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

Presented by
Yifeng Wang

SAND2018-9465PE for UUR
Nanoscience: Size-Dependent Material Properties

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

Size-dependent CdS band gap
(Lüning et al., 1999, Solid State Communication)
Nanogeochemistry: Understand emergent properties of geochemical systems under nano-scale structural constraints or organizations.

Rule of thumb: <100 nm

Nanogeochemistry

Wang (2014) Chemical Geology

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

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

Structure of Clays

Clarkson et al. (2012)
Model Systems for Studying Nanopore Confinement

Wang et al. (2008)

\[
Q = \int_{pK_{\text{min}}}^{pK_{\text{max}}} \frac{f(pK)}{1 + 10^{-pK+pH}} d(pK)
\]
Model Systems for Studying Nanopore Confinement (cont.)

\[ f(pK) \]

- Nanoporous alumina
- Activated alumina particles

\[ \Delta pH = 1.00 \]
\[ \Delta pH = 0.75 \]
\[ \Delta pH = 0.50 \]

Surface Charge on Activated Alumina Particles (C/m²)

1:1 line

Effect of nanopore confinement

- 0.1 M NaCl
- 0.01 M NaCl
- D.I. Water

Effect of Nanopore Scale Pore Space Confinement

Fraction of Surface Species

\[ SOH^+ \]
\[ SOH^- \]
\[ SOH \]

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.

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

Postulations:
- Water molecules in nanopores are more restrained.
- $\text{H}_4\text{SiO}_4 = \text{SiO}_2(s) + 2\text{H}_2\text{O}$ opptn
- $\text{M(H}_2\text{O)}_n^{z+} = \text{M}^{z+} + n\text{H}_2\text{O}$ inner sphere
- $\text{Na}^+ + \text{Cl}^- = \text{NaCl}^0$ 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

Bulk phase fluids (Unconfined or pore size > ~100 nm)

EOS = f(P, T, composition)

Nanofluids (Confined in nanopores, pore size < ~100 nm)

EOS = f(P, T, composition, pore size, surface chemistry)

Overall goal: (1) Obtain a fundamental understanding of CH₄-CO₂-H₂O (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 Nangeochemical Studies at Sandia National Laboratories

Synthesis of nanoporous materials

Isolation of kerogen from Mancos shale

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

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

http://www.pflotran.org/applications.html
PFLOTAN: Reactive transport modeling

TRAMANTO: Classical Density Functional Theory modeling
Low pressure gas sorption measurements

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

<table>
<thead>
<tr>
<th>Model Substances</th>
<th>Temp, °C</th>
<th>Gas Mixture, volume percent</th>
<th>Pressure, bar</th>
<th>Sorption Capacity, mg/g</th>
<th>Sorption Rate, mg/g min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DARCO activated carbon</td>
<td>25</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>28</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>11</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>9.0</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>2.1</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>1.8</td>
<td>0.10</td>
</tr>
<tr>
<td>Montmorillonite, &lt;75 μm</td>
<td>25</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>2.8</td>
<td>$4.7 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.30</td>
<td>$9.6 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.19</td>
<td>$6.7 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.18</td>
<td>$5.1 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.12</td>
<td>$3.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>Crushed Shale</td>
<td>25</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.29</td>
<td>$3.3 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.21</td>
<td>$2.7 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>85% CH₄ + 15% CO₂</td>
<td>1</td>
<td>0.16</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Experimental measurement of sorption capacity and sorption rate for a model substance at an elevated temperature and pressure

<table>
<thead>
<tr>
<th>Model Substances</th>
<th>Temp, °C</th>
<th>Gas Mixture, volume percent</th>
<th>Pressure, PSI</th>
<th>Sorption Capacity (mixture) mg/g</th>
<th>Sorption Rate, mg/g min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite, &lt;75 mm</td>
<td>50</td>
<td>90% CH₄ + 10% CO₂</td>
<td>300</td>
<td>190</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Kerogen

Density
Sample 1: 1.172g/cm³
Sample 2: 1.287g/cm³

Average :1.22±0.04 g/cm³
Experiment: 1.28±0.3g/cm³


Over-mature kerogen molecules

Ho, et al, Scientific Reports 28053

Methane sorption and extraction from kerogen

Graph showing:
- Extraction rate over time (ps) for different pressures (atm).
- Adsorption vs. pressure (atm) with curves for Total-1, Excess-1, Total-2, and Excess-2.

Legend:
- Sample 1: 47% Fast, 50% Slow, 3% Unrecoverable
- Sample 2: 30% Fast, 35% Slow, 35% Unrecoverable
Implication to decline curve

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

Bulk

In kerogen nanopores
Differential retention of CO\textsubscript{2} and CH\textsubscript{4} in kerogen

Fuel 220, 1-7, 2018

Kerogen preferentially retains CO\textsubscript{2} over CH\textsubscript{4}
Pore specific effects on enhanced gas recovery

Pore size effect

- **CO₂**: Pore is too small for the invasion of CO₂
- **CH₄**: Pore is big enough for the invasion of CO₂
Pore specific effects on enhanced gas recovery

Pore shape effect

Graphene slit-pore

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

Pore is too small for the invasion of CO2
Assume that water thin films block the pore entrance.

CO₂ invades through water and replaces CH₄ in the nanopore.
Kerogen Swelling upon Gas Sorption (PCCP, 2018)

![Graph showing volumetric strain (%)](image1)

- **He**
- **CH₄**
- **CO₂**

![Graph showing total uptake (mmol/g)](image2)

- **CO₂**
- **CH₄**

Mathematical equation:

\[ Y = 0.3173X^2 - 0.5485X + 2.107 \]

\[ R^2 = 0.9891 \]
Sorption-desorption hysteresis and chemo-mechanical coupling (?)
Emergent transport properties in nanopores: Isotopic fractionation

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

M - Molecular weight

Wang (2018)
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
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.