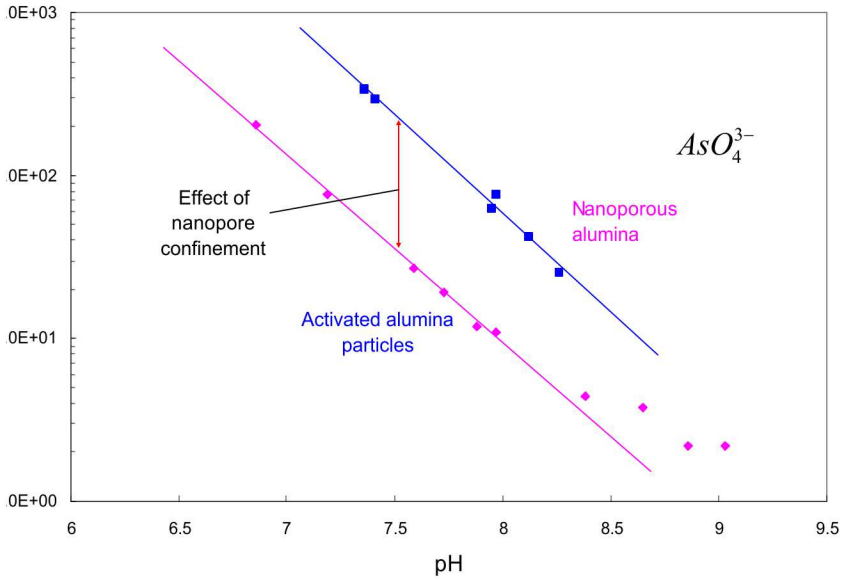




Wang et al., 2002, JCIS; 2003, Geology

Nanoconfinement and Ion Sorption

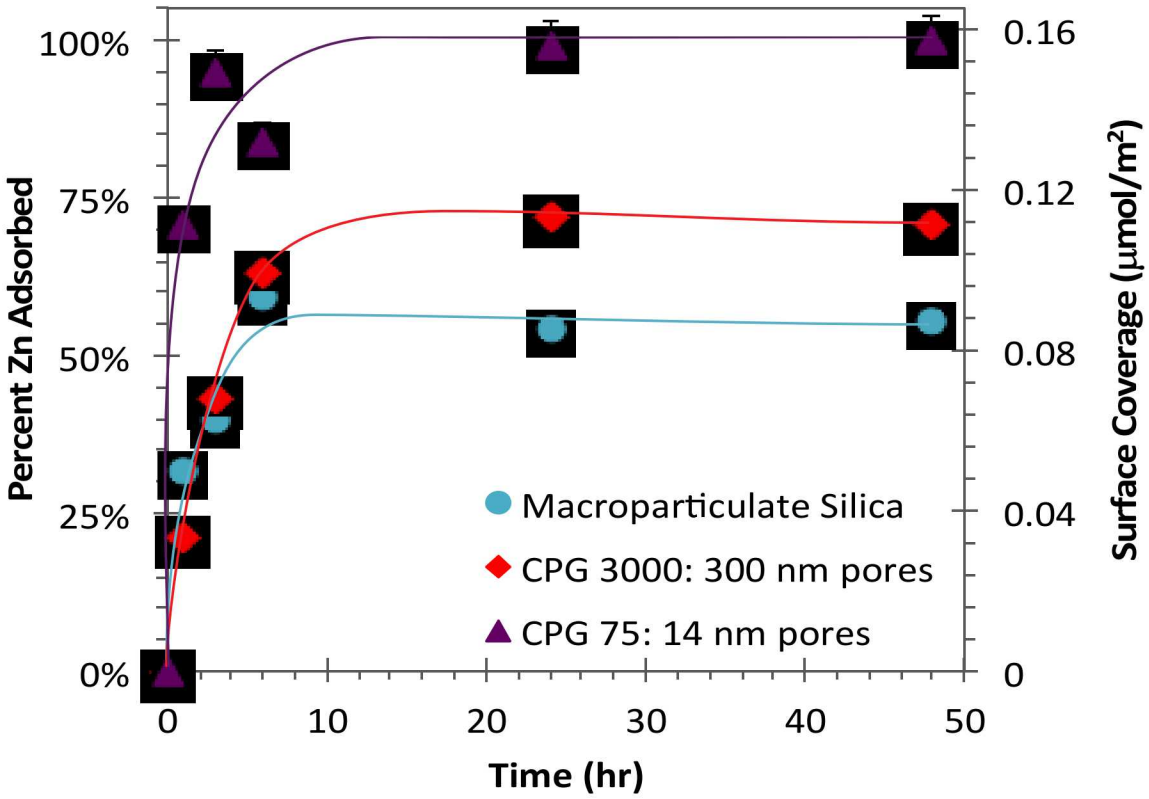




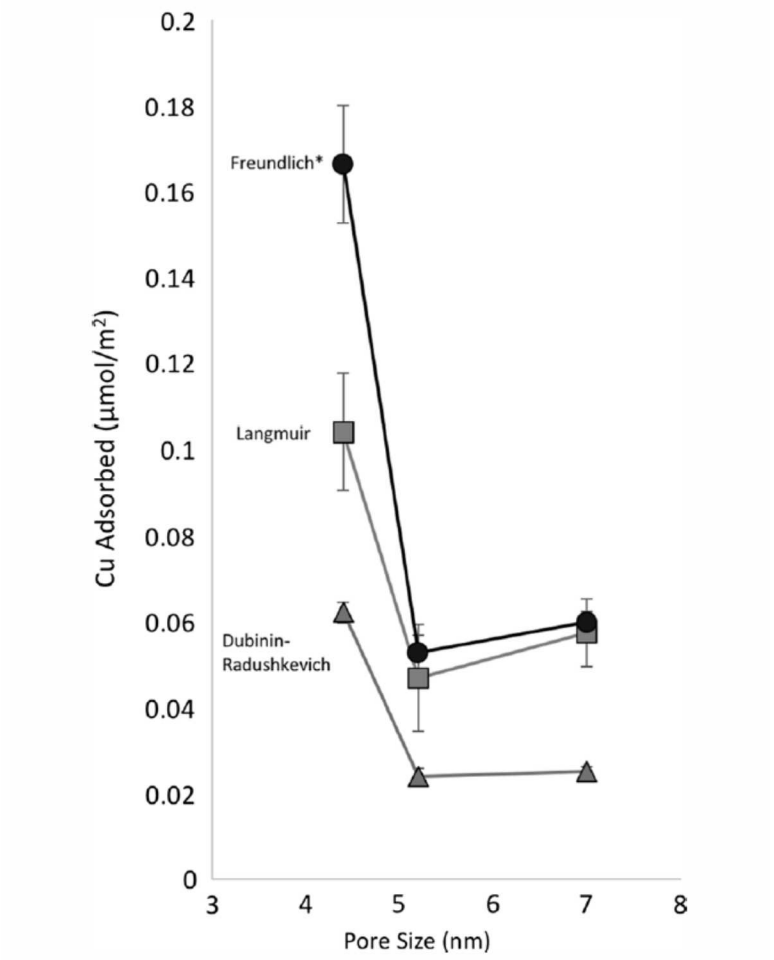
Nanopore confinement enhances ion sorption onto a solid-water interface for both cations and anions.

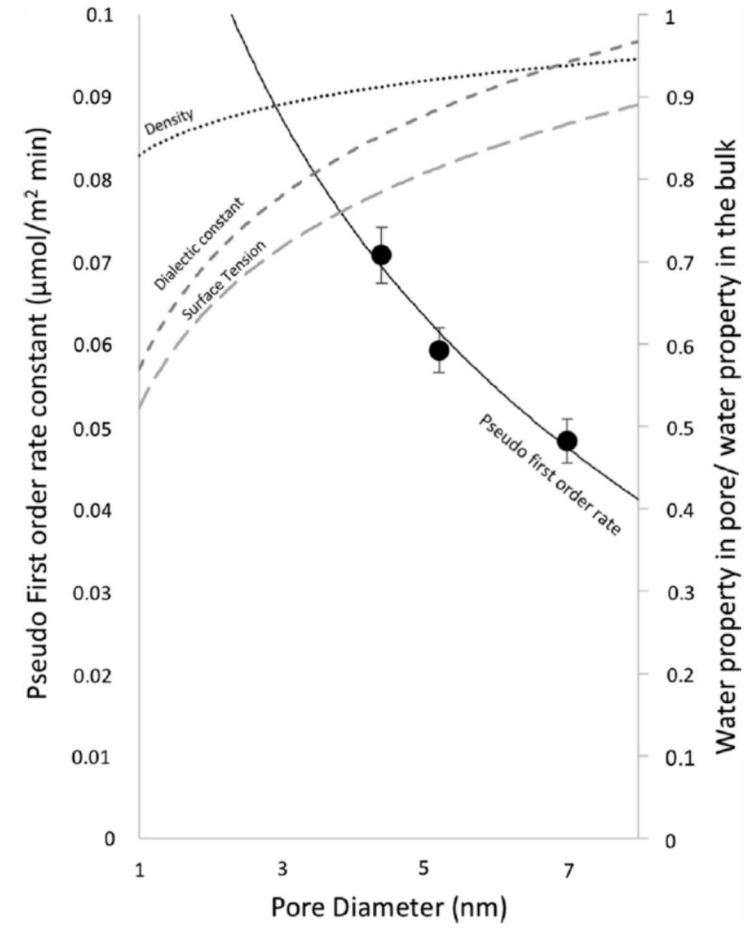
Wang et al., 2003, Mat. Res. Soc. Symp. Proc.; 2003, Geology

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

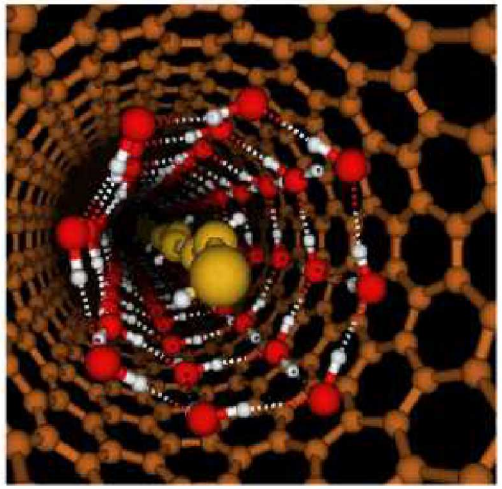


Cu(II) sorption onto mesoporous silica (Knight et al., 2018)

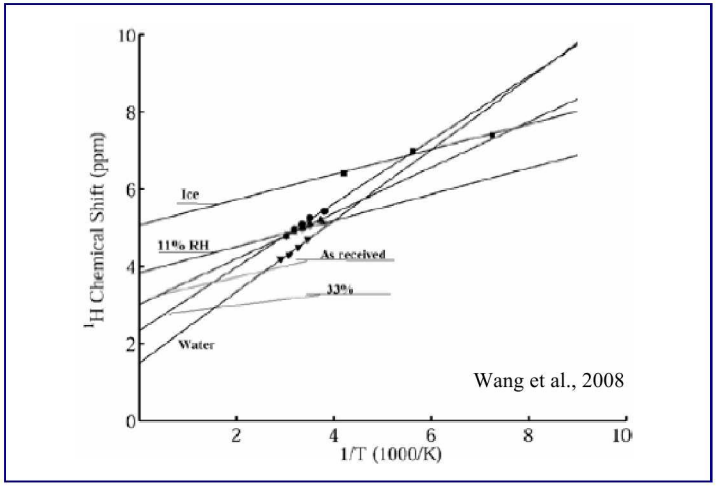




Effect of Nanopore Confinement on Water



Kolesnikov et al., 2004



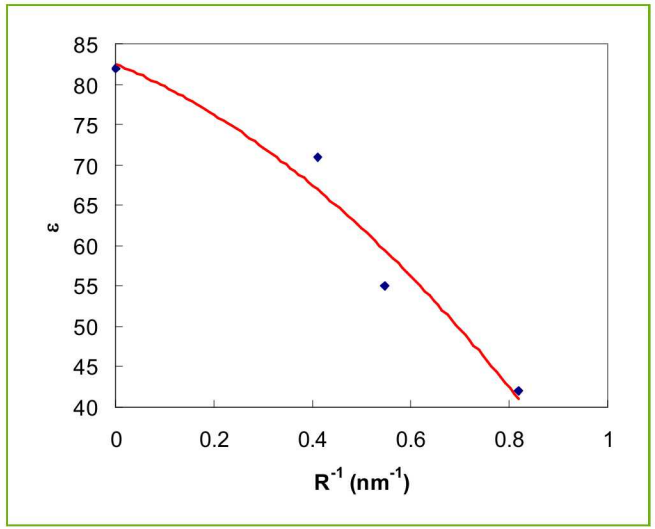
Postulations:

Water molecules in nanopores are more restrained.

$H_4SiO_4 = SiO_2(s) + 2H_2Opptn$

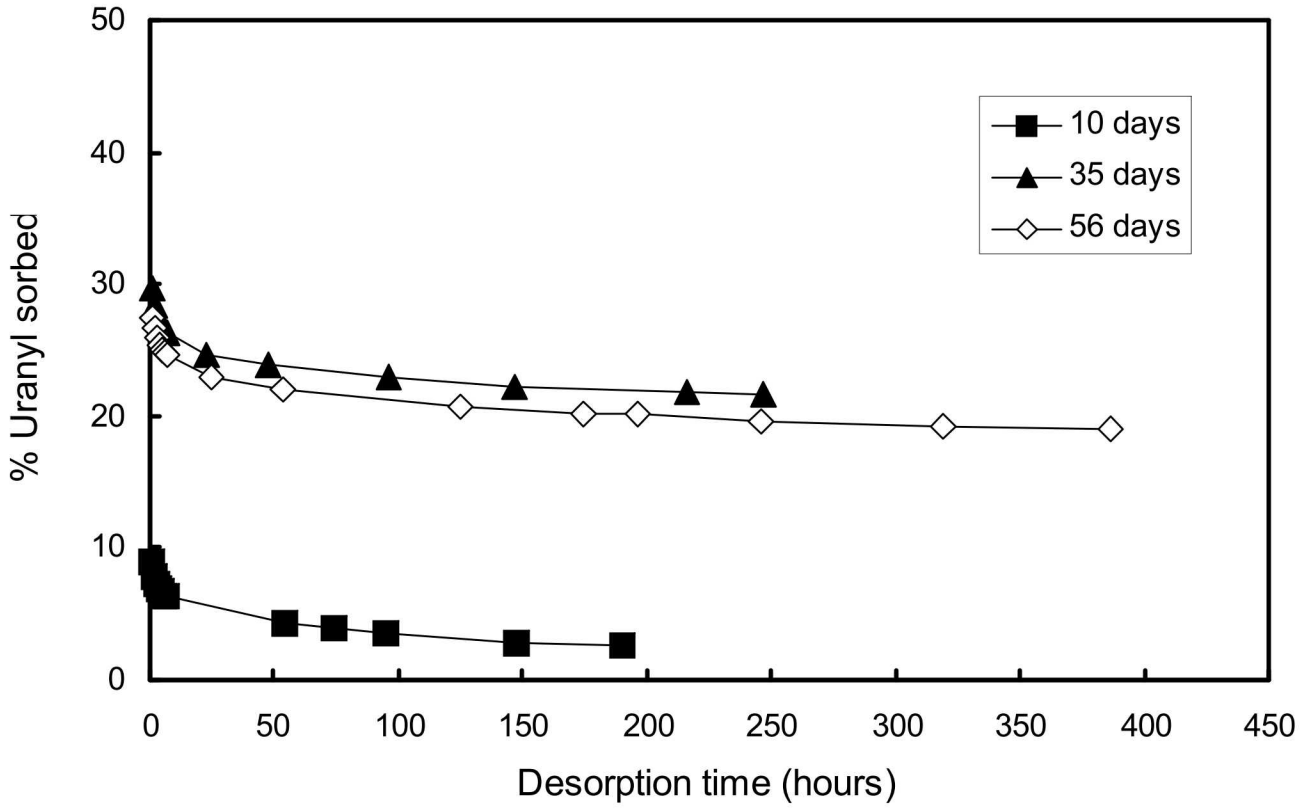
$M(H_2O)_n^{z+} = M^{z+} + nH_2O$ inner sphere

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



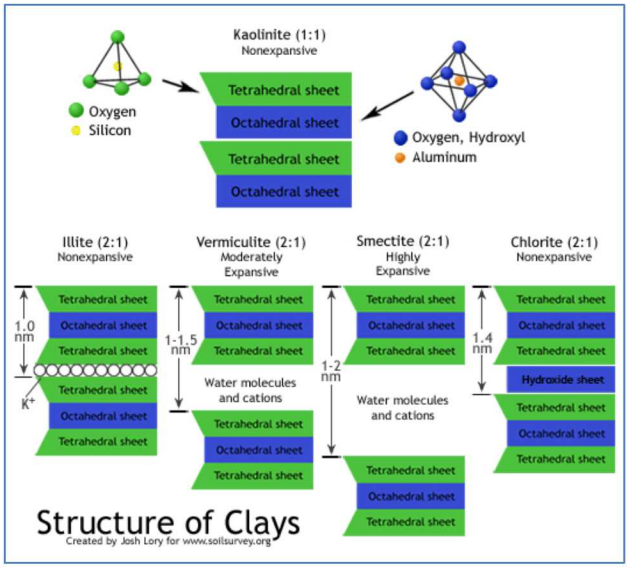
Senapati & Chandra, 2001, J. Phys. Chem.

Uranyl Desorption from Synthetic Porous Goethite

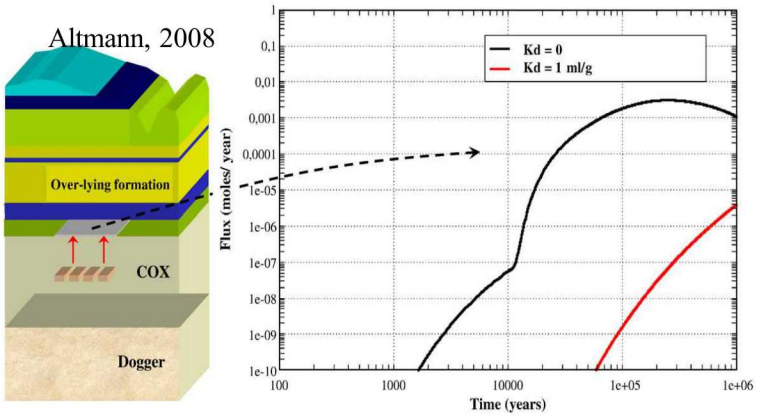


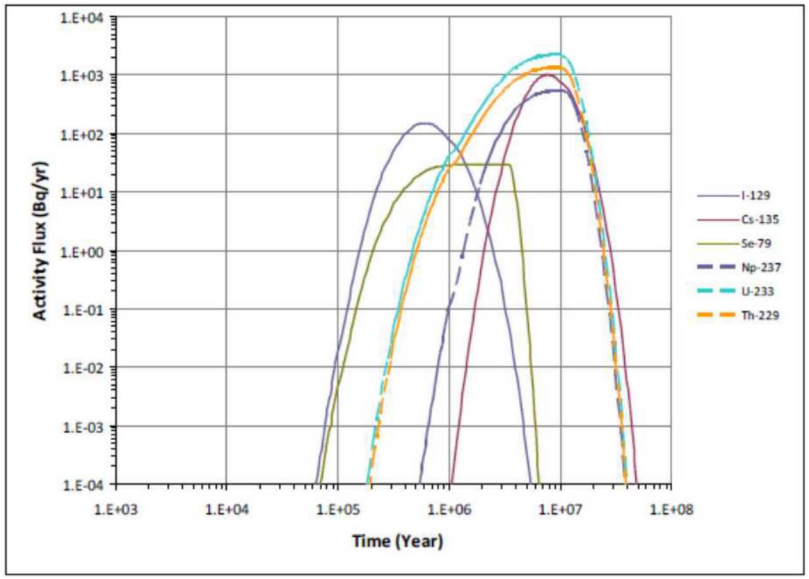
Wang et al., 2003, Geology

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



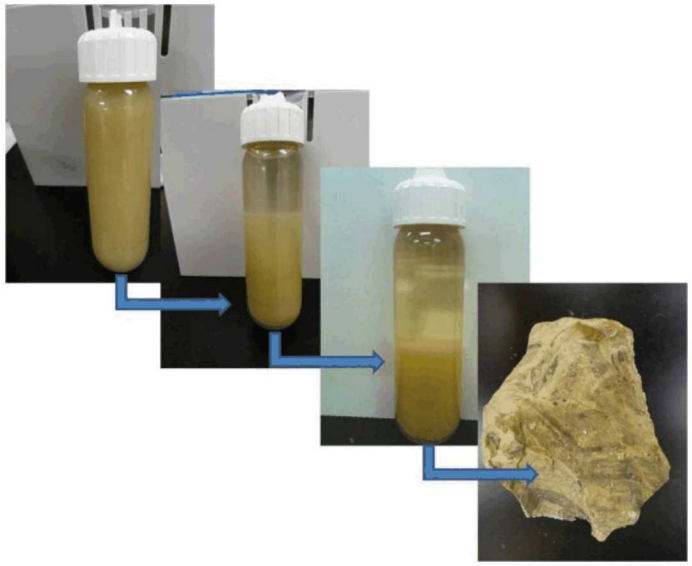


Generic clay repository

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

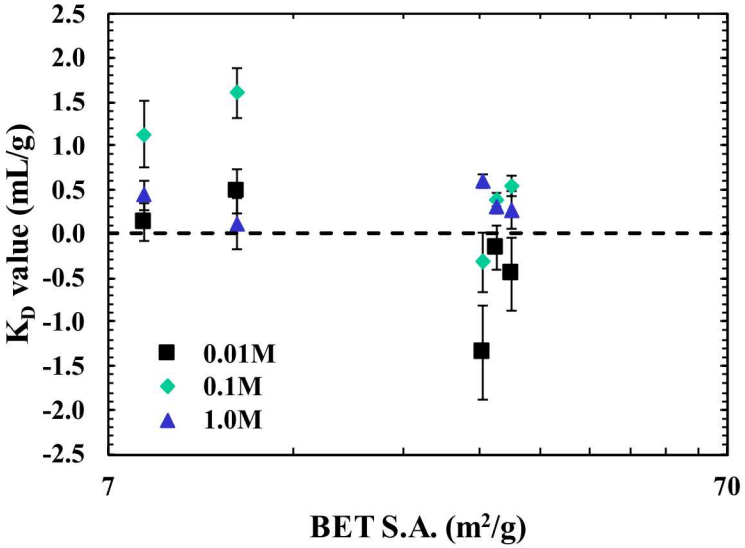
Concentration (M)	NaCl	NaBr	KCl
1.0	X		
0.1	X	X	X
0.01	X		

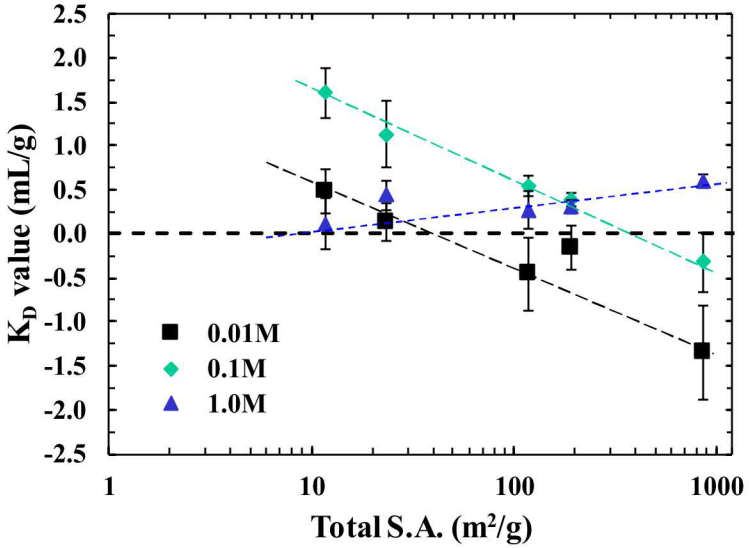
Iodide uptake is dependent on ionic composition of swamping electrolyte.

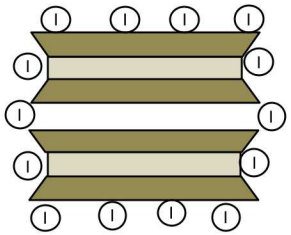
		CEC meq/100g	K_D [mL/g] (Std. Dev.)		
			NaCl	NaBr	KCl
Layered	Kaolinite	4.61	1.61 (0.28)	0.02 (0.63)	-0.01 (0.22)
	Ripidolite	6.03	1.13 (0.38)	-0.16 (0.72)	-0.31 (0.17)
	Illite	27.61	0.54 (0.12)	0.13 (0.002)	-0.50 (0.24)
	Illite.Smectite	30.39	0.38 (0.08)	-0.01 (0.11)	-0.49 (0.11)
	Montmorillonite	151.92	-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)

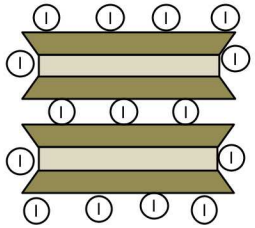
All electrolytes at 0.1M

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

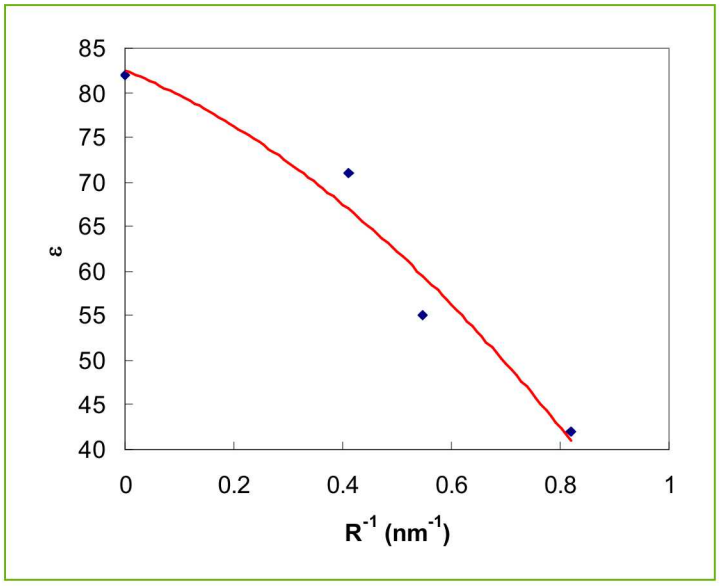


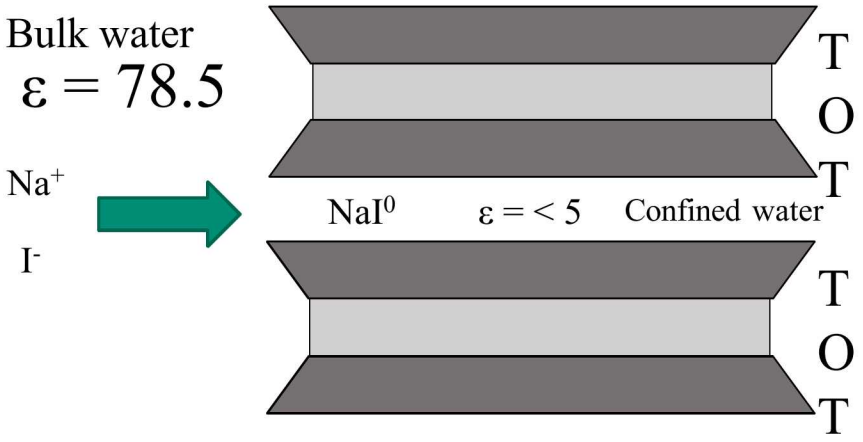




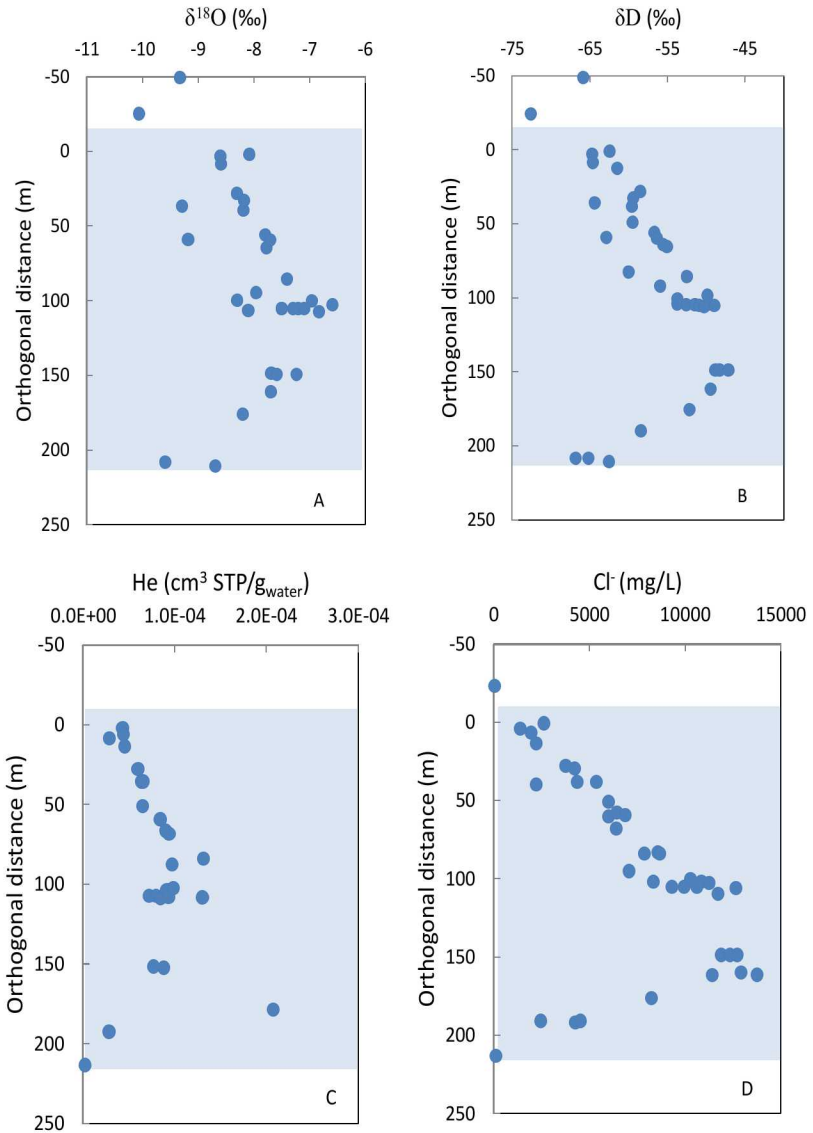


Data is consistent with ion pair formation caused by reduced dielectric constant of confined water.





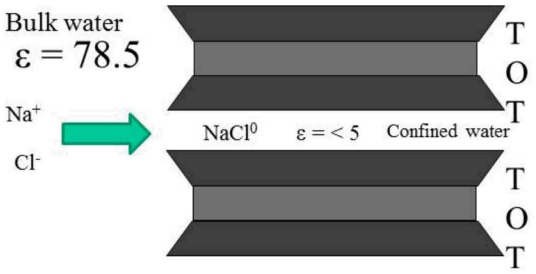
Senapati & Chandra, 2001, J. Phys. Chem.



Tracer measurements at Mont Terri site (Switzerland)

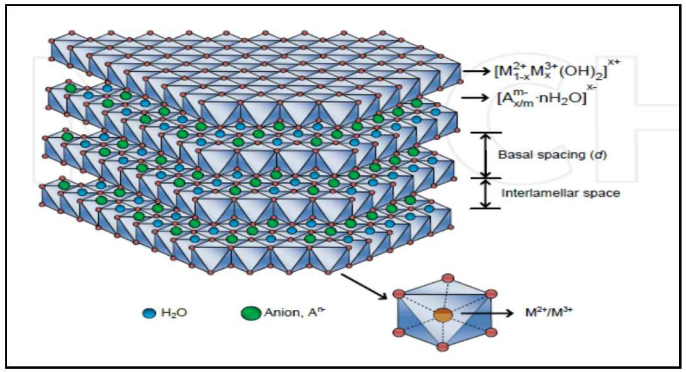
Mazurek et al. (2011)

- 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.

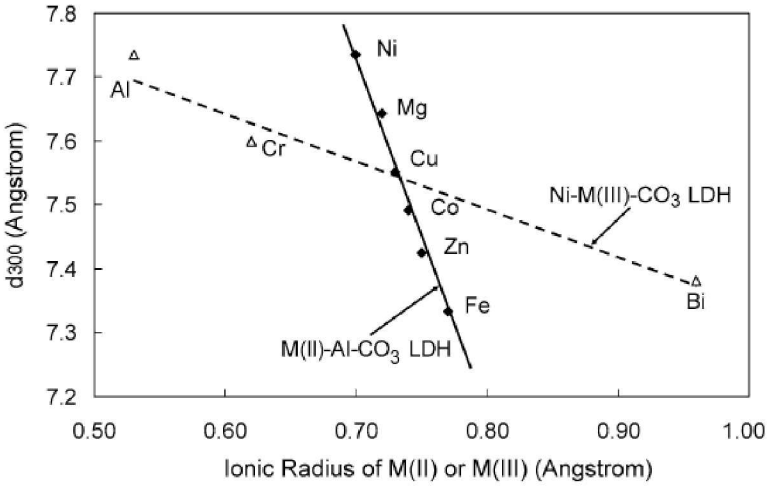


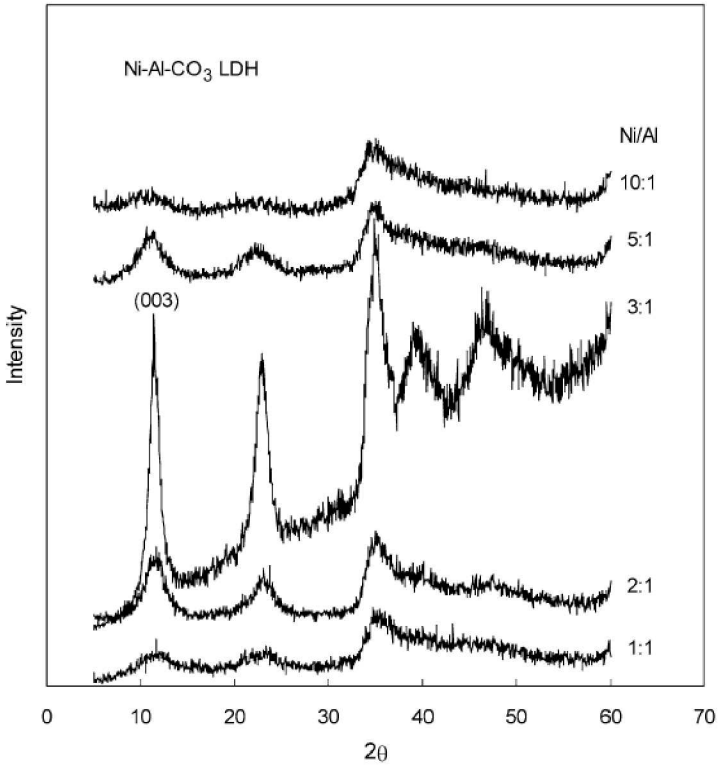
Miller et al. (2015)

Manipulation of Layered Double Hydroxide (LDH) Structure



Tronto et al. (2013)

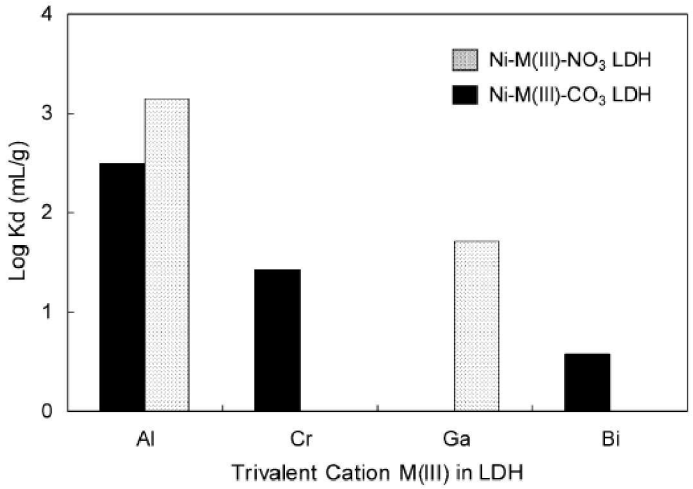


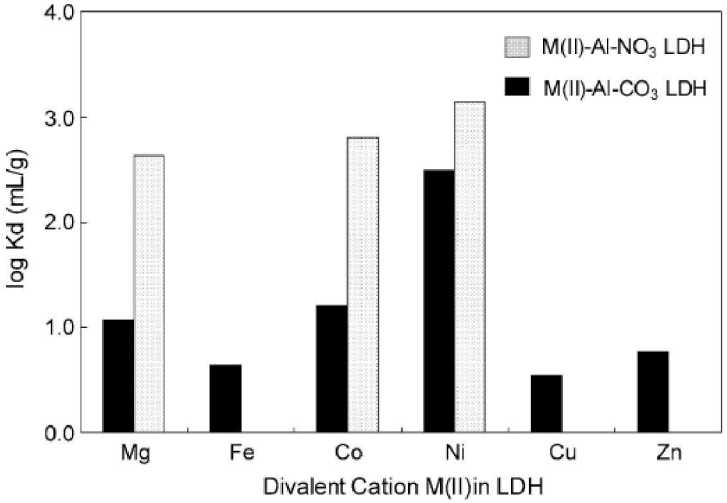


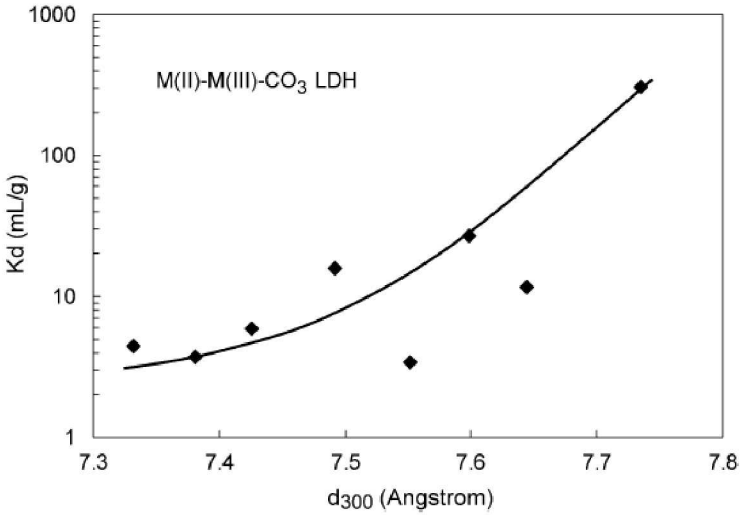
Wang and Gao (2006)

Sandia National Laboratories

Pertechnetate Sorption on LDHs



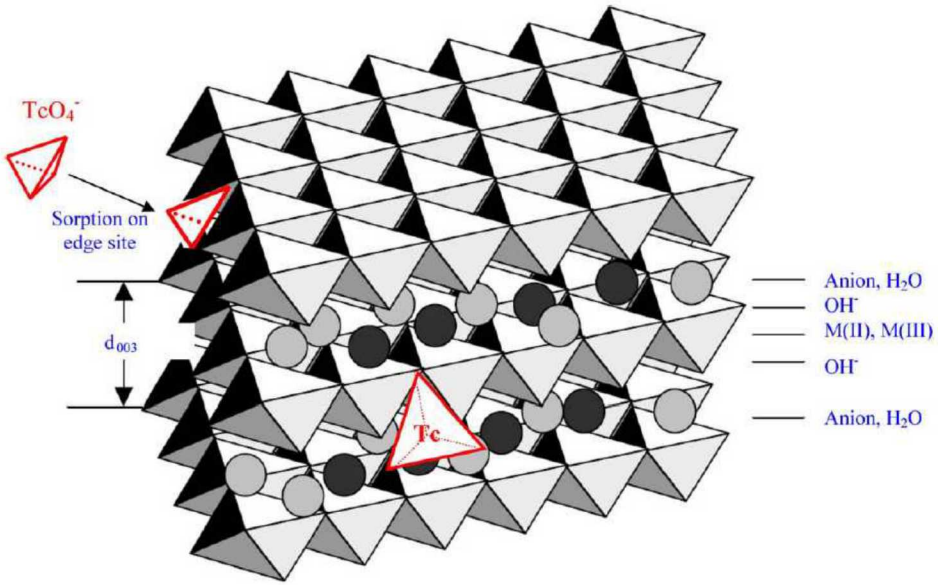




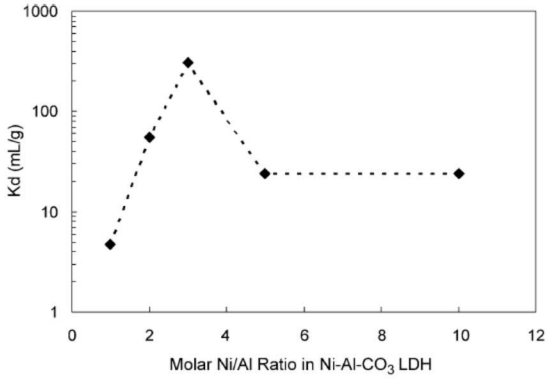
Further expansion of interlayer spacing (by intercalating SO_4^{2-}) diminishes sorption (Kd = ~0).

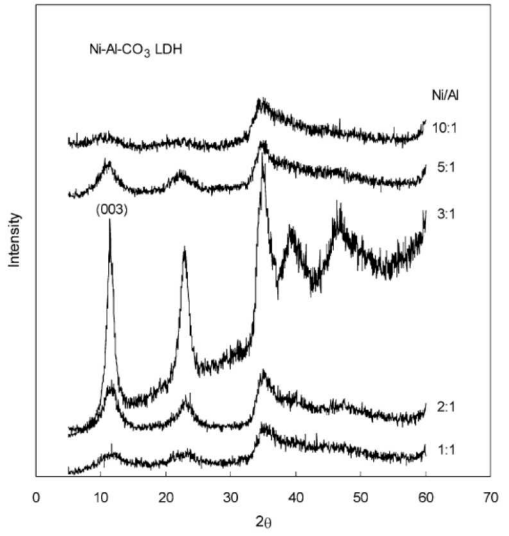
Wang and Gao (2006)

Pertechnetate Sorption on LDHs (cont.)



Wang and Gao (2006)





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!

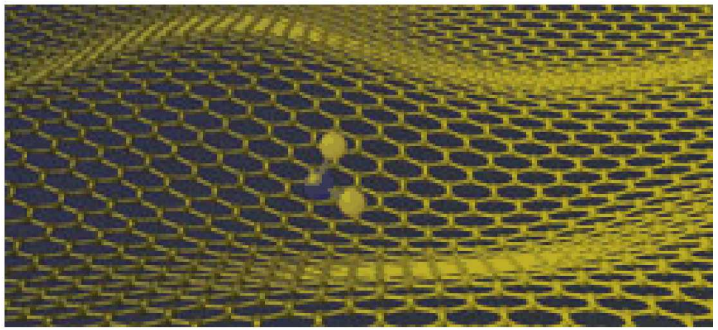
- Measurements on "isolated", unconfined surfaces may not be representative of actual geologic materials.

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:

A. Miller
H. Gao
Ed Matteo
J. Kruichak
Y. Xiong
C. Bryan
J. Brinker
T. Ho
G. Xu
H. Xu (Univ. of Wisconsin)
M. Ding (Los Alamos National Lab)

Funding sources:

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This research is supported by DOE LDRD program, DOE OCRWM S&T Program, DOE-UFD (SFWST) program, NETL, and the National Science Foundation.