Iodine interactions with clays and the relationship to surface charge and clay texture

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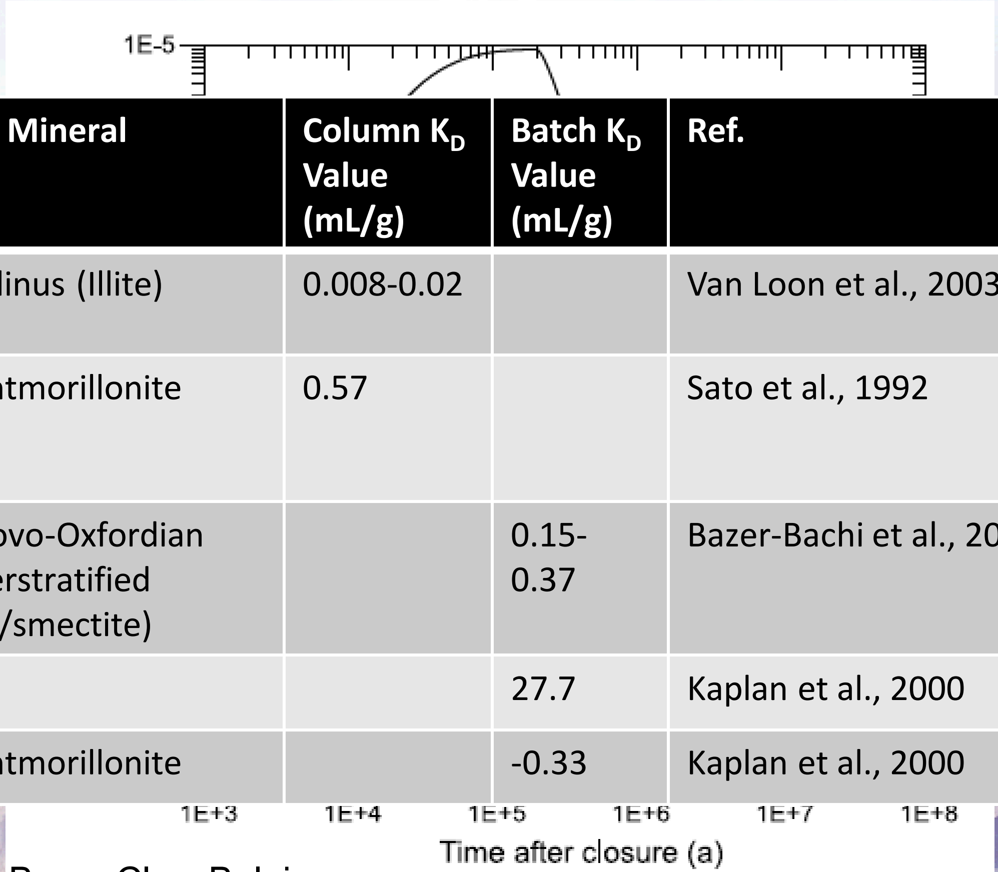
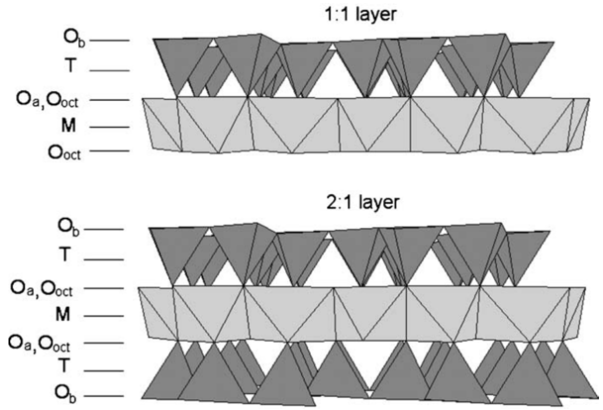
Clay Mineral	Column K_D Value (mL/g)	Batch K_D Value (mL/g)	Ref.
Opalinus (Illite)	0.008-0.02		Van Loon et al., 2003
Montmorillonite	0.57		Sato et al., 1992
Callovo-Oxfordian (Interstratified illite/smectite)		0.15-0.37	Bazer-Bachi et al., 2006
Illite		27.7	Kaplan et al., 2000
Montmorillonite		-0.33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



Boom Clay, Belgium
Mallants et al., 2001. Journal of Nuclear Materials, 298, 125-135.

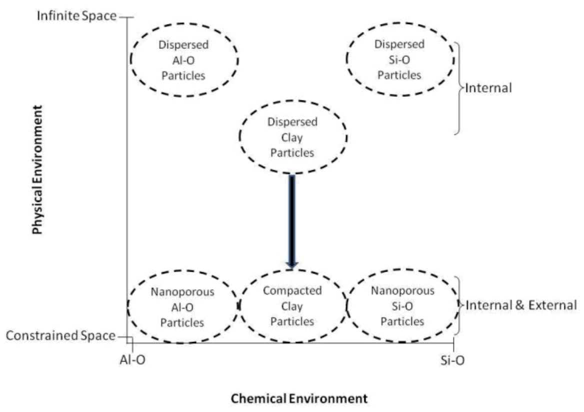
This talk compares physical/chemical relationships that may lead to disparate iodine sorption behavior

Clay mineralogy



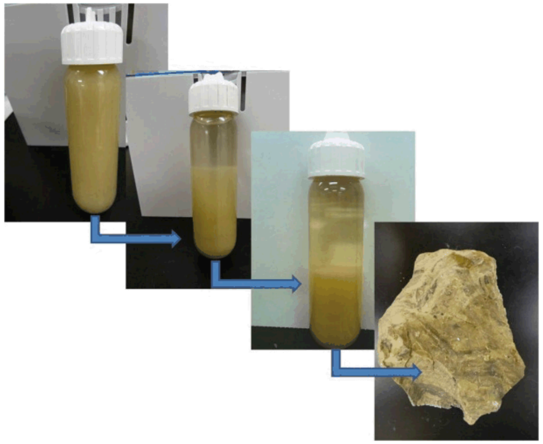
Handbook of Clay Science, Eds.: Bergaya, F., Theng, B.K.G., Lagaly, G.; Elsevier, 2006.

Potential reasons for anion interactions

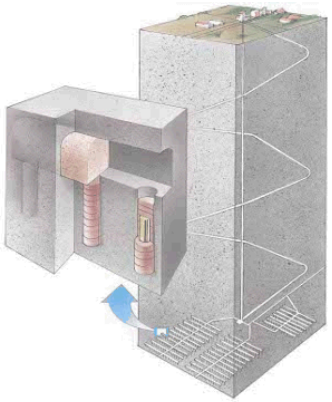


Miller, A.W., Wang, Y. (2012). *Environ.Sci. Technol.* **DOI:** 10.1021/es203025q.

Experimental conditions/results



Repository implications



http://www.dalton.manchester.ac.uk/our-research/waste-management/

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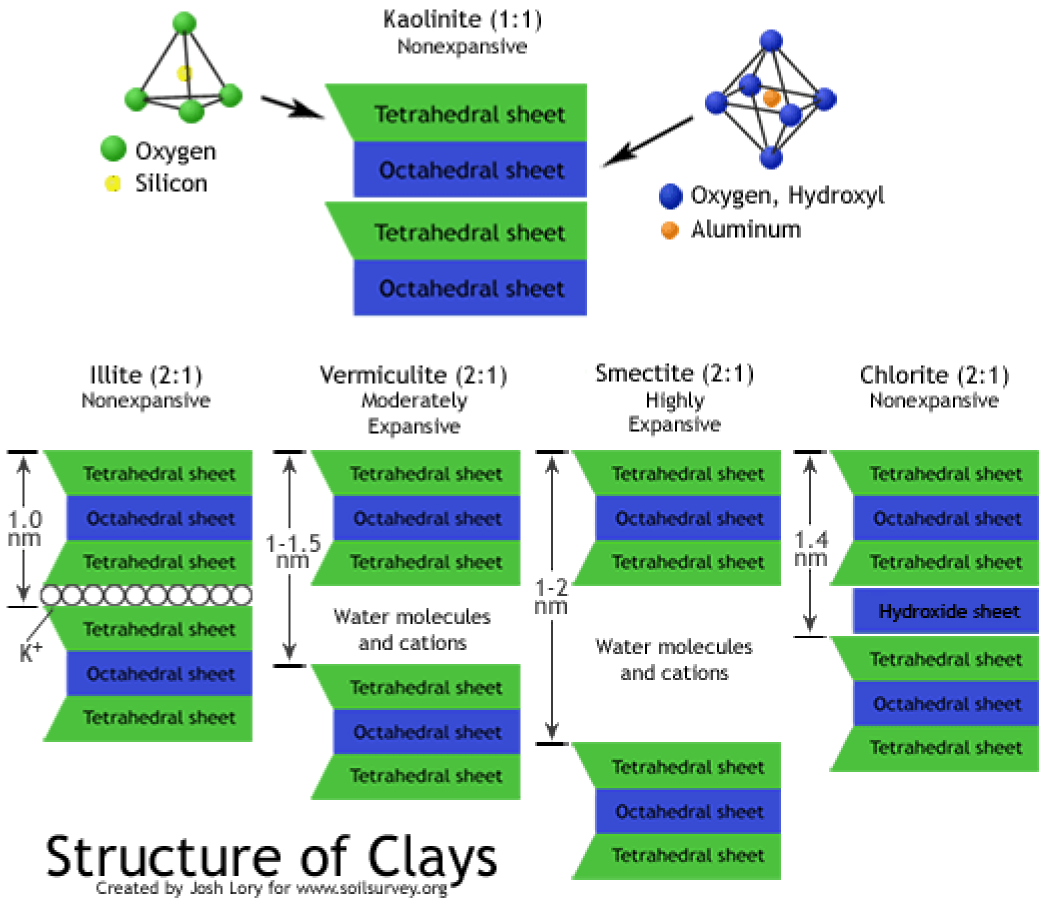
Clays are (Mg, Al)-silicates with sheets, layers, edges and interlayers.



http://soils.missouri.edu/tutorial/page8.asp

Surface Charge Separation

Cation Exchange Capacity

$$\equiv X - Na^{+} + K^{+} \leftrightarrow \equiv X - K^{+} + Na^{+}$$

Edge Exchange

$$\equiv AlO^{-} + H^{+} \leftrightarrow \equiv AlOH$$

$$\equiv AlOH + H^{+} \leftrightarrow \equiv AlOH_2^{+}$$

$$\equiv SiO^{-} + H^{+} \leftrightarrow \equiv SiOH$$

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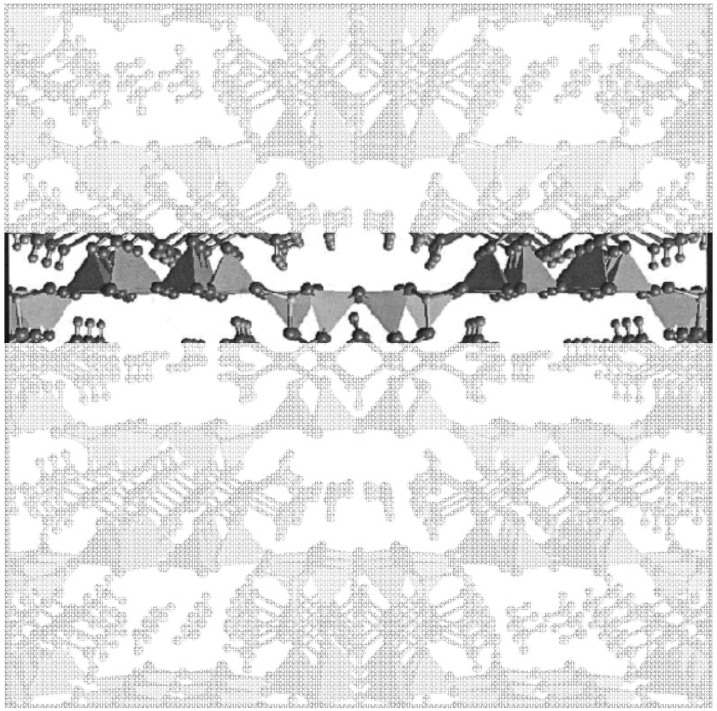
Fibrous clays have columnar voids for water inclusion



Fois et al., 2003. **Microporous and Mesoporous Materials**. 57, 263-272.

http://backreaction.blogspot.com/2008/03/cookies-palygorskite-and-maya-blue.html

Clays have a fixed negative charge, how can an anion (iodine) interact with a clay particle?

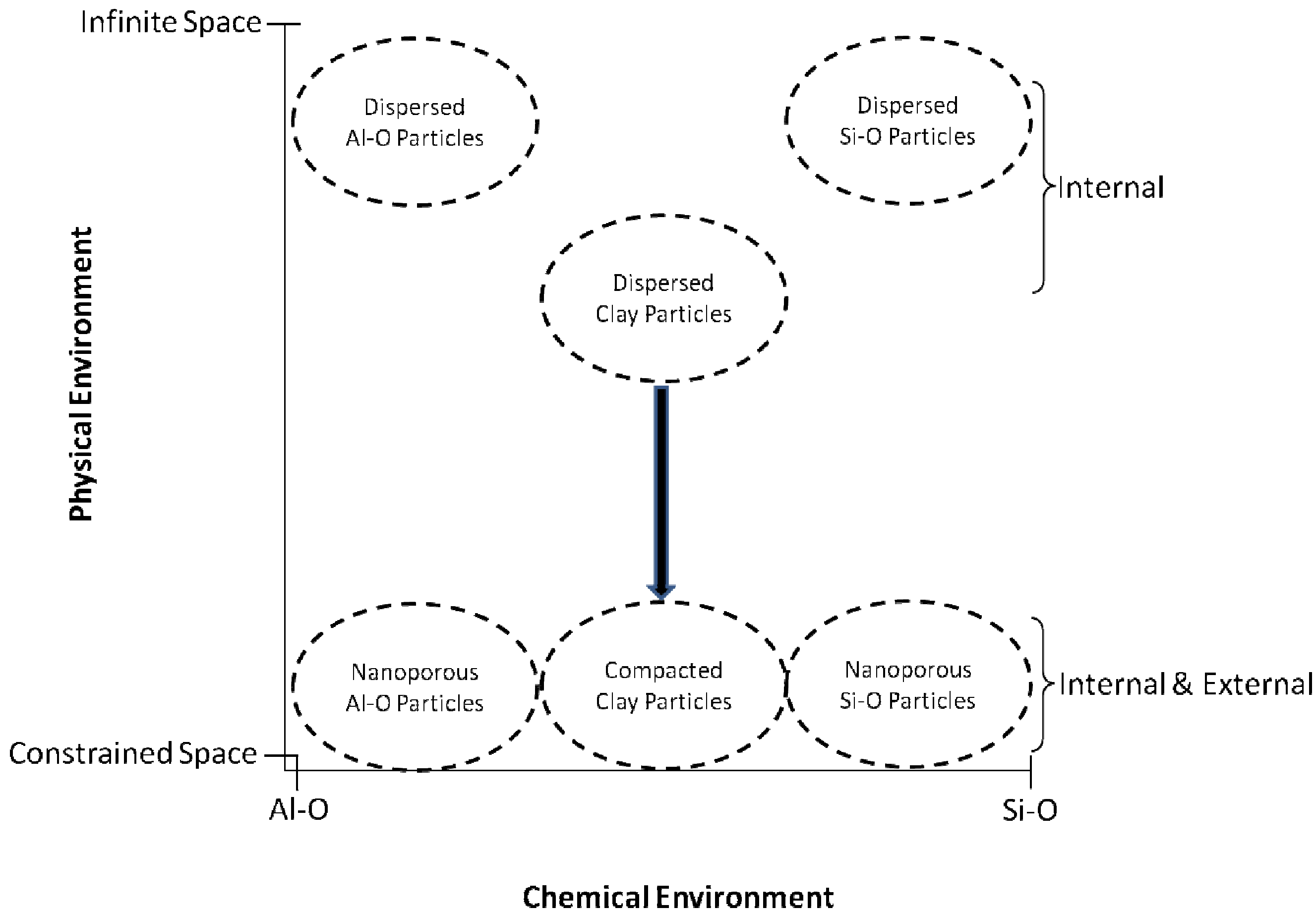
1. **They aren't.**
   - Impure radiotracers
   - Isotopic exchange with natural iodine
   - Uptake into carbonate minerals

2. **Iodine redox reactions**
   - Iodide/iodate/iodine all possible
   - Iodate generally more surface reactive
   - Redox transformations are enhanced by COx clay
   - Clay oxic state is important

3. **Clays are not pure**
   - Organic matter
   - Reduced iron in clay structure
   - Presence of other reduced minerals (e.g., pyrite)

4. **Nano-environments**
   - Heterogeneous charge environments
   - Forced overlap in compacted systems

Clay particle proximity has the potential to change observed reactivity



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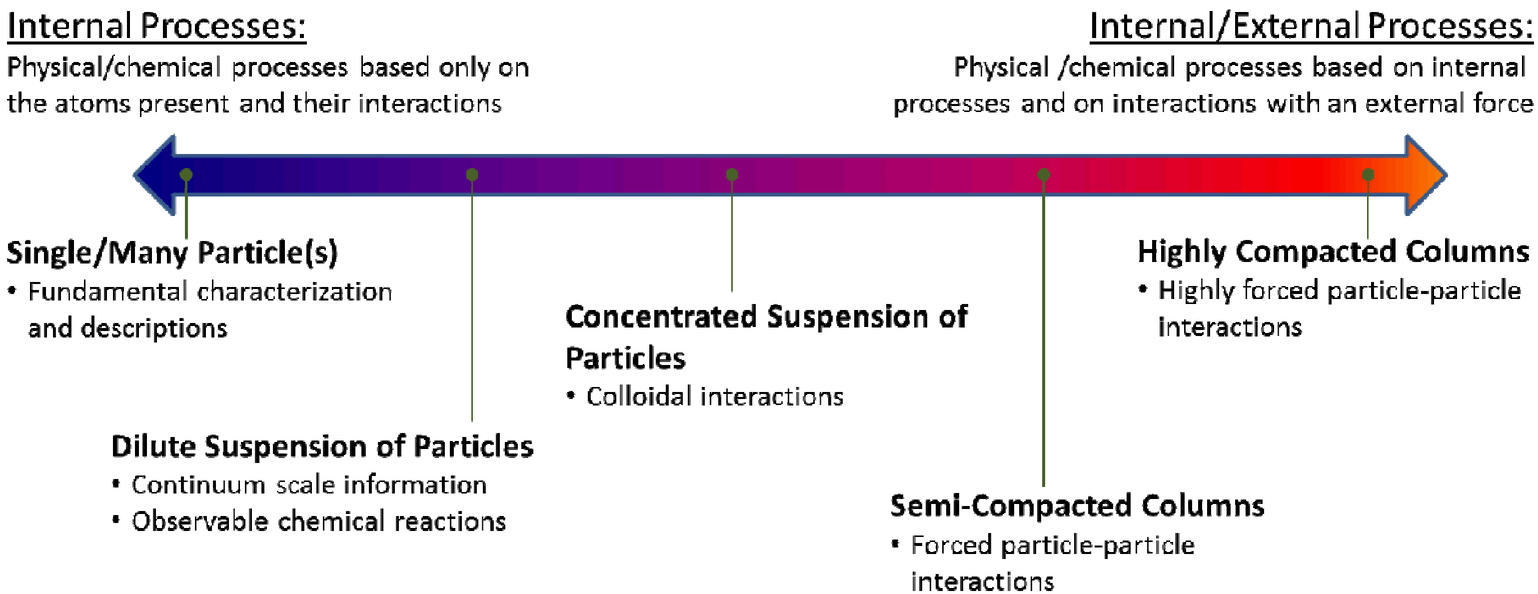
Particle-particle interactions create nano-environments



- As solids concentration increases chemical (and charge) environment changes
  - Single/Many Particles: No particle-particle interactions (by definition)
  - Dilute Suspensions: No particle-particle interactions (by assumption)
  - Concentrated Suspensions: DLVO type interactions, possible polymerization of clay particles
  - Semi-Compacted Column: Overlapping double layers
  - Highly-Compacted Columns: Overlapping double layers and compression of the interparticle space

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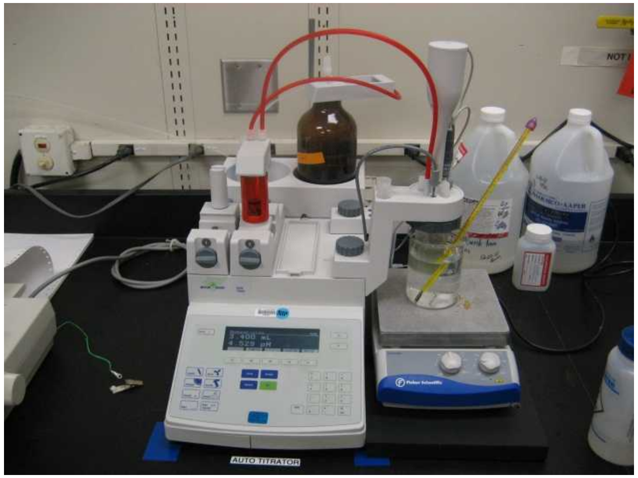
Surface titrations and batch sorption experiments were completed to characterize the clay surface environment

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

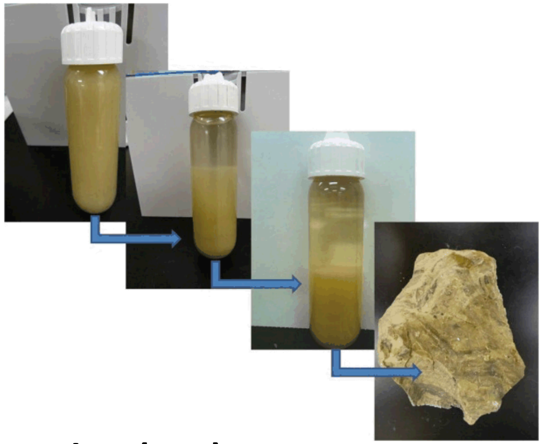
- Kaolinite
- Ripidolite
- Illite
- Illite/Smectite
- Montmorillonite
- Palygorskite
- Sepiolite

Titrations:



- Ionic strengths: 0.01M, 0.1M, and 0.5M NaCl
- Solid:Liquid ratio: 20g/L
- Continuous nitrogen sparge
- pH range: 2.5-10.5

Sorption experiments:



- **Methylene Blue (MB)**
    - Na-exchanged clays
    - Variable amounts of MB were added until clay surface was saturated
- **Iodide**
    - Initial iodide concentrations: 1.3, 10.1, 50 mg/L ($1x10^{-5}$, $8x10^{-5}$, $3.9x10^{-4}$ M)
    - Ionic strength: 0.1M NaCl
    - Solid:Liquid ratio: 100g/L
    - No specific pH control; 'natural' pH of clay
    - Seven day reaction time

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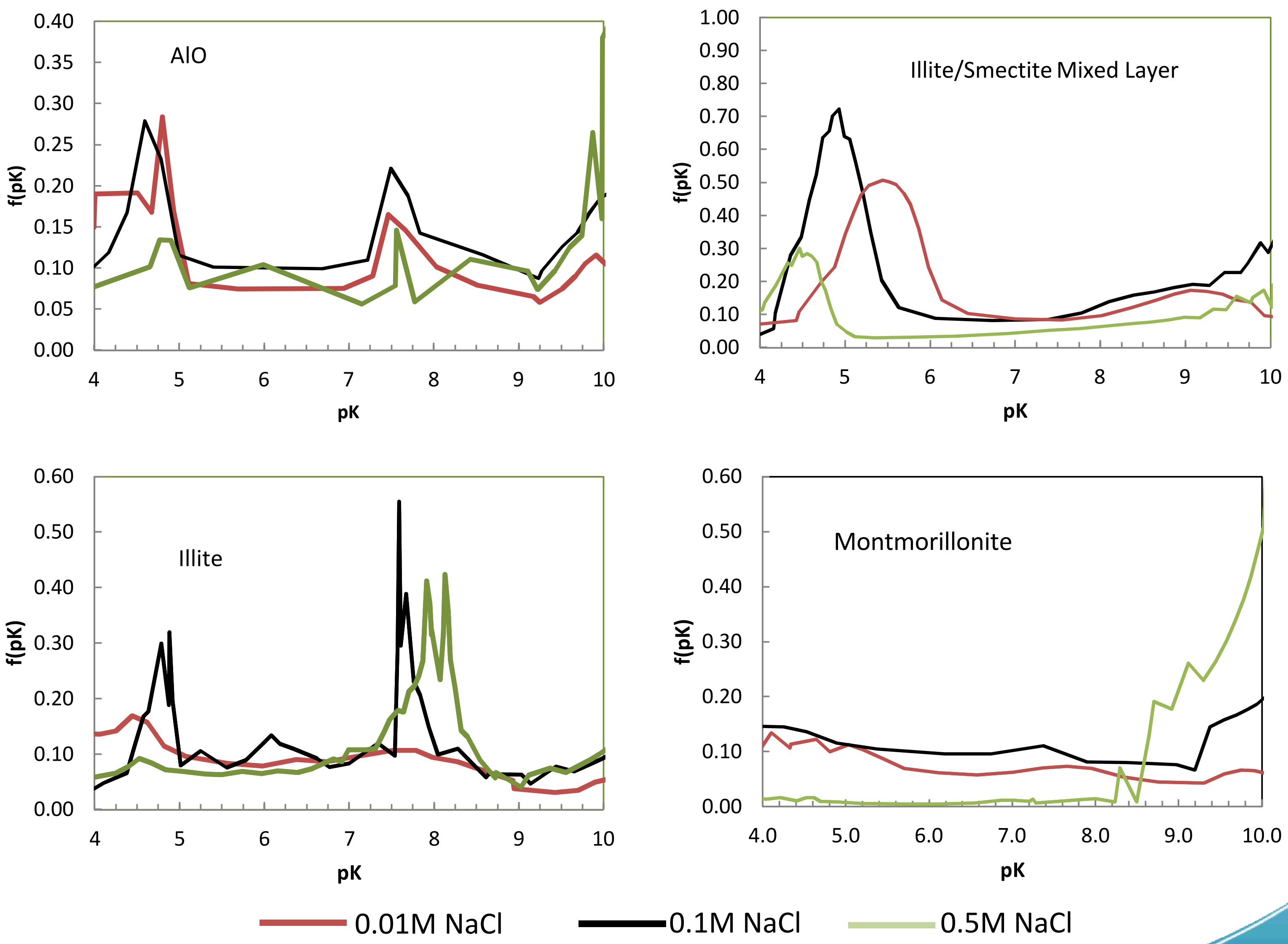
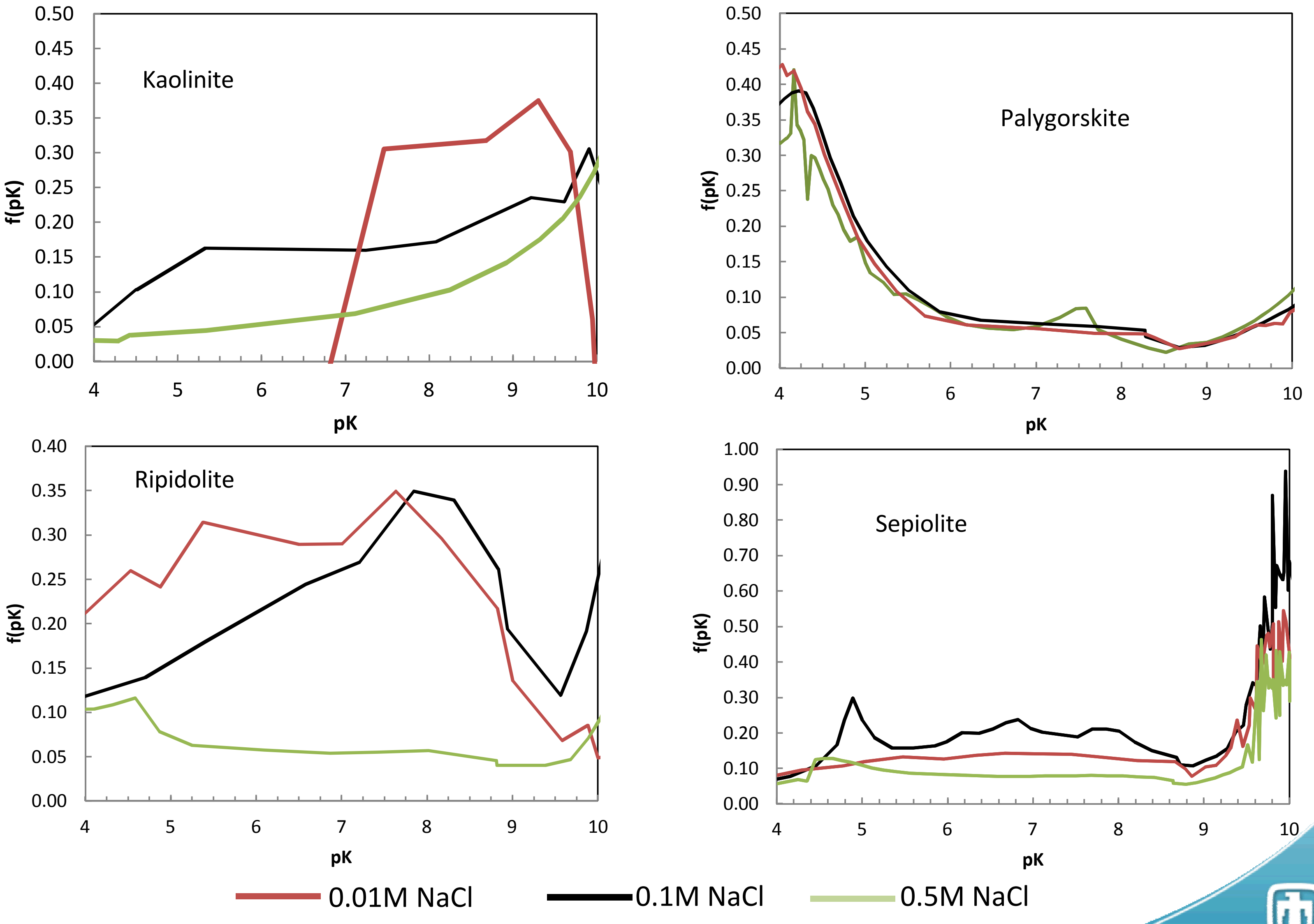
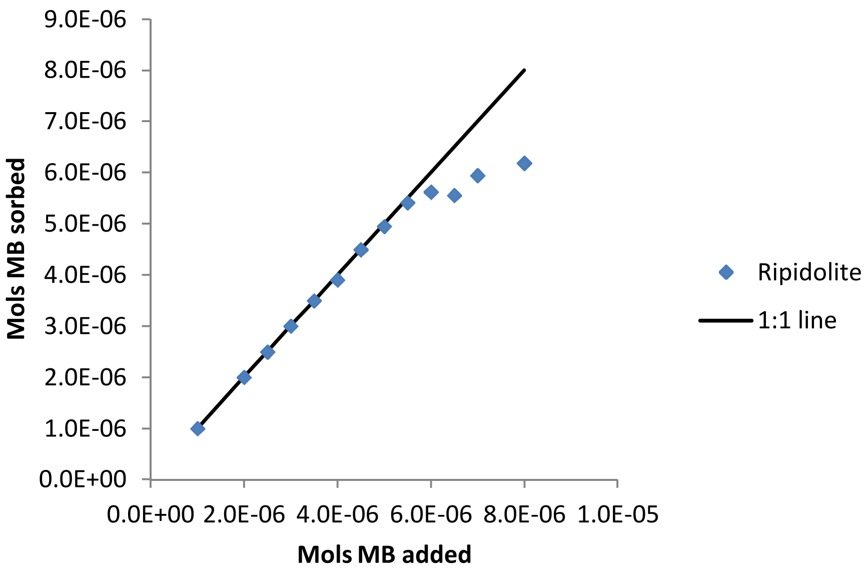
Clays' pK_a distribution is more heavily affected by ionic strength relative to AlO.



Fibrous clay distributions are less affected than layered clays.

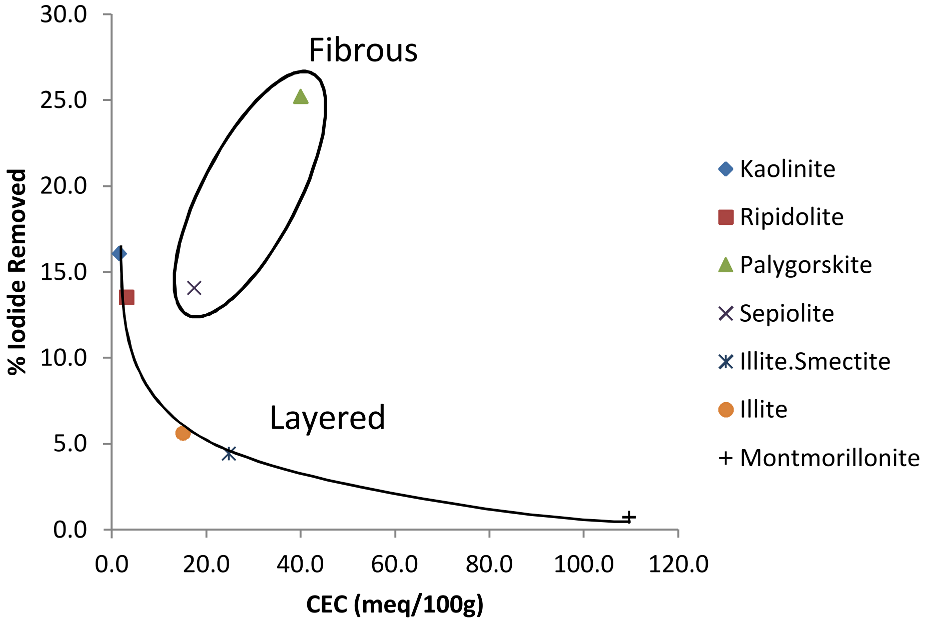


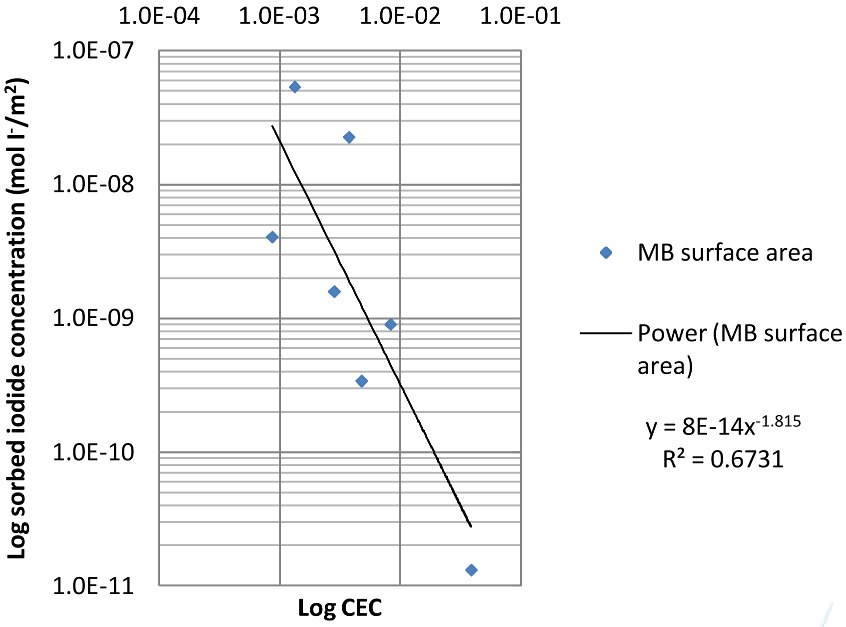
MB surface areas deviate from BET (N_2) surface area.



	BET S.A (m^2/g)	CEC (meq/100g)	CEC (meq/m^2)	Calc. MB S.A (m^2/g)
Kaolinite	11.31	1.50	1.33E-03	11.76
Ripidolite	8.02	3.00	3.74E-03	23.49
Illite	31.46	14.98	4.76E-03	117.21
Illite.Smectite	29.82	24.69	8.28E-03	193.23
Montmorillonite	28.29	109.53	3.87E-02	857.17
Sepiolite	201.43	17.41	8.64E-04	136.27
Palygorskite	141.52	39.96	2.82E-03	625.45

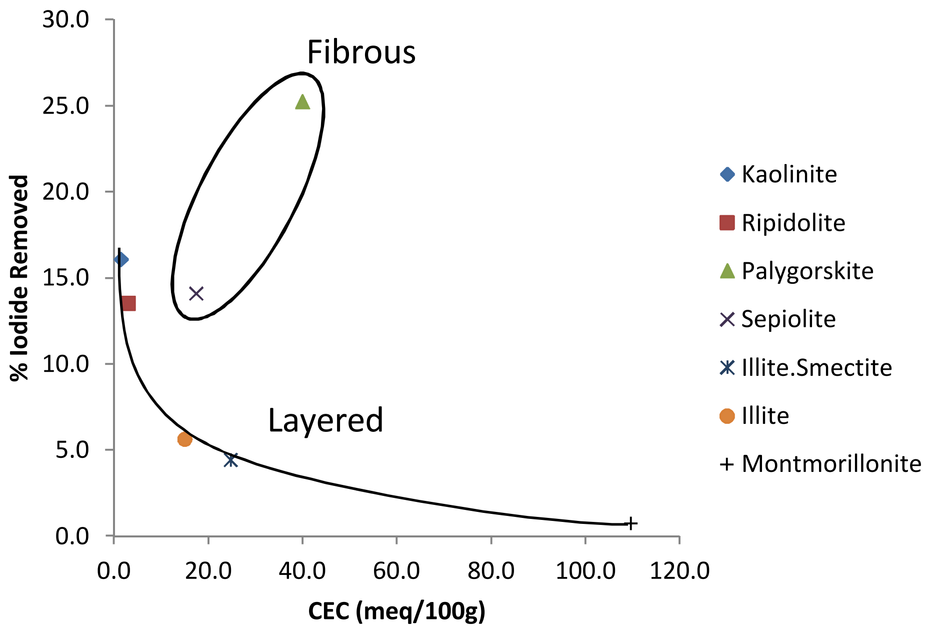
Iodide removal trends with CEC for layered clays, but not fibrous clays.





In summary, underlying clay structures play a clear role in determining iodide sorption.

- Clays have more complicated surface behaviors than those observed for simple metal oxides.
- For layered clays, higher CEC (larger negative charge) led to smaller iodide sorption.
- Results suggest that anion interaction with clay minerals is possible, though mechanisms are still unclear
- Fibrous clays have higher sorption capacities for iodide than layered clays.



Repository Implications:

- Most work with clays is focused on illite (host rock) and montmorillonite (backfill)
- Fibrous clays may allow for more significant anion retardation than montmorillonite