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Nanogeochemistry: Nanophases, Nanostructures and Their Reactivity in Natural Systems

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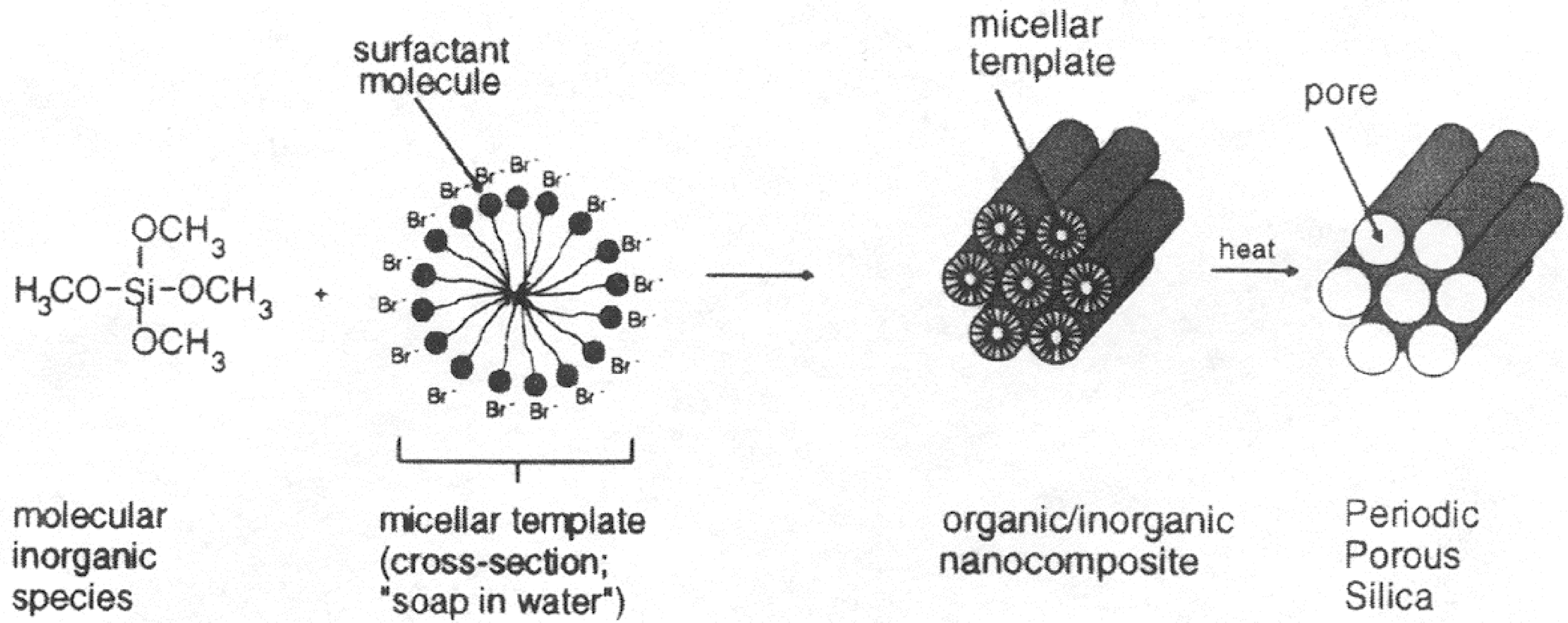
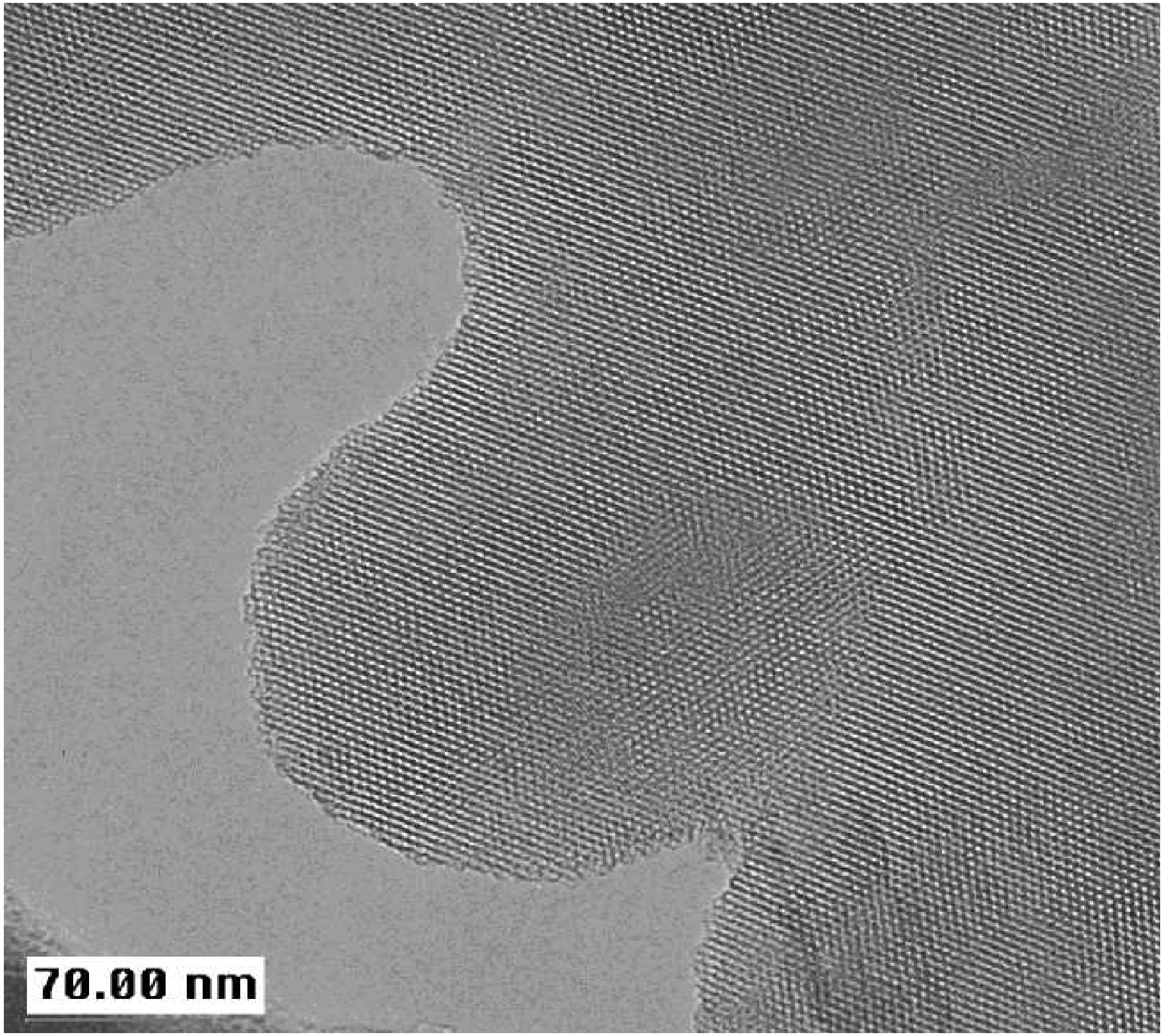


surfactant molecule
micellar template
pore
OCH3
H3CO-Si-OCH3
OCH3
+
Br⁻
heat
molecular inorganic species
micellar template (cross-section; "soap in water")
organic/inorganic nanocomposite
Periodic Porous Silica

Mesoporous Silica



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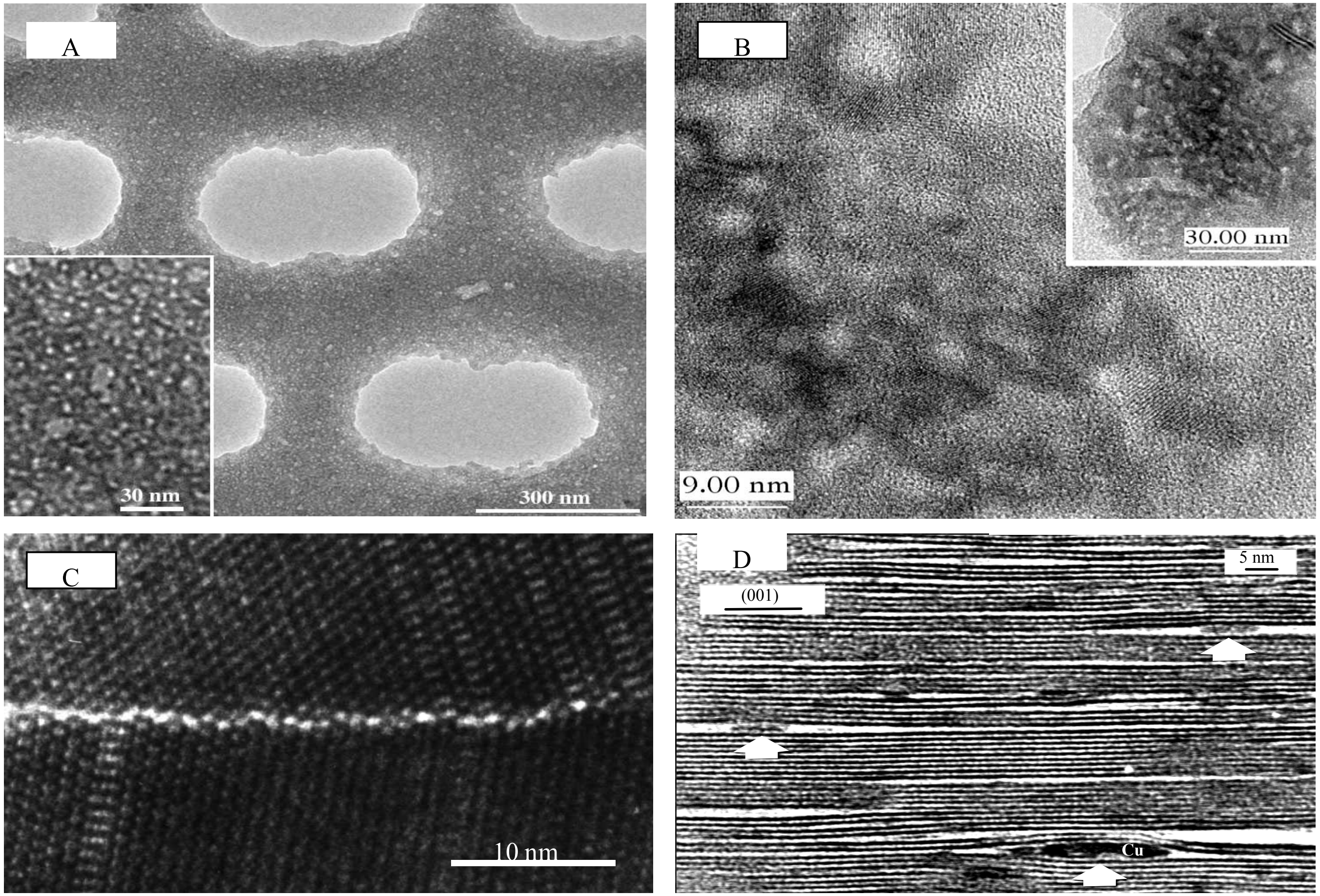
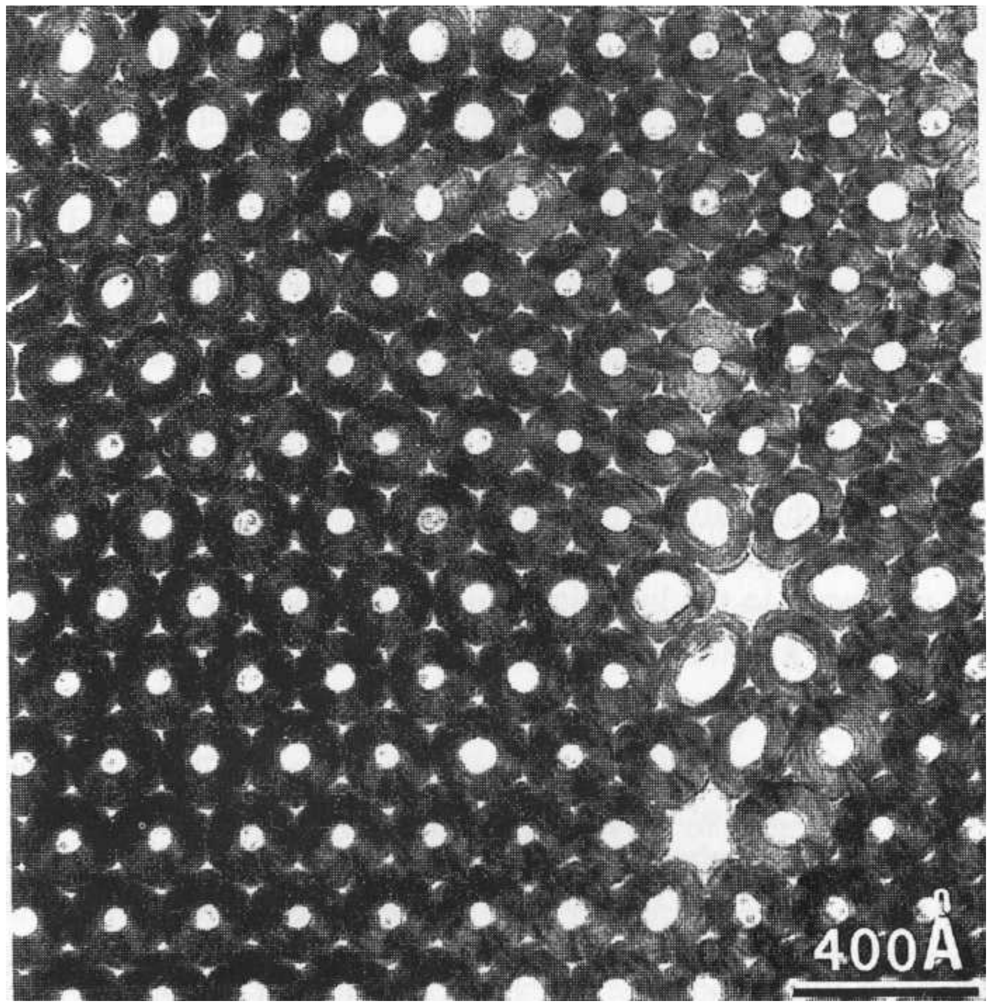
Nanopores in Geologic Materials

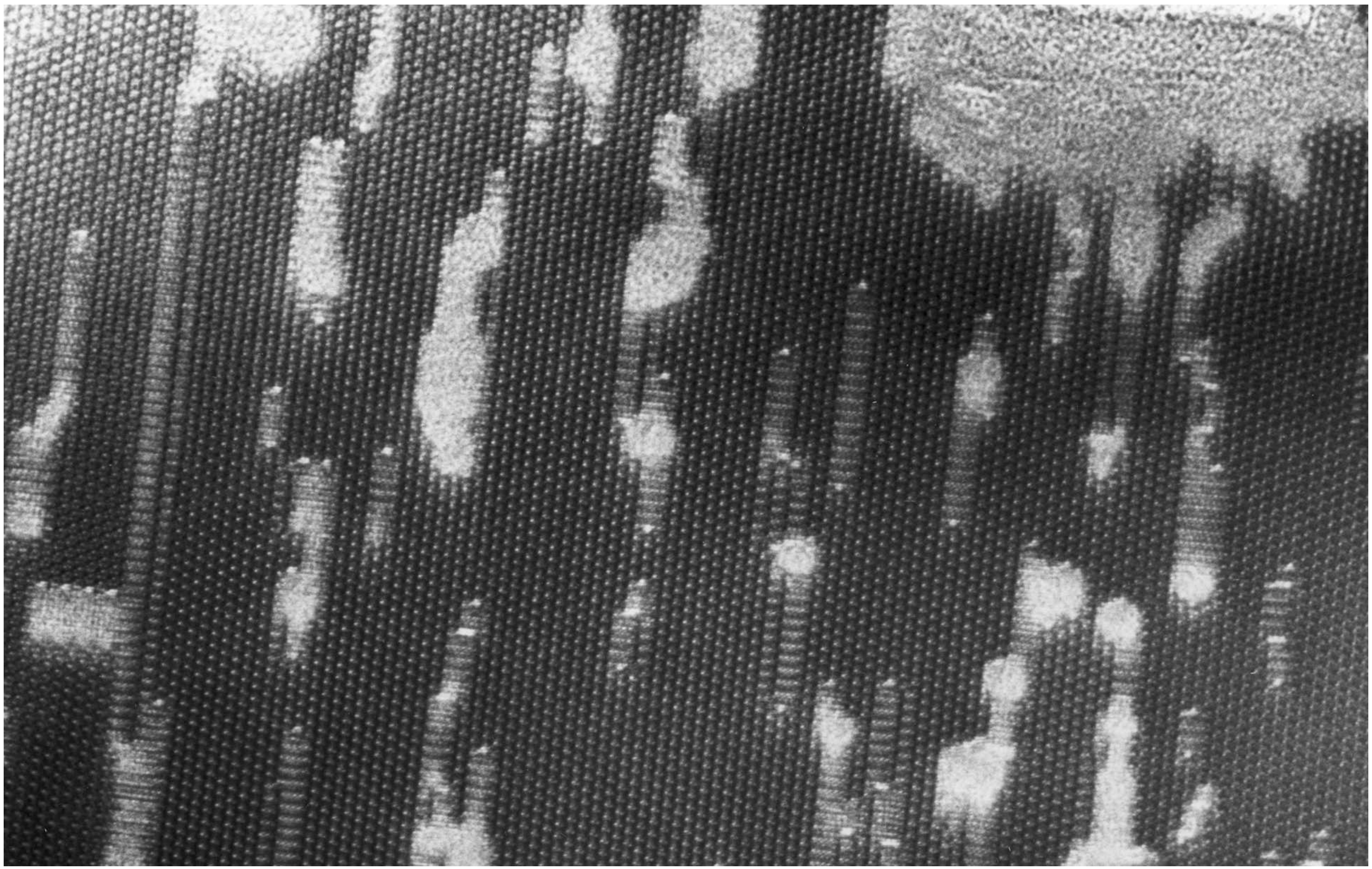


Natural Nanotubes: Chrysotile



Baronnet, 1992

Nanopores at Reaction Front of Amphibole Weathering



Nanopore Distribution in Geologic Materials

B-horizon soils (Görres et al., 2000):

< 100 nm	10 to 40% of total porosity
> 1 μm	> 60% of total porosity

Georgia kaolinite (Tardy and Nahon, 1985):

< 10 nm	~ 100% of total porosity

Surface area for a given pore volume is inversely proportional to the pore diameter. The contribution of nanopores to the total surface area in those materials is very high, probably over 90%.

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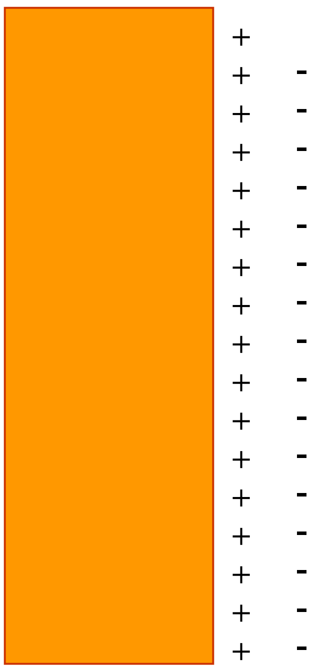
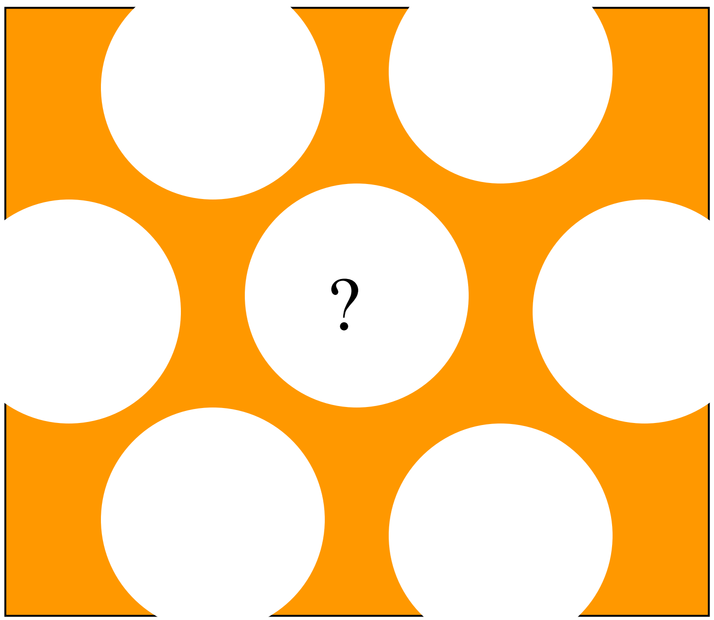
Electric Double Layer (EDL) in A Confined Environment



Unconfined



Confined

Hypothesis: Nanopore space confinement creates a different surface complexation environment, which would affect overall ion sorption on mesoporous materials.

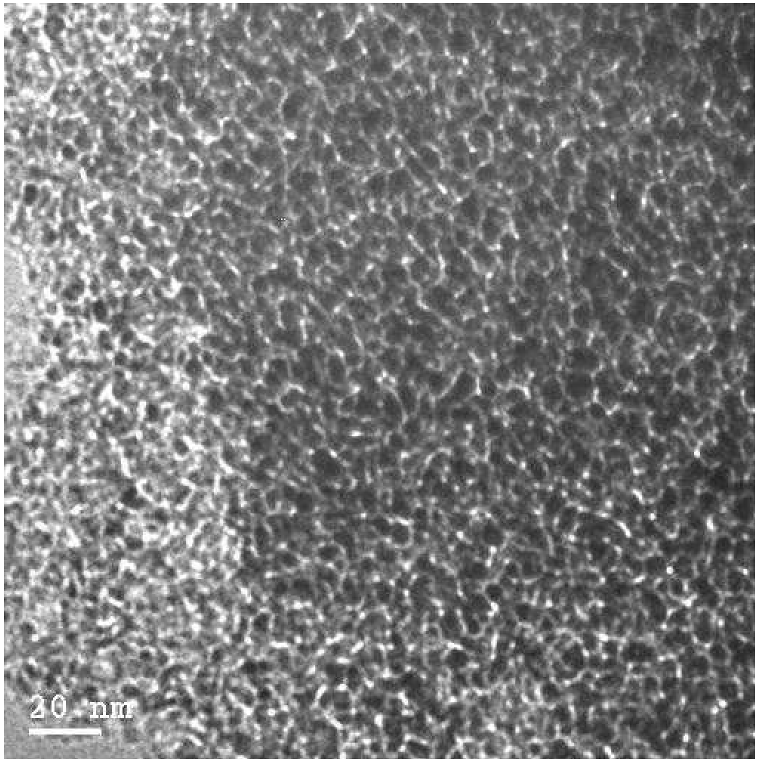
Methodology: pH titrations, sorption experiments

Materials Used in Experiments

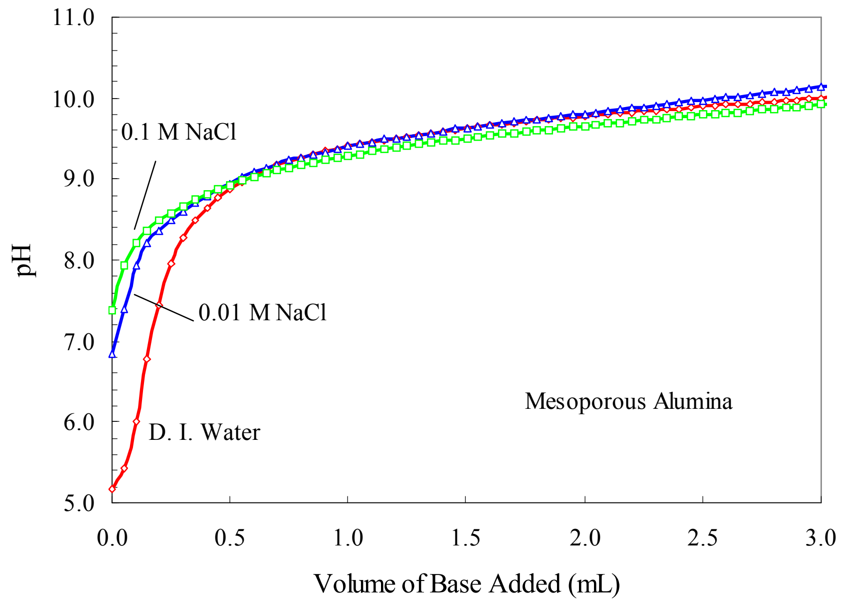
- Mesoporous alumina
  - Reported pore size: 6.5 nm
  - Surface area: ~ 284 m^2/g
- Activated alumina particles
  - Particle size: 80 - 200 mesh
  - Surface area: on the order of 118 m^2/g
  - Similar to mesoporous alumina in surface chemical composition and crystallinity

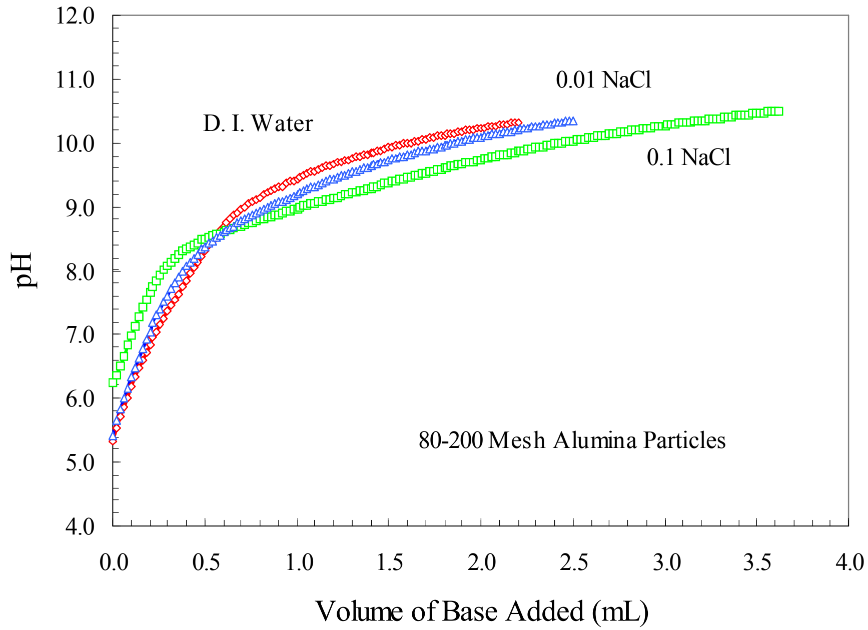
Mesoporous Alumina

- Worm-hole-like structures
- Pore size: ~ 2 nm x 10 nm x 10 nm
- Phase: γ–Al_2O_3



pH Titration Results

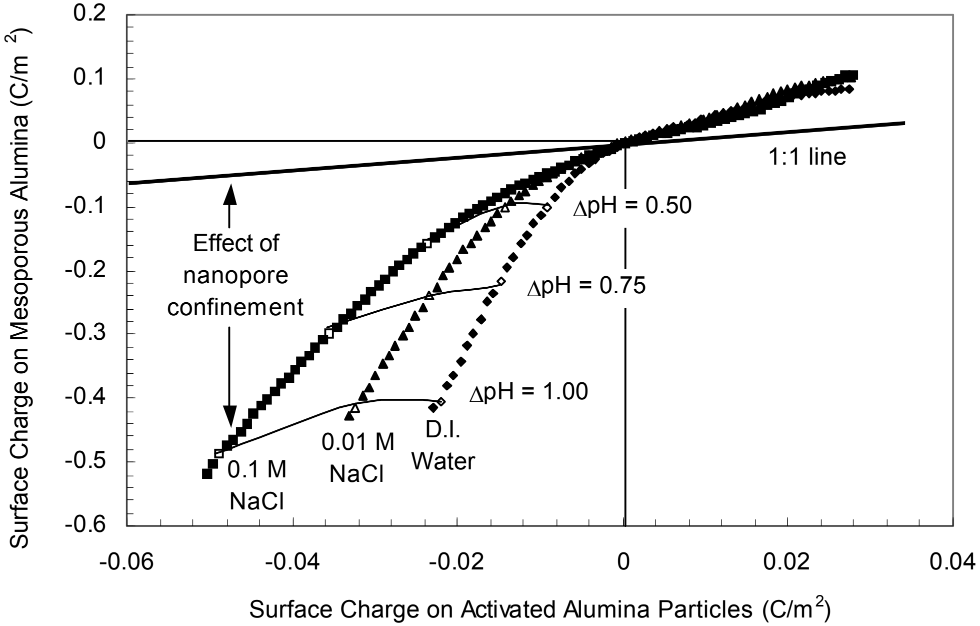




Point of Zero Charge (PZC):

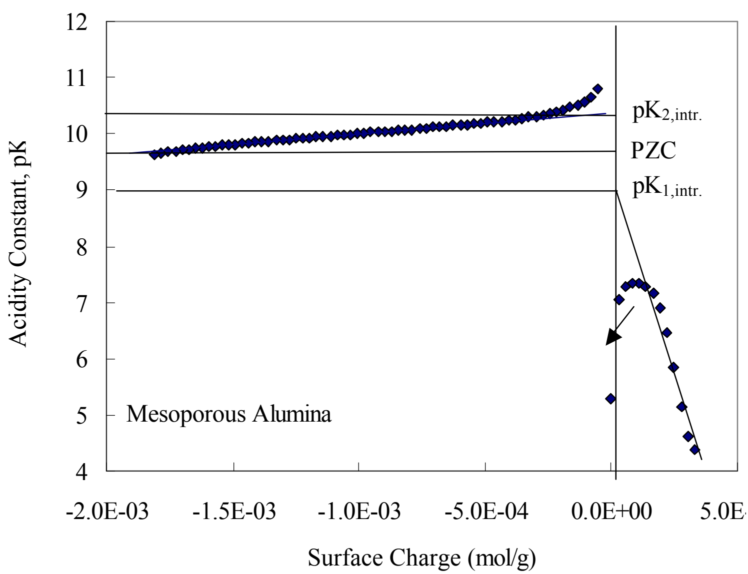
Mesoporous alumina: ~ 9.0
Activated alumina particles: 8.6
Reported data: 8.7 – 9.1

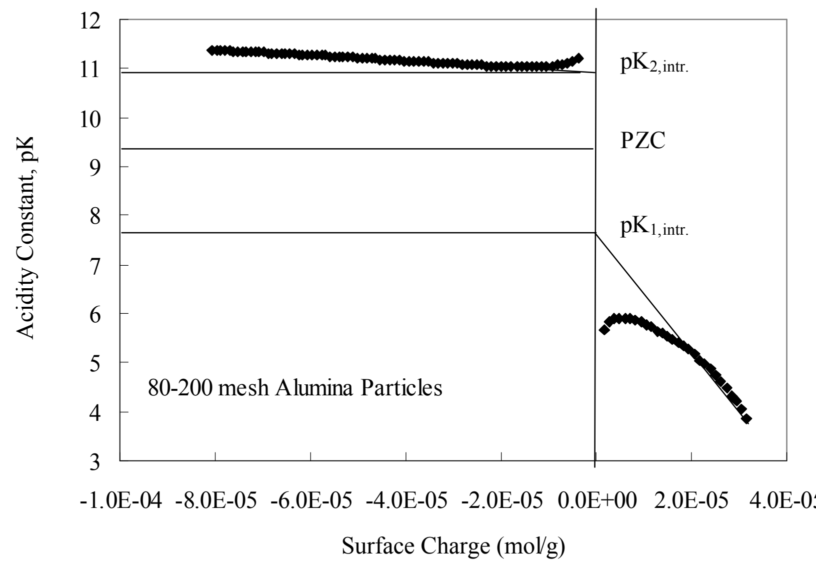
Surface Charges: Mesoporous vs. Non-mesoporous Materials



If the difference in surface charge were controlled by the difference in surface area, the resulting curve would be a single straight line.

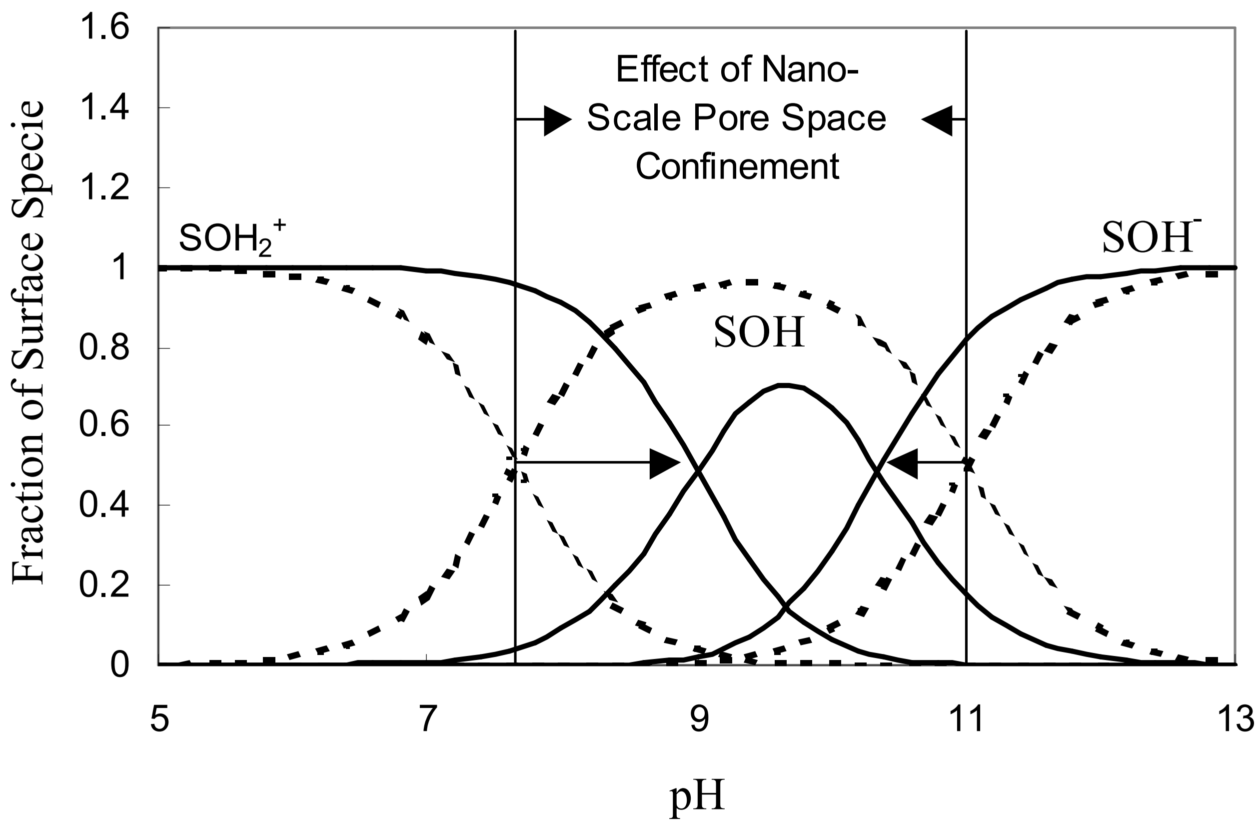
Effect of Nanopore confinement on Surface Acidity Constants





$$K_{app} = K_{int} \exp(-k\sigma)$$

Effect of Nanopore Confinement on Acidity Constants



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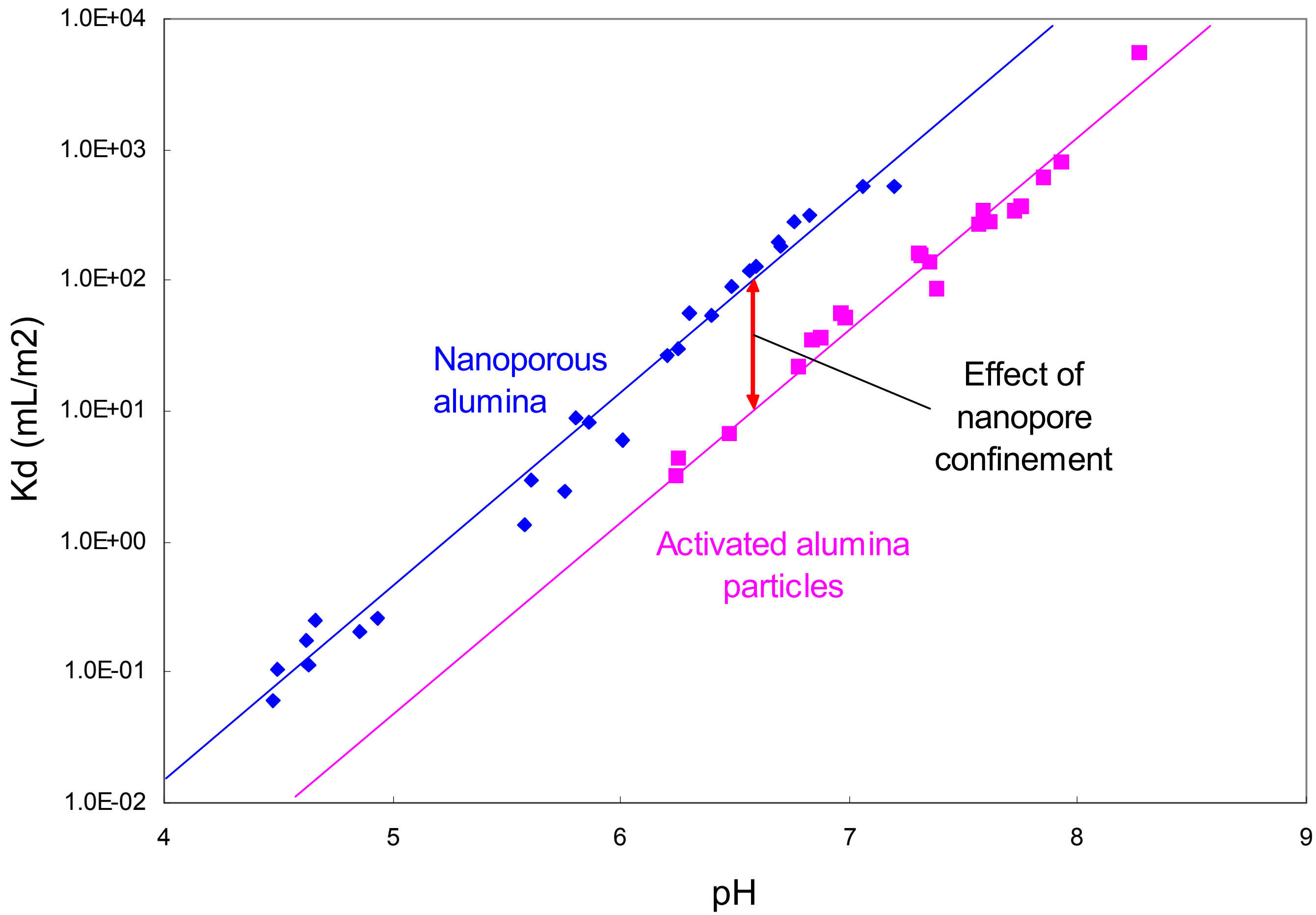
Zn Sorption Experiments - Kd



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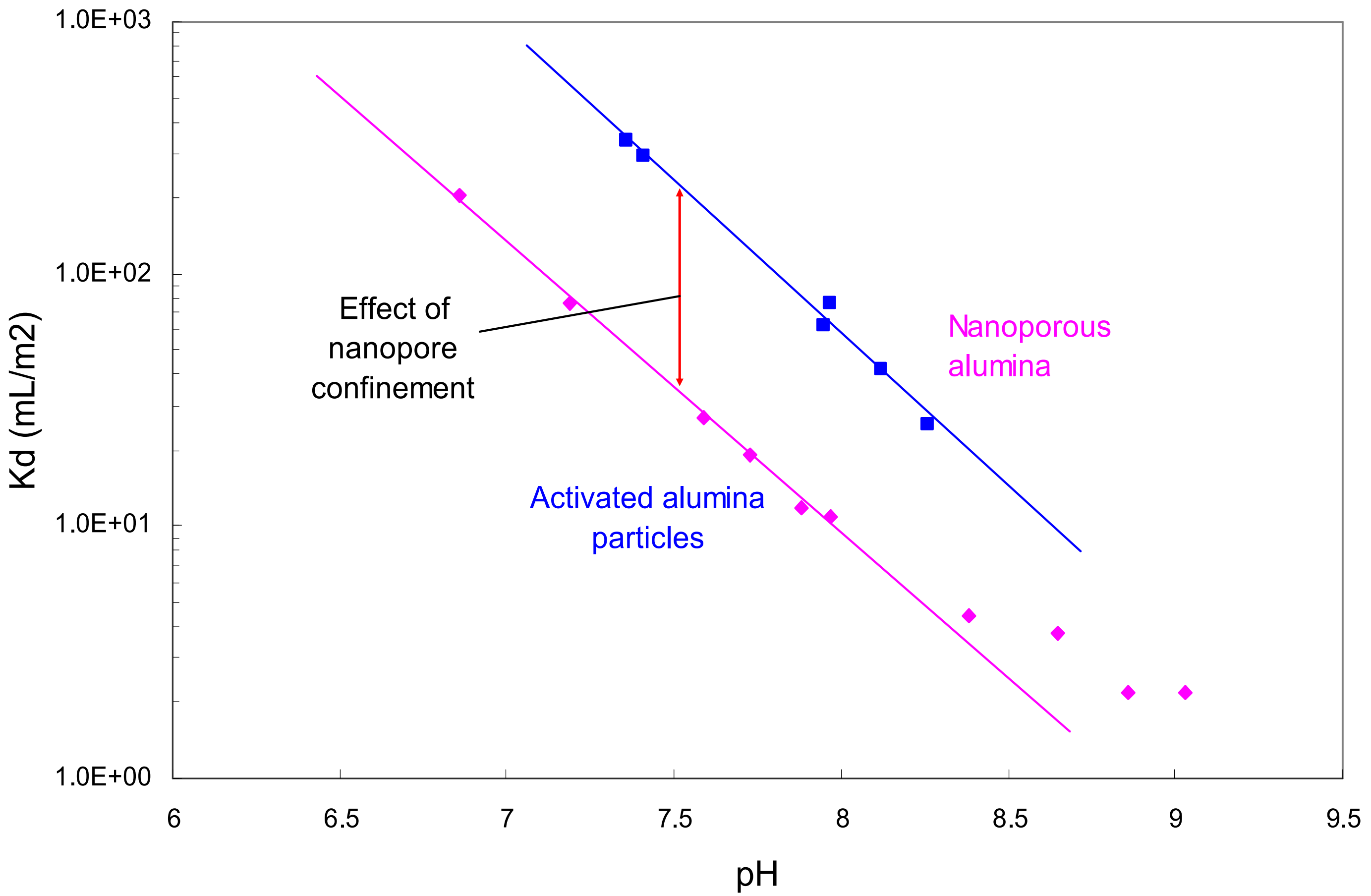
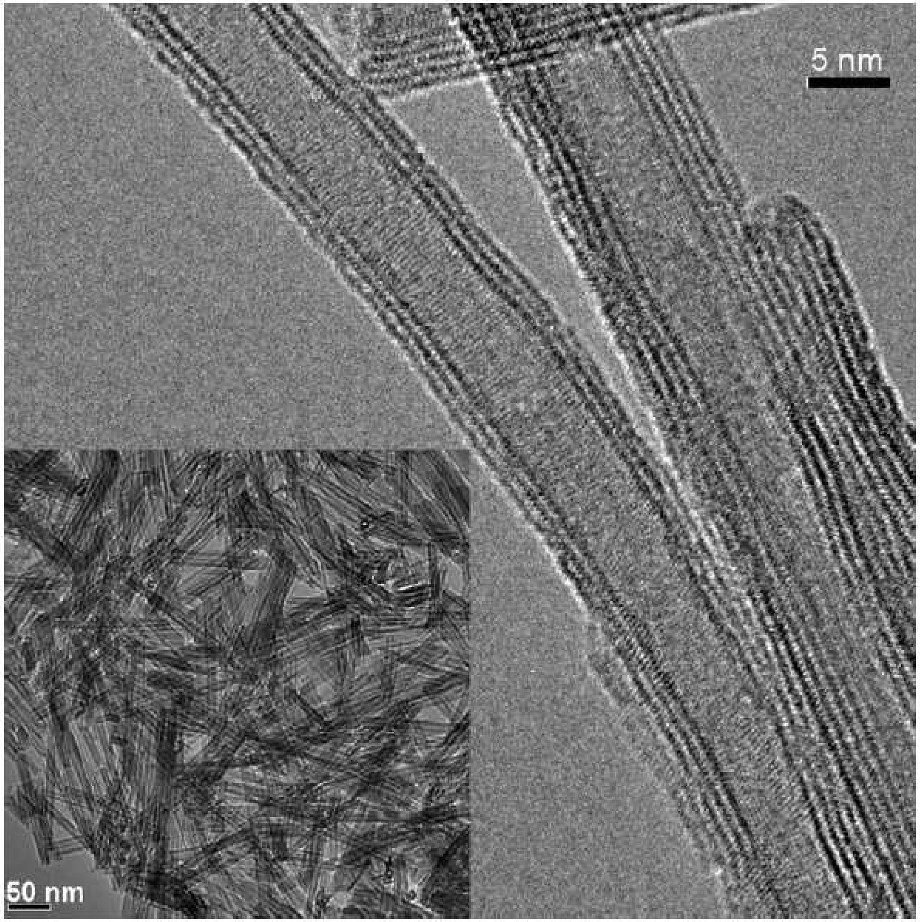
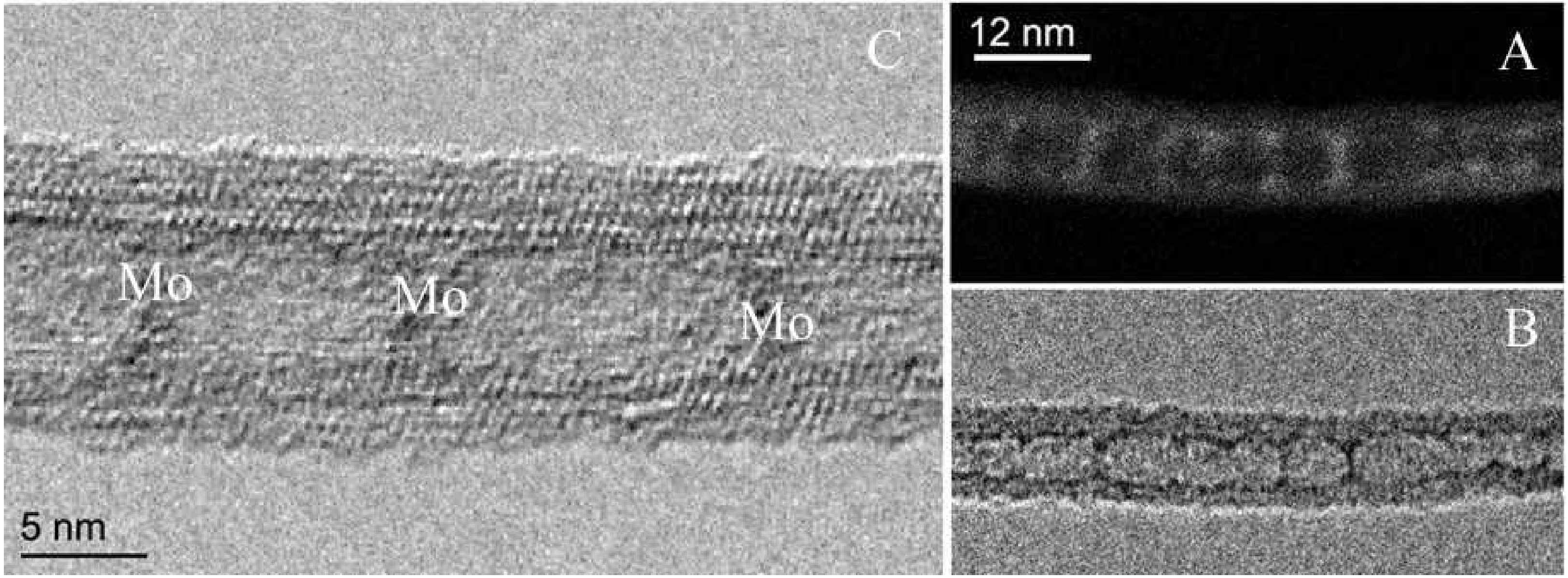
As Sorption Experiments - Kd



Synthesis of TiO_2 Nanotubes



Preferential Enrichment of Mo in TiO_2 Nanotube



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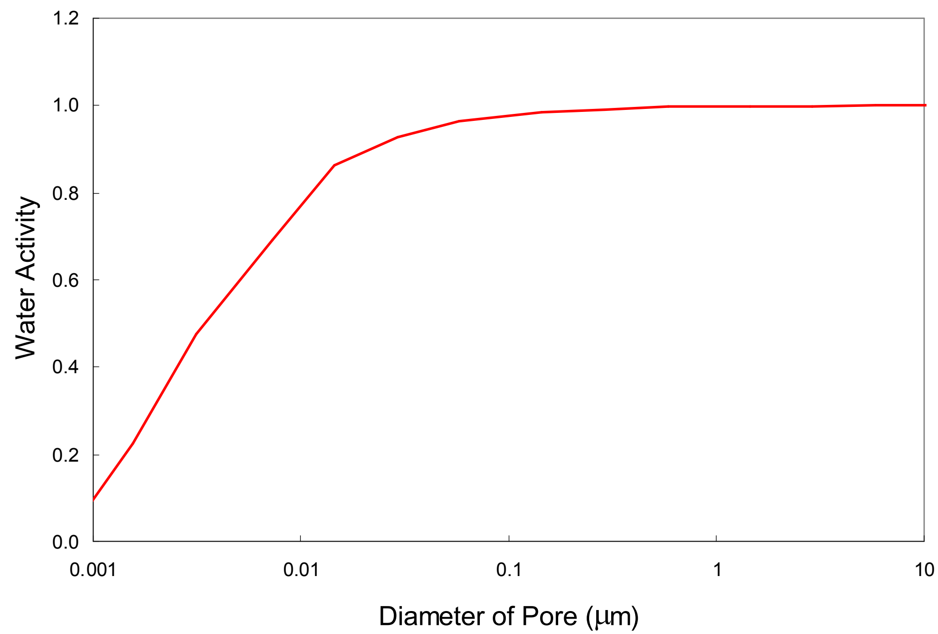
Effect of Nanopore Confinement on Solvent

Observations:

- The hysteresis width between meelting and solidification decreases as the pore size decreases (Denoyel and Pellenq, 2002).
- Water in nanopores is similar to supercooled water at ~ 30 K (Teixeira et al., 1997).
- Water vapor pressure decreases with the decrease in water saturation degree.

  Kelvin's equation (e.g., Hiemenz, 1986): $\ln(a_w) \propto -1/r$.



Postulations:

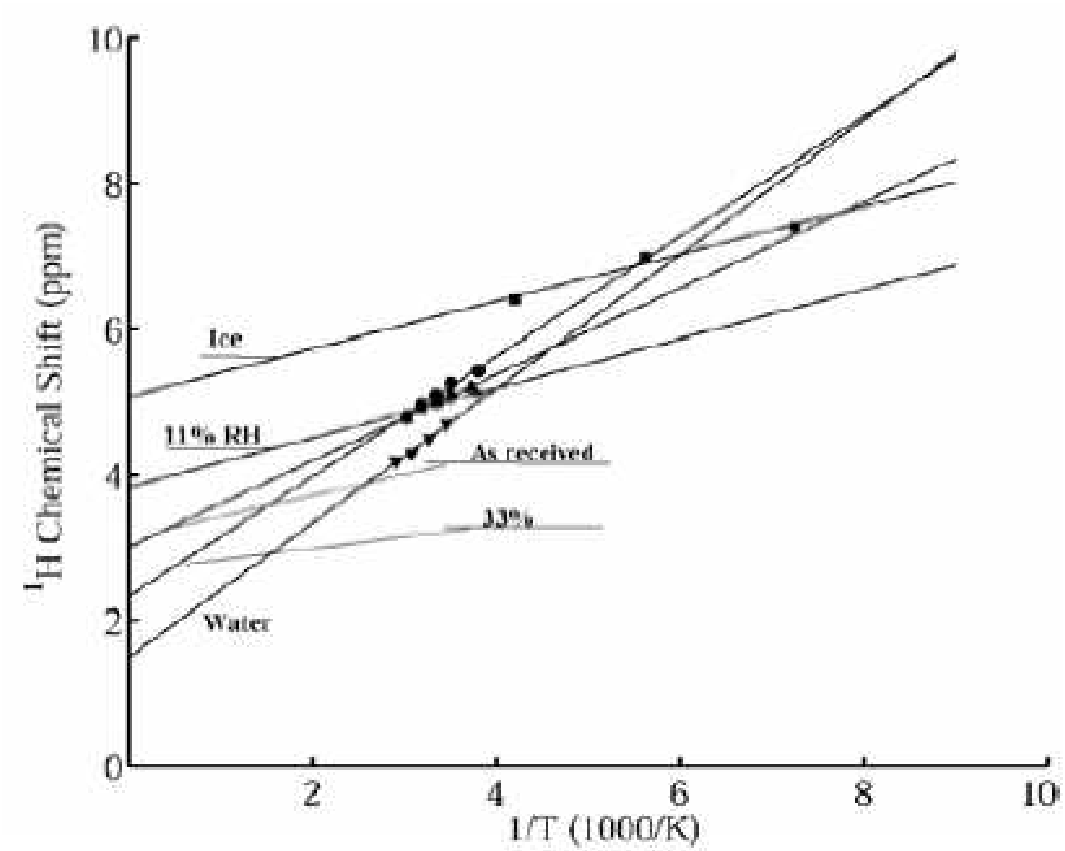
Water activity in nanopores is much lower.

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

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

Water and H^+ Mobility in Nanopores: NMR Data

NMR data indicate different water and H^+ mobility in nanopores as compared to an unconfined water-solid interface.



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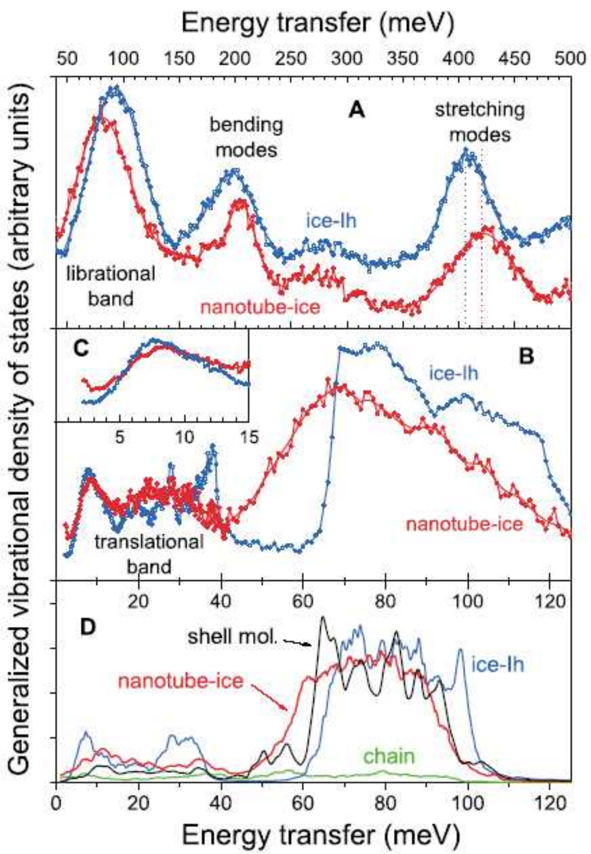
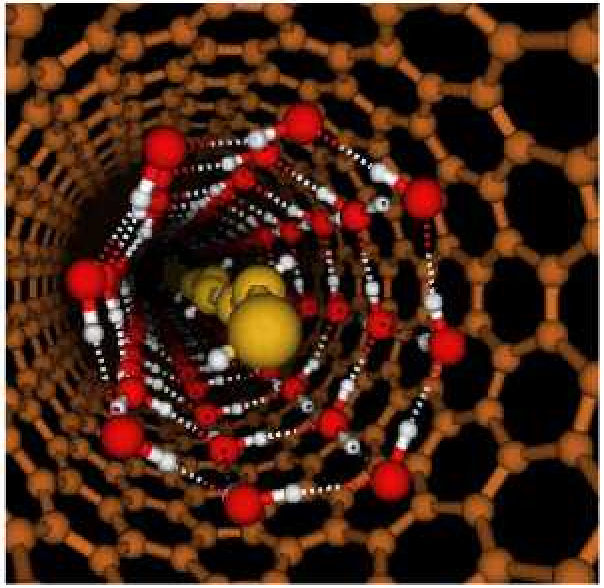
Water in SWNT





Kolesnikov et al., 2004

Effect of Nanopore Confinement on Geochemical Mass Transfers

- Preferential enrichment: Mass transfers from large pores to nanopores.
- High chemical affinity: Chemical species are more strongly bound in nanopores.
- Two sorption sites vs. same sorption sites with two different confinement environments.
- Bioavailability: Nanopores are two small for microbes to access.

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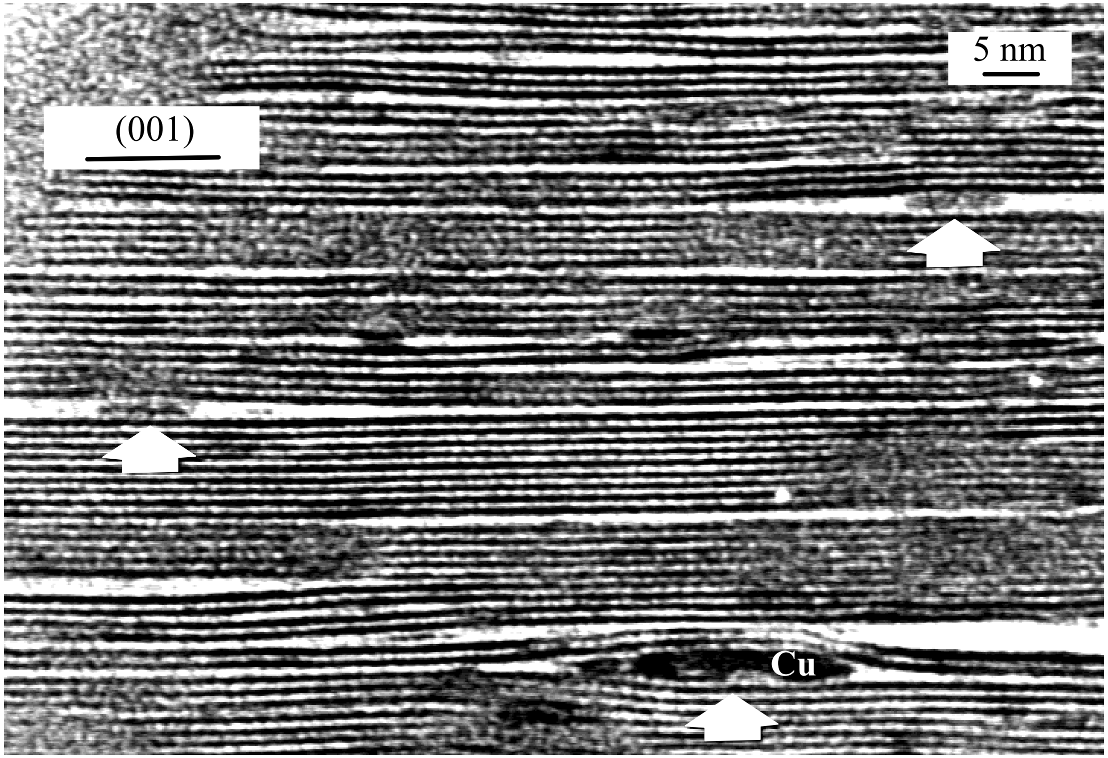
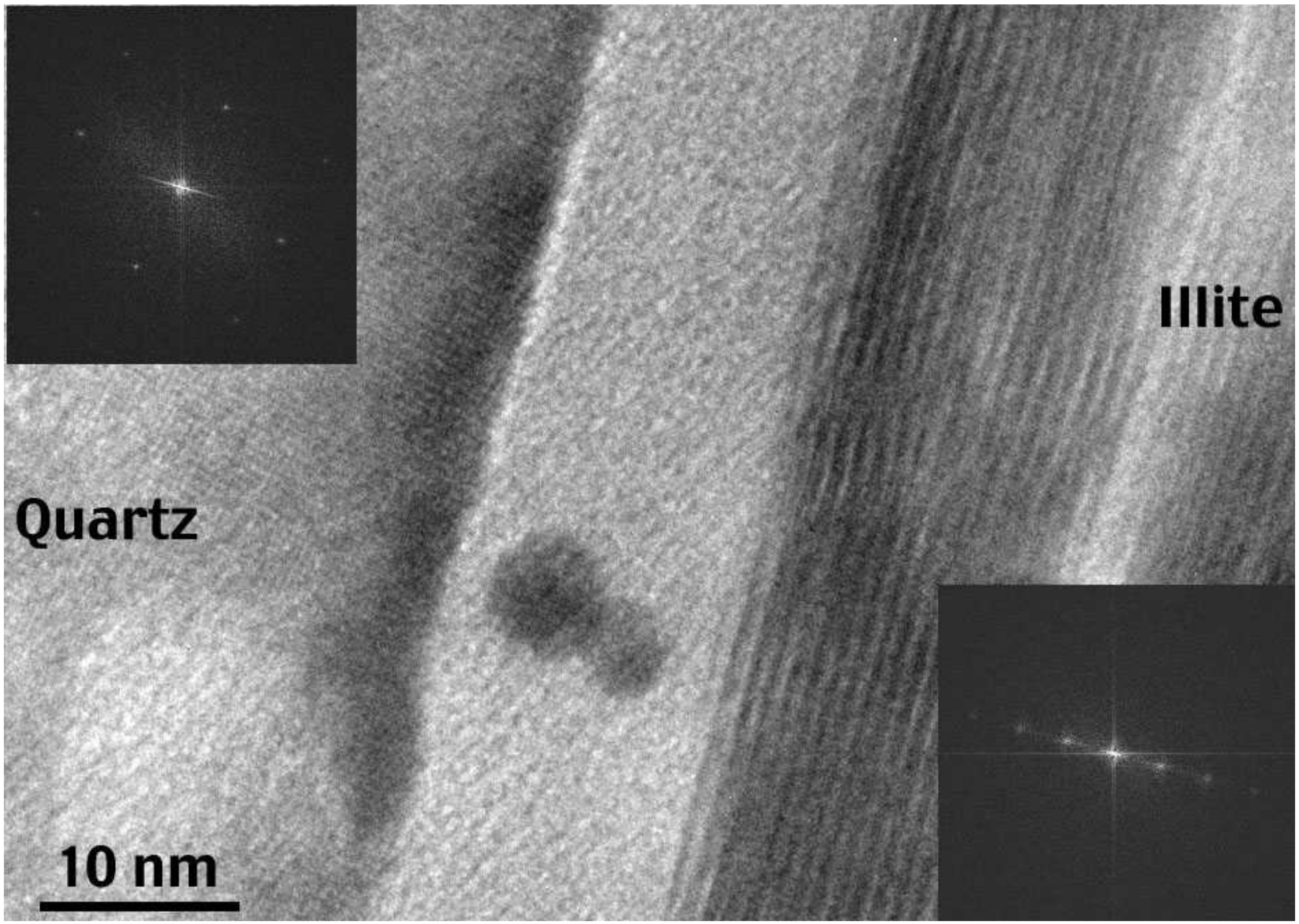
Preferential Enrichment of Trace metals



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

Nanometer Au Particles at a nanoporous Boundary between Quartz and Illite



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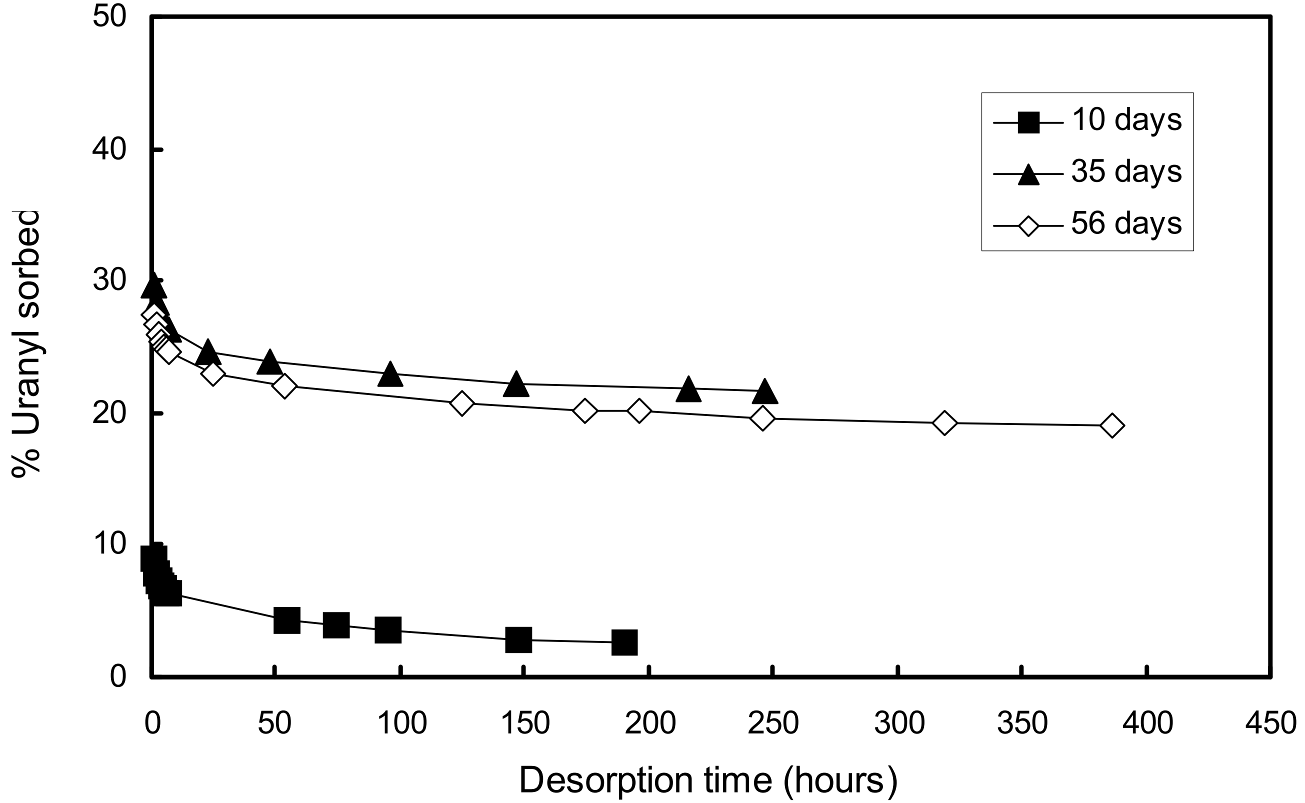
Uranyl Desorption from Synthetic Porous Goethite



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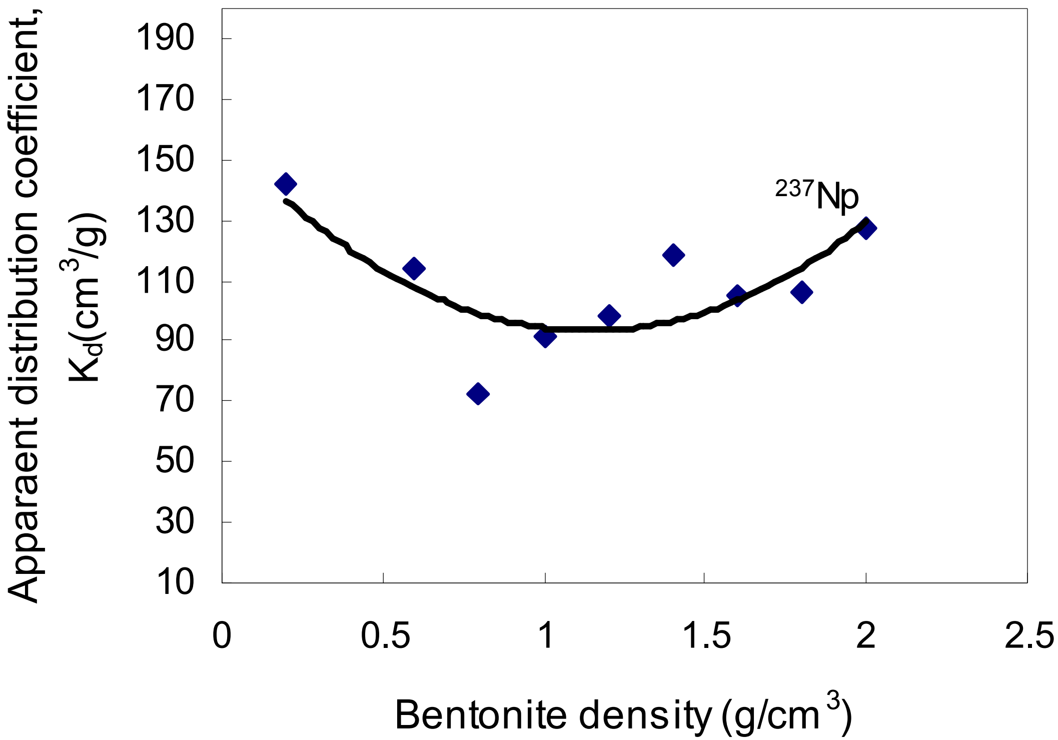
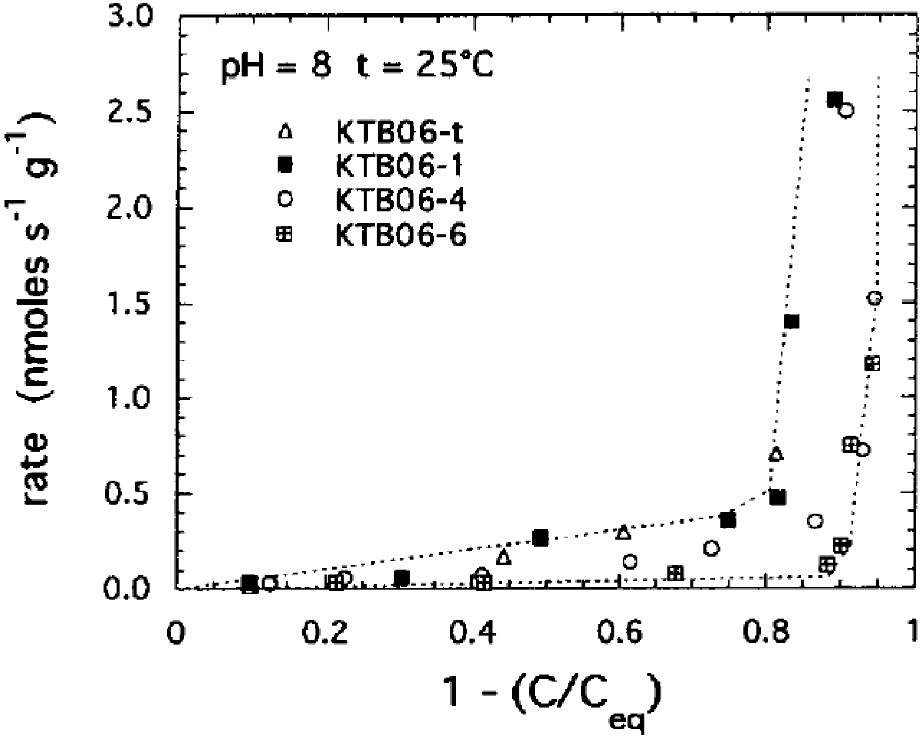
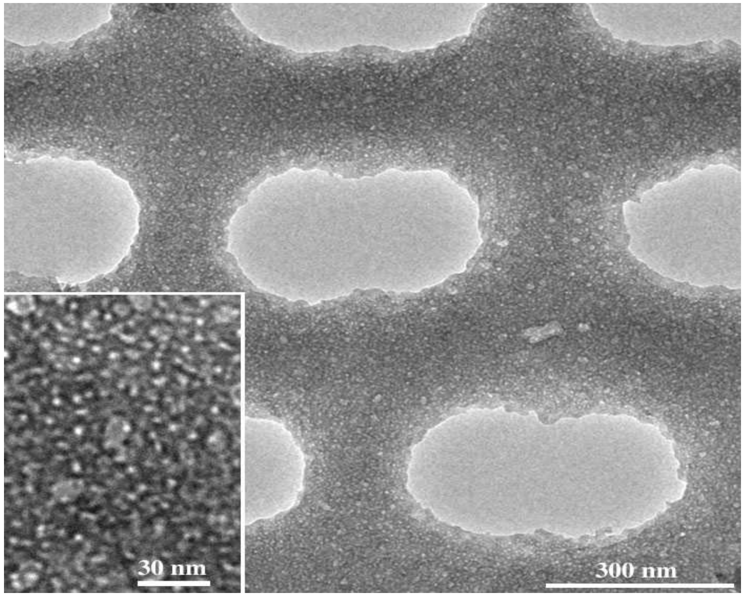
Integrity of Material Structure vs. Sorption Experiments



Conca & Wright (1992)

Dissolution Kinetics of Biogenic Silica





Van Cappellen and Qiu, 1997

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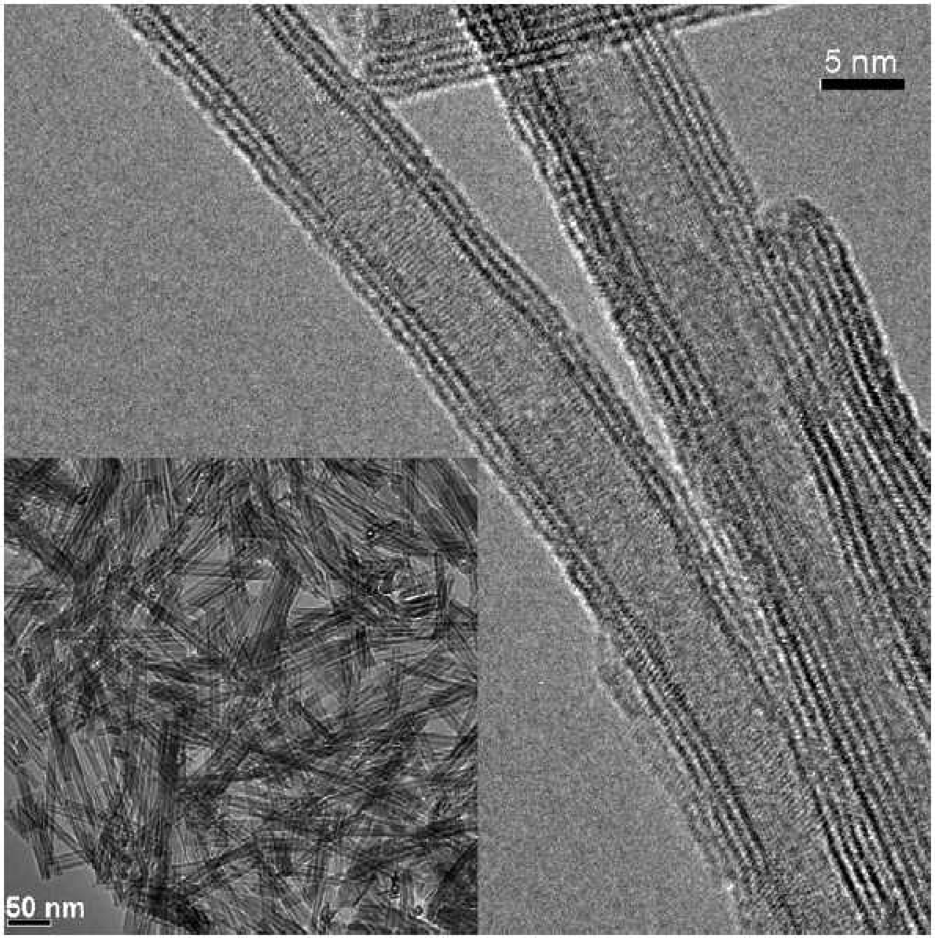
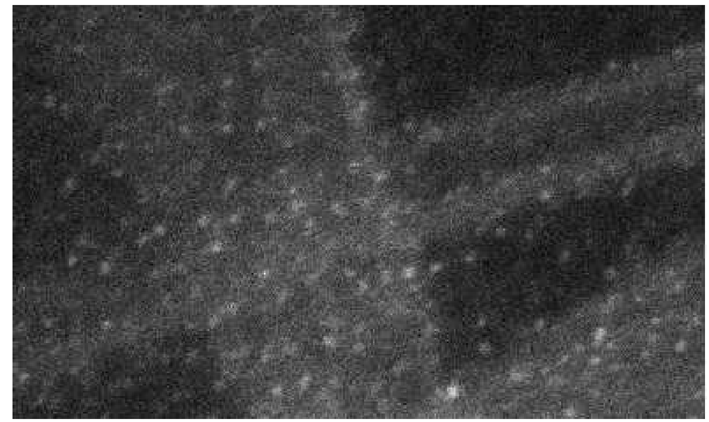
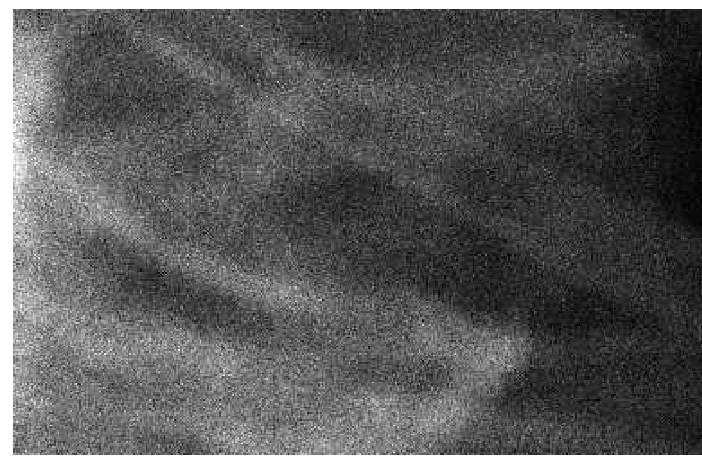
TiO_2 Nanotubes as Photocatalyst







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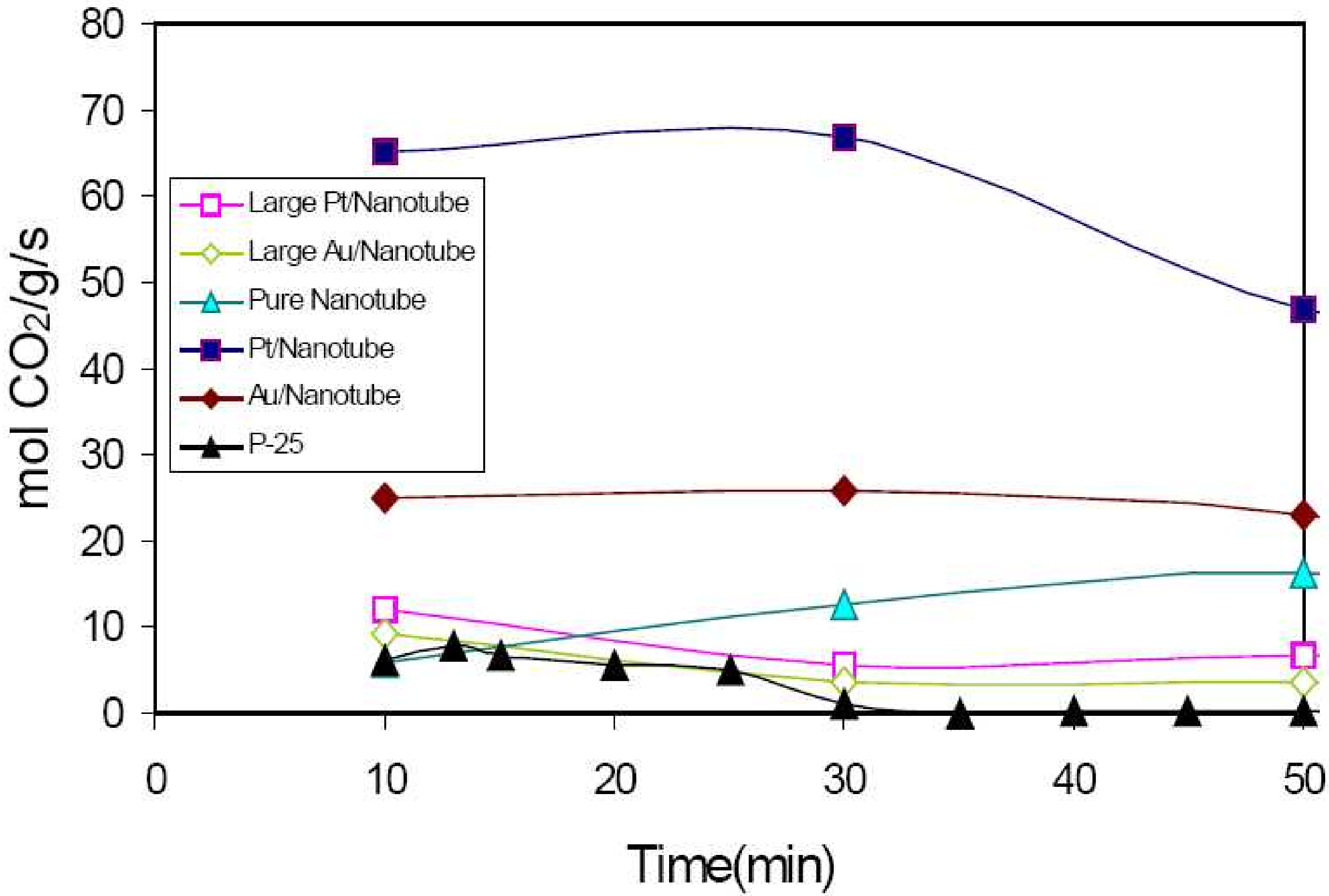
Acetaldehyde Oxidation under UV Irradiation



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Conclusions

- Effects of nanopore confinement:
  - Enhancement of sorption
  - Preferential enrichment
- Geochemical implications
  - Fate of subsurface contaminants
  - Bioavailability
  - Reversibility vs. irreversibility
- Engineering implications:
  - Reactive barrier materials
  - High performance adsorbents & catalysts

Acknowledgments

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