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Used Fuel Disposition Campaign

Sorption Capacity in Clay Minerals for UFD Applications

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UFD Working Group Meeting

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Sorption Capacity in Clay Minerals for UFD Applications

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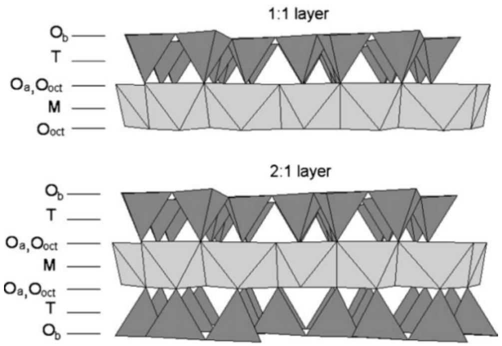
PART 1: Iodide sorption behavior

Clay mineralogy

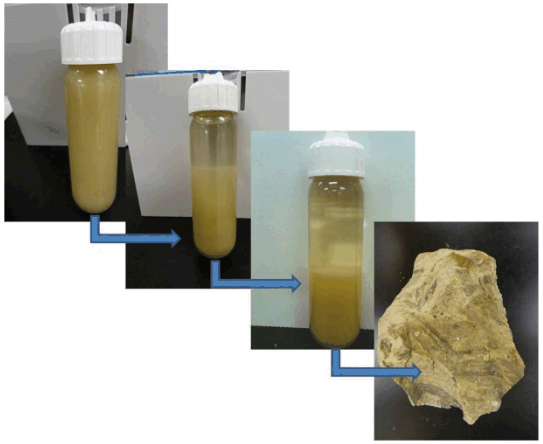


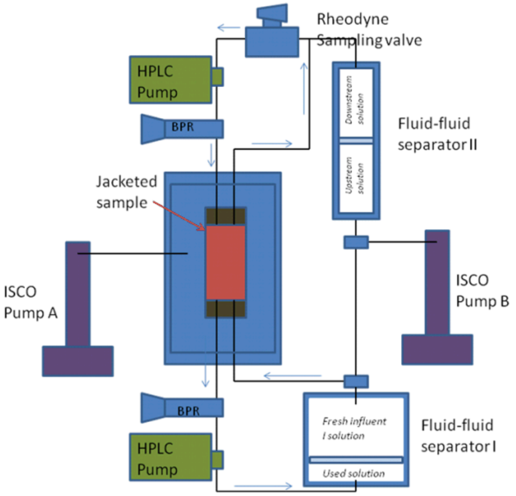
***Handbook of Clay Science**, Eds.: Bergaya, F., Theng, B.K.G., Lagaly, G.; Elsevier, 2006.*

Potential reasons for anion interactions

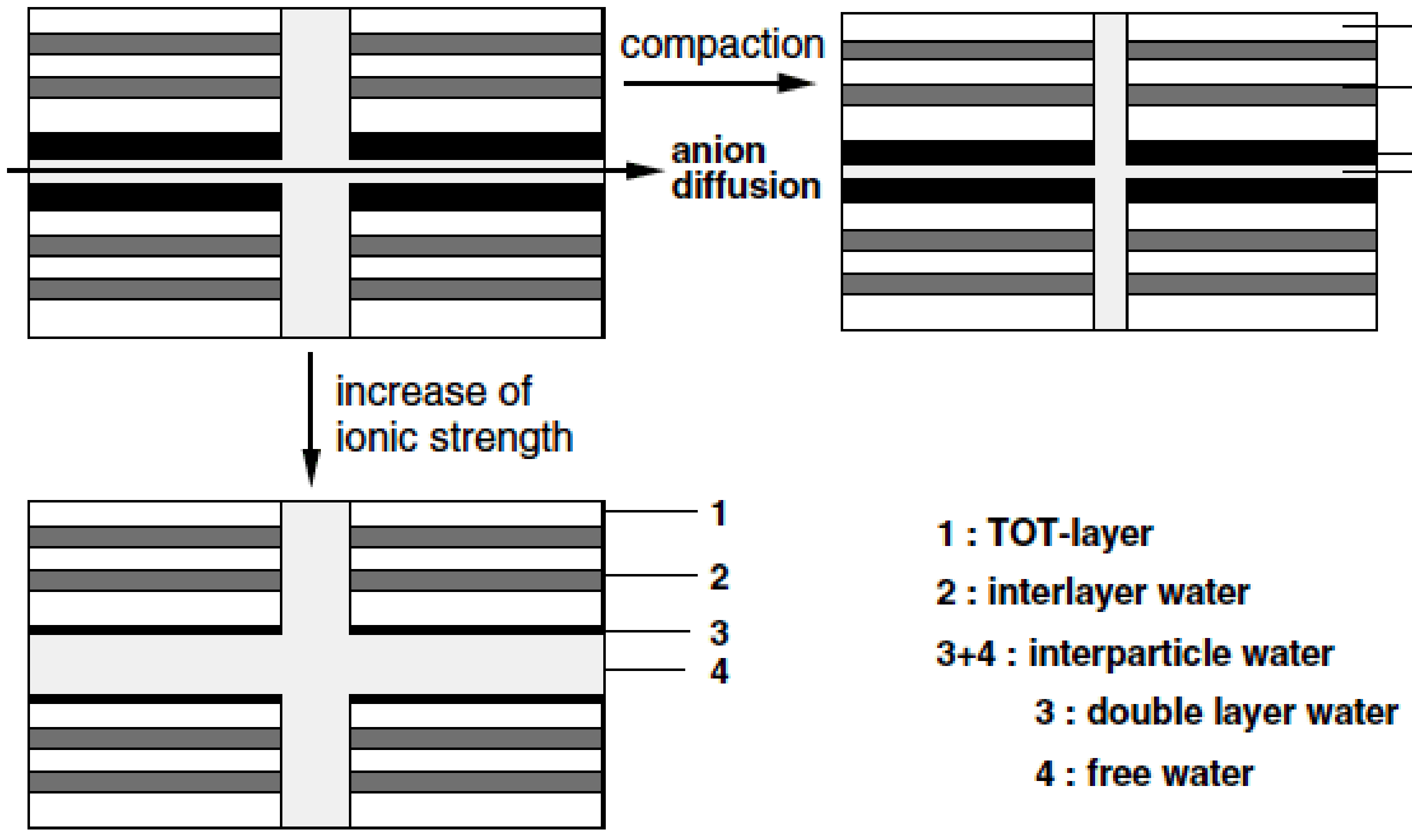
1. *Interactions?… what interaction?*
2. *Iodine redox -> oxyanions*
3. *Clays impurities*
4. *Nano-environments*

Experimental conditions/results





Anion Exclusion in Clays



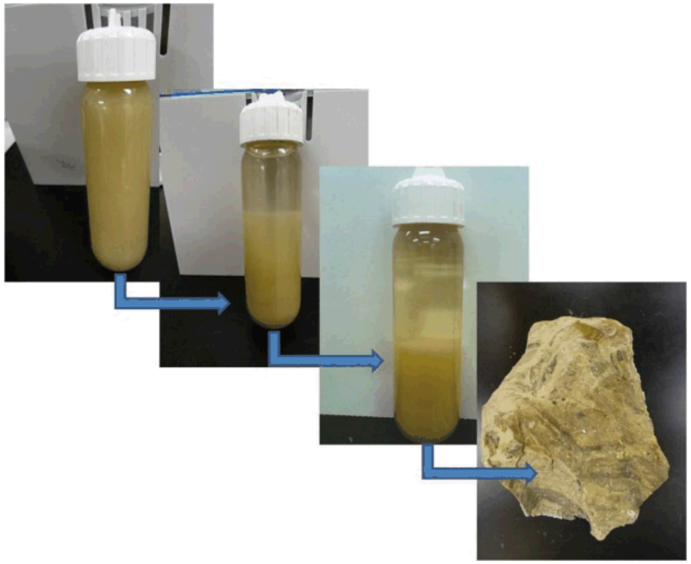
L.R. Van Loon et al. / Applied Geochemistry 22 (2007) 2536–2552

Several types of 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*

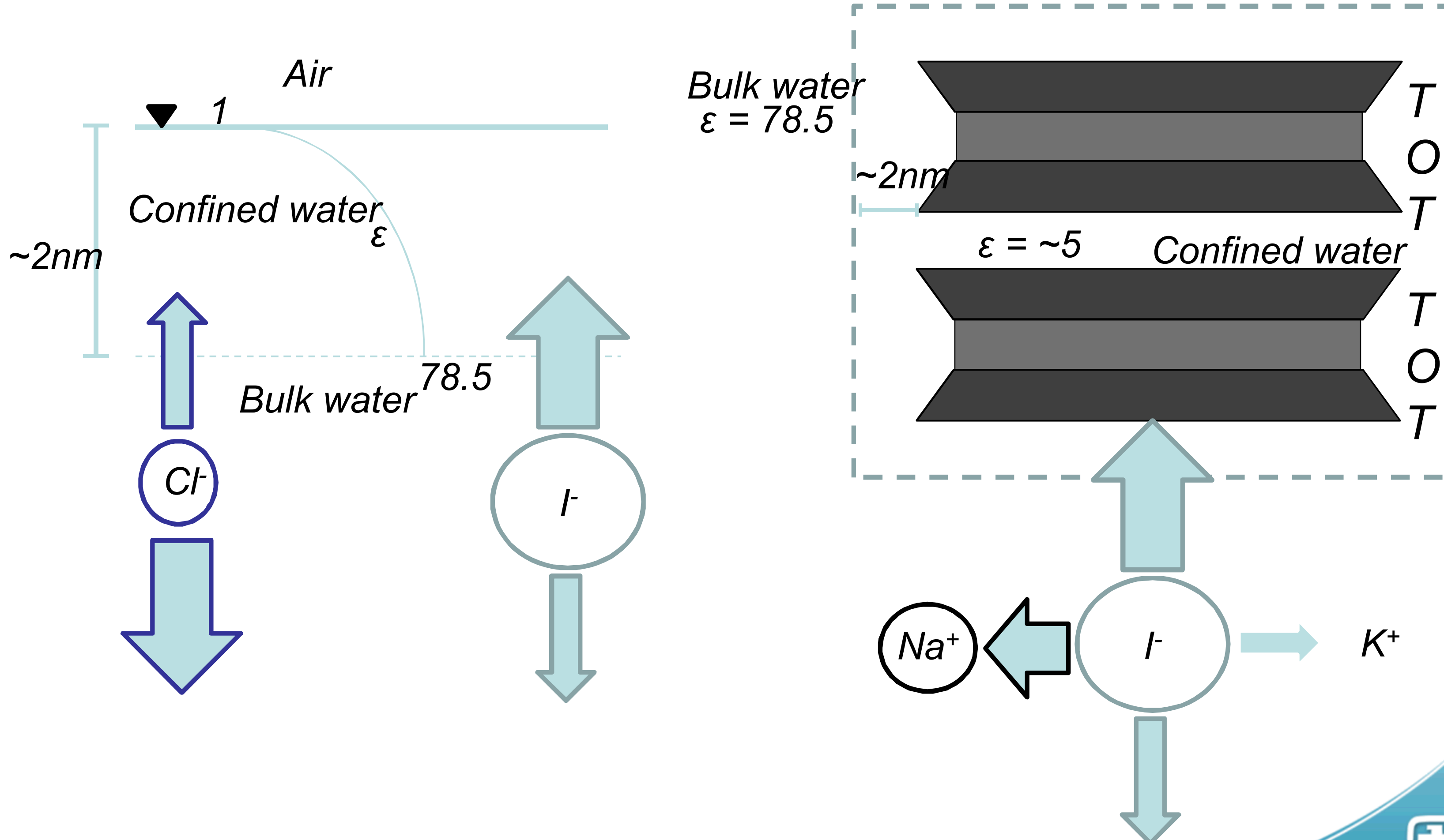


Sorption experiments:

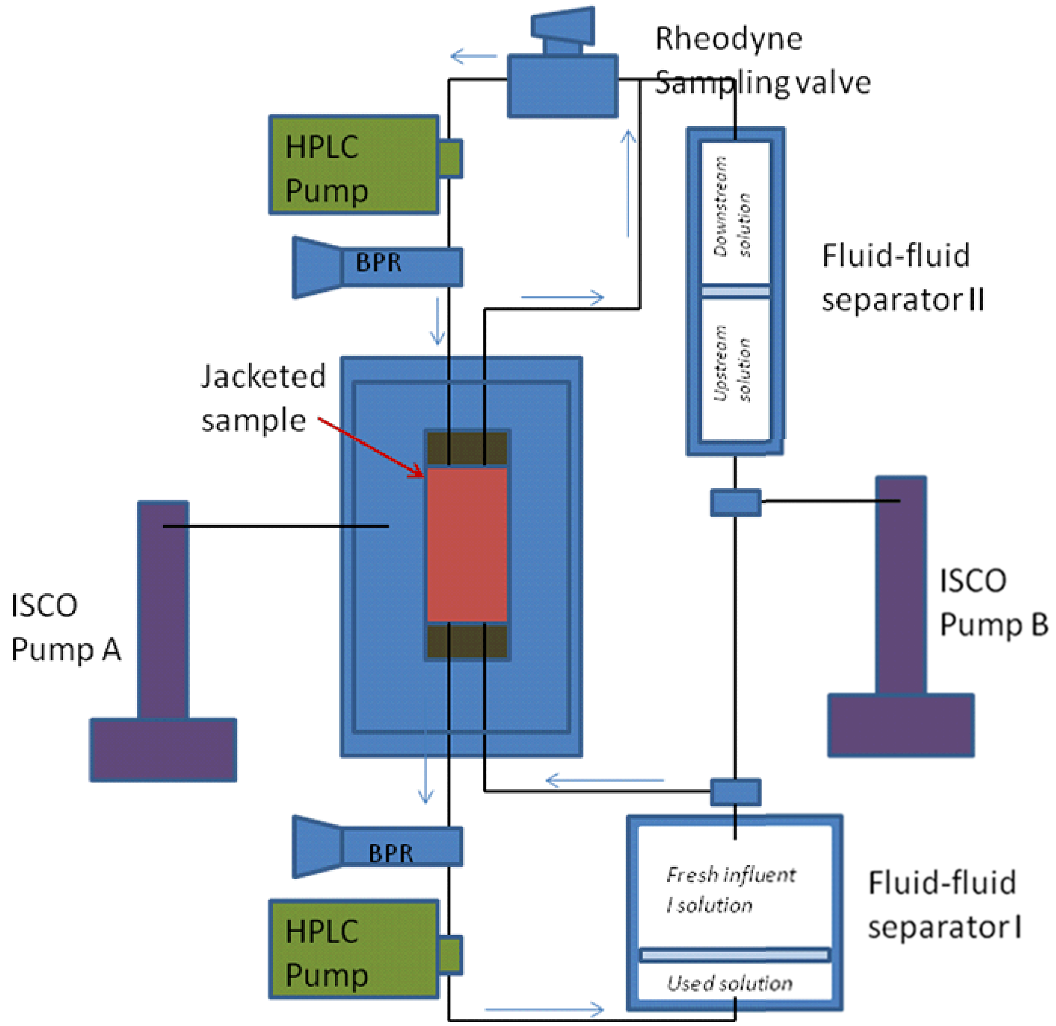
- ***N_2 BET***
- ***Methylene Blue (MB)***
  - *Na-exchanged clays*
  - *Variable amounts of MB were added until clay surface was saturated*
- ***$BaCl_2$ Exchange***
  - *Excess of barium displaces native cations*
  - *Measure native cation release*
- ***Iodide***
  - *Solid:Liquid ratio: 100g/L*
  - *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		

Data is consistent with ion pair formation caused by surface induced changes to water structure.

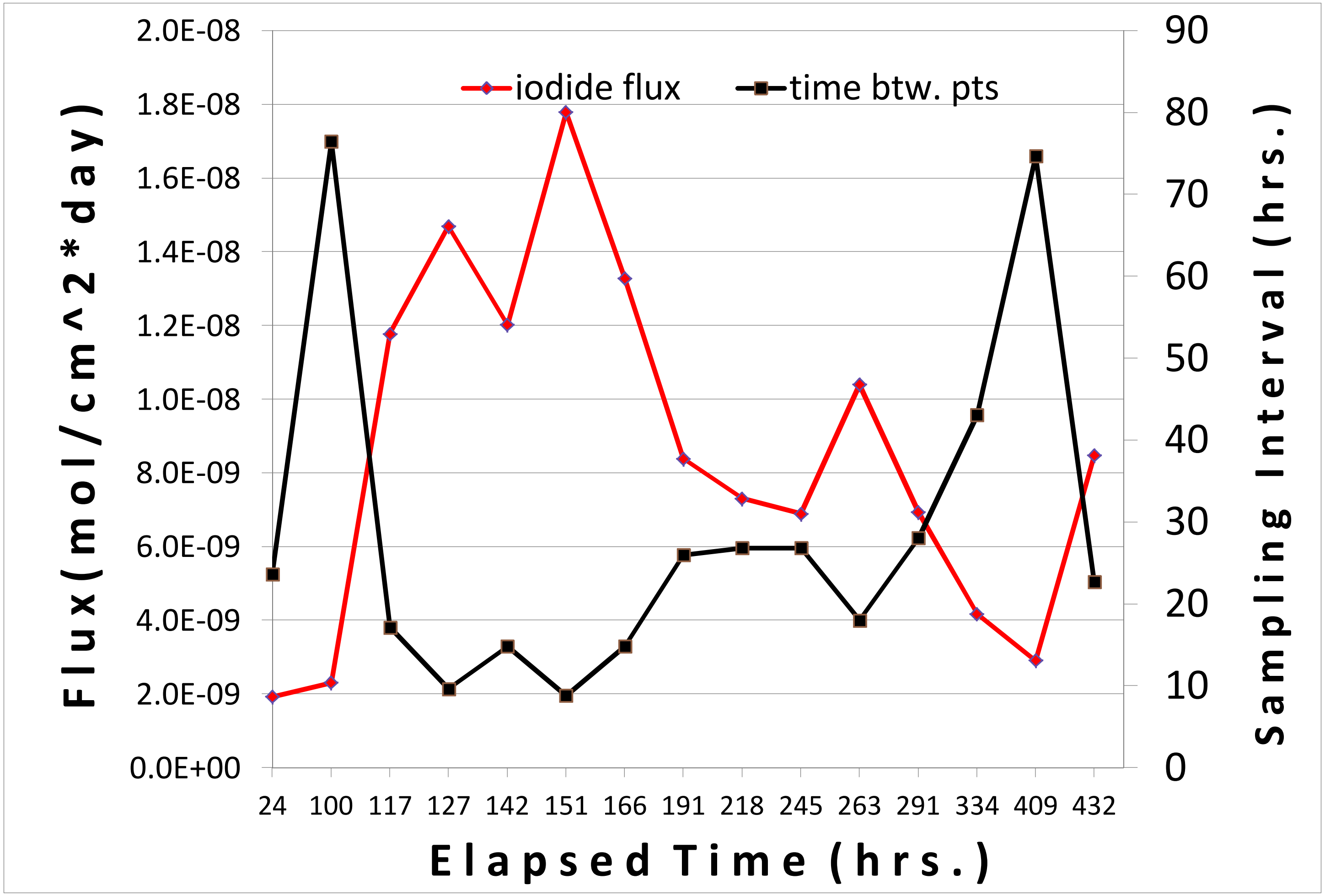


Diffusion studies are underway completed in a constant pressure system.



Schematic courtesy of Tom Dewers

Sampling Rate is Critical!



Part 2 -- Thermal Effects – Heated Clay Experiments

- **Materials**
  - Illite, Illite-Smectite, Smectite, Palygorskite
- **Methods**
  - Heat clays for 1 hr., at ambient pressure in air
  - External surface area via BET (N2 adsorption)
  - CEC via BaCl2 exchange

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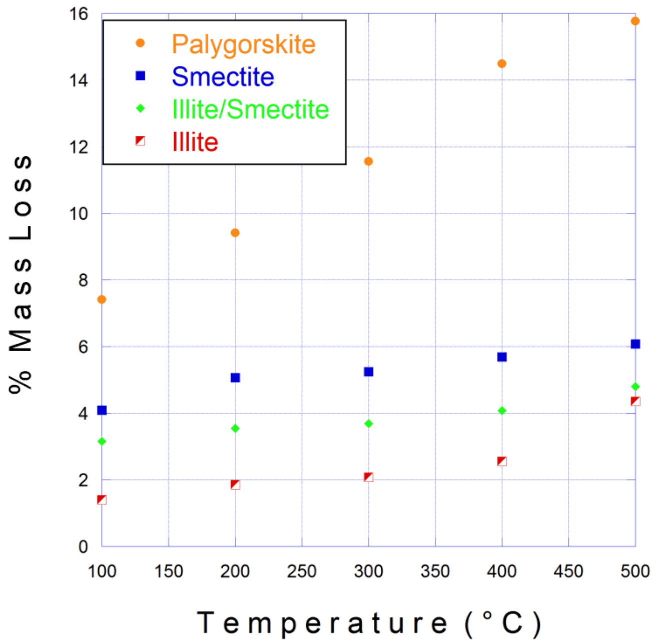
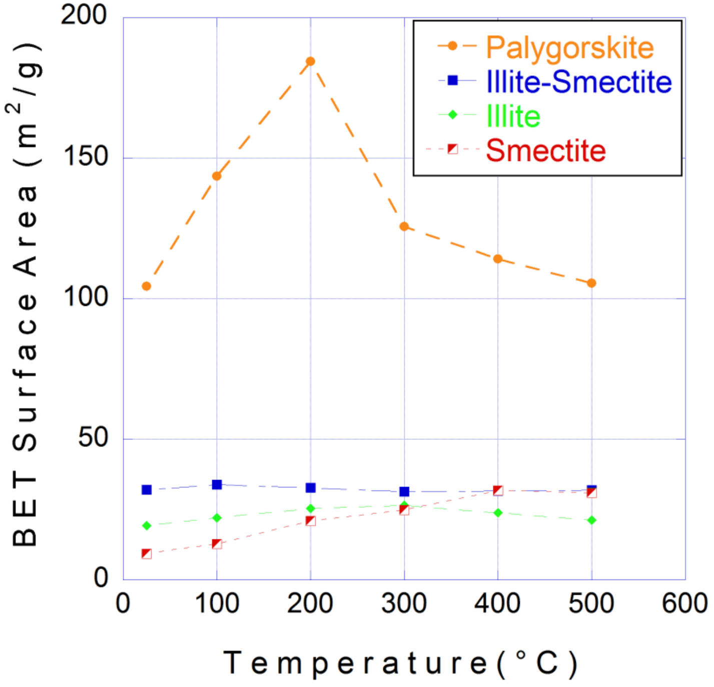
Results I -- Mass Loss on Heating

Clay morphology matters





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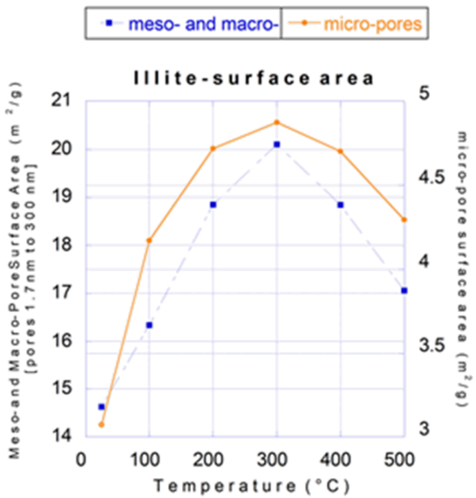
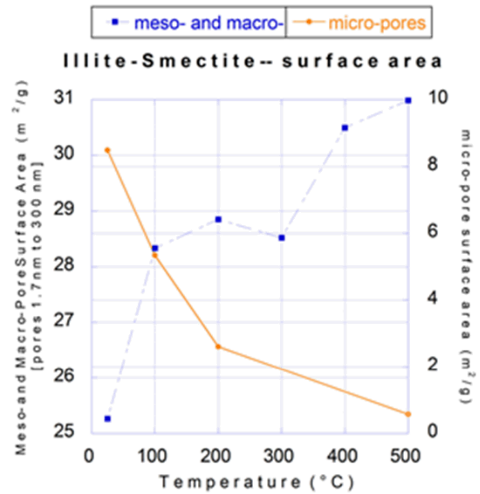
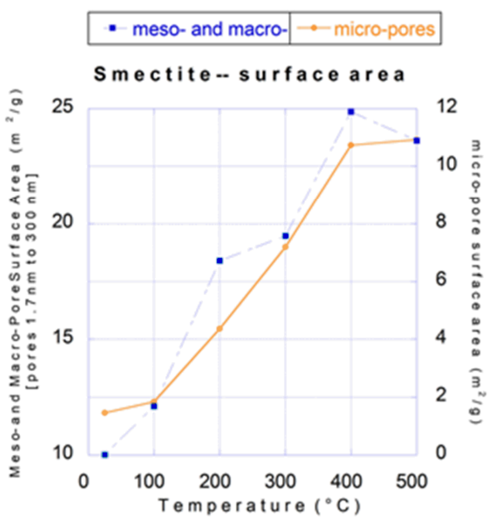
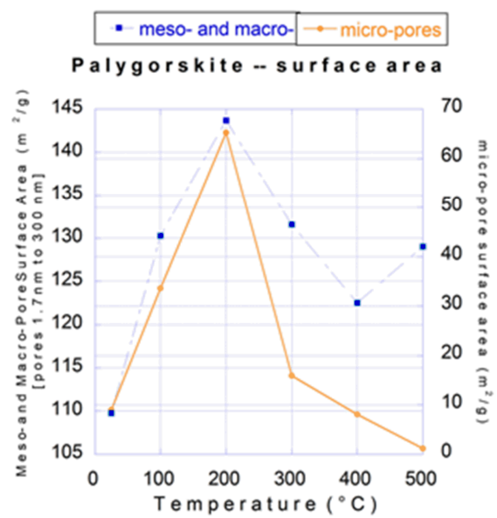
Results II – Pore Size Distributions









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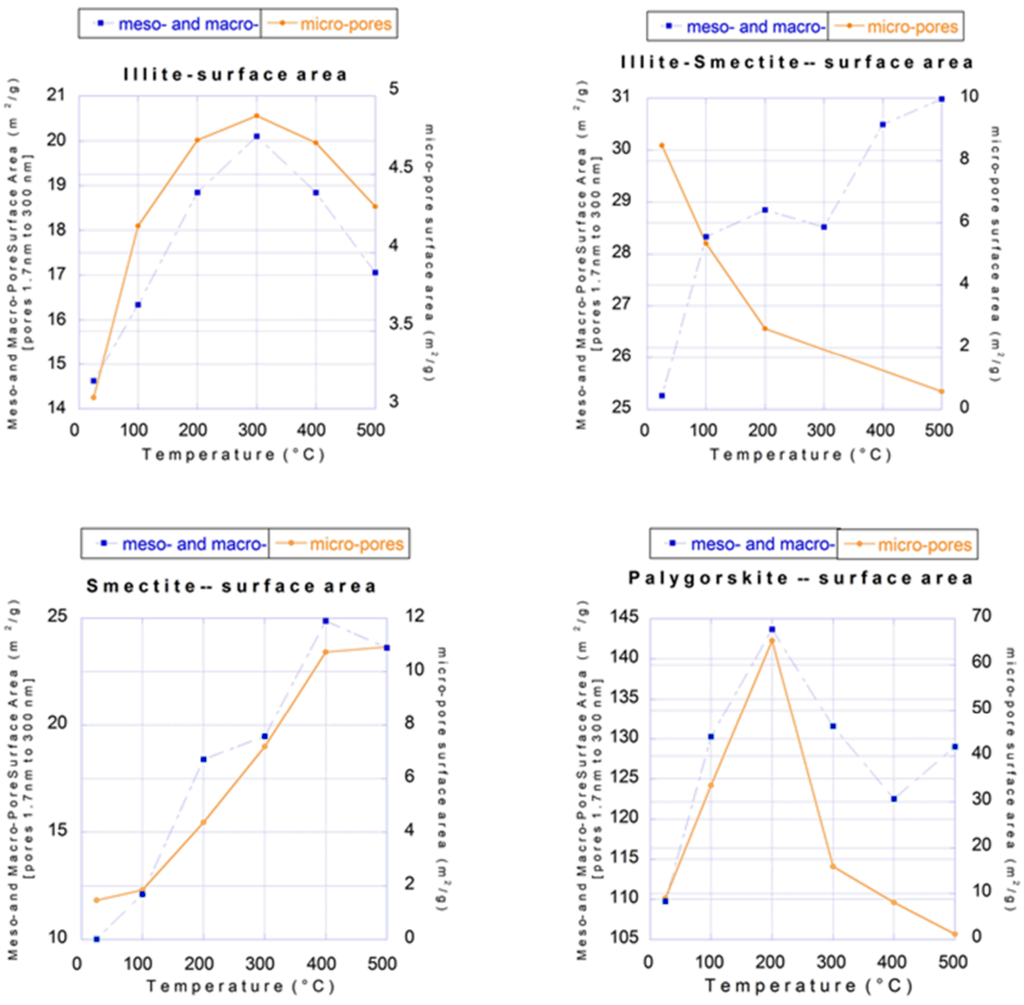
Results II – Pore Size Distributions



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Conclusions and Next Steps
Part 2. Thermal Treatments and CEC

- **Thermal treatments show significant effects on CEC for all four clays studied.**
- **Illite and Illite-Smectite, 20-fold and 10-fold increases at 100C, respectively.**
- **For montmorillonite, the significant increase in CEC at 400 °C is perhaps of only of marginal importance.**
- **Next, investigate heating duration, water content/humidity, and effect on compaction and swelling.**

Back-Up Slides

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

Iodide uptake is dependent on ionic composition of swamping electrolyte.

		CEC meq/100g	K_D [mL/g] (Std. Dev.)		
			$CaCl_2$	$CaBr_2$	$MgCl_2$
Layered	Kaolinite	4.61	0.34 (0.35)	-0.34 (0.28)	0.09 (0.43)
	Ripidolite	6.03	0.16 (0.33)	-0.05 (0.01)	0.22 (0.66)
	Illite	27.61	1.02 (0.22)	-0.48 (0.32)	0.37 (0.01)
	Illite.Smectite	30.39	0.87 (0.16)	-0.30 (0.09)	0.90 (0.34)
	Montmorillonite	151.92	0.56 (0.18)	-2.16 (0.53)	-1.70 (0.47)
Fibrous	Sepiolite	8.98	-0.43 (0.12)	0.52 (0.25)	-0.35 (0.37)
	Palygorskite	29.22	0.41 (0.78)	0.80 (0.41)	0.48 (0.10)

All electrolytes at 0.05M

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