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Spent Fuel and Waste Science and Technology

Illitization Experiments on Cation Exchanged Smectite

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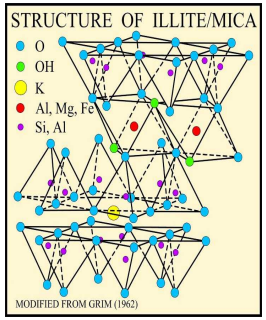
Background and Motivation

- **Illitization: the formation of illite from smectite clay by diagenetic processes**
- **Hydrothermal reaction (or hydrous pyrolysis) used in laboratory experiments to control diagenetic reactions**
- **Dependent on:**
  - Time
  - Temperature
  - K^+ concentrations
  - Solid to liquid ratio
- **Important for heat effects on hydrothermal alteration of bentonites (used for barrier systems)**
- **Typically thought to take a long time for conversion**

Source: Roaldset et al. Clay Minerals 33, 147-158, 1998.

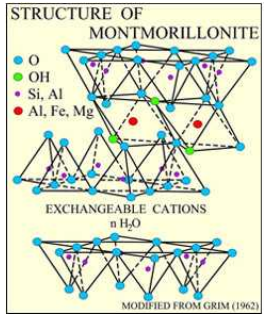
The Conversion of Smectite to Illite

Stoichiometric relationship of reaction empirically derived from Huang et al. (1993).



$$2Na_{0.4}(Al_{1.47}Mg_{0.29}Fe_{0.18})Si_4O_{10}(OH)_2 + 0.85K^+ + 1.07H^+$$

Na-Smectite



$$1.065K_{0.8}(Al_{1.98}Mg_{0.02})(Si_{3.22}\,Al_{0.78})O_{10}(OH)_2 + 4.6SiO_2 + 0.36Fe(OH)_3 + 0.56Mg^{2+} + 0.8Na^+ + 0.9H_2O$$

Illite

- **If silica concentration decreases (i.e. dissolves), then conversion could be faster.**
- **Calculated amount of smectite in 150mL of liquid to convert to 1 mole of illite based on the solubility of SiO_2 at 200ºC.**
- **Optimal amount was ~0.169 g smectite to 150 mL liquid, or loading of 1:1000 (S:L)**
- **Altered loading to see if there is a critical point for conversion**

Source: Huang et al. *An Experimentally Derived Kinetic Model for Smectite-to-Iliite Conversion and its Use as a Geothermometer.* Clays and Clay Minerals, Vol. 41, No. 2, 162-177, 1993.

Experimental Procedures

Sample Preparation

<75μm fraction

Crush and sieve SWy-2 Na-Smectite

<2μm fraction

Suspension and settling of <75μm fraction

Exchanges

Exchange <2μm fraction with 1M KCl, CsCl, and NH4Cl

Hydrothermal Alteration

Parr Vessel Reaction

Place exchanged clay in Parr Vessel at various load ratios

Conversion Investigation

XRD Analysis

001 peak from oriented and glycolated mounts

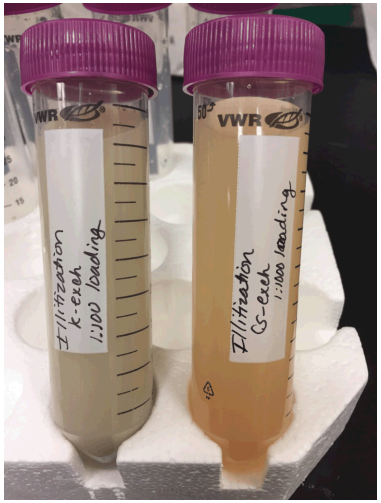
Cation Exchange Capacity

$BaCl_2$ exchange method by Hendershot and Duquette (1986)

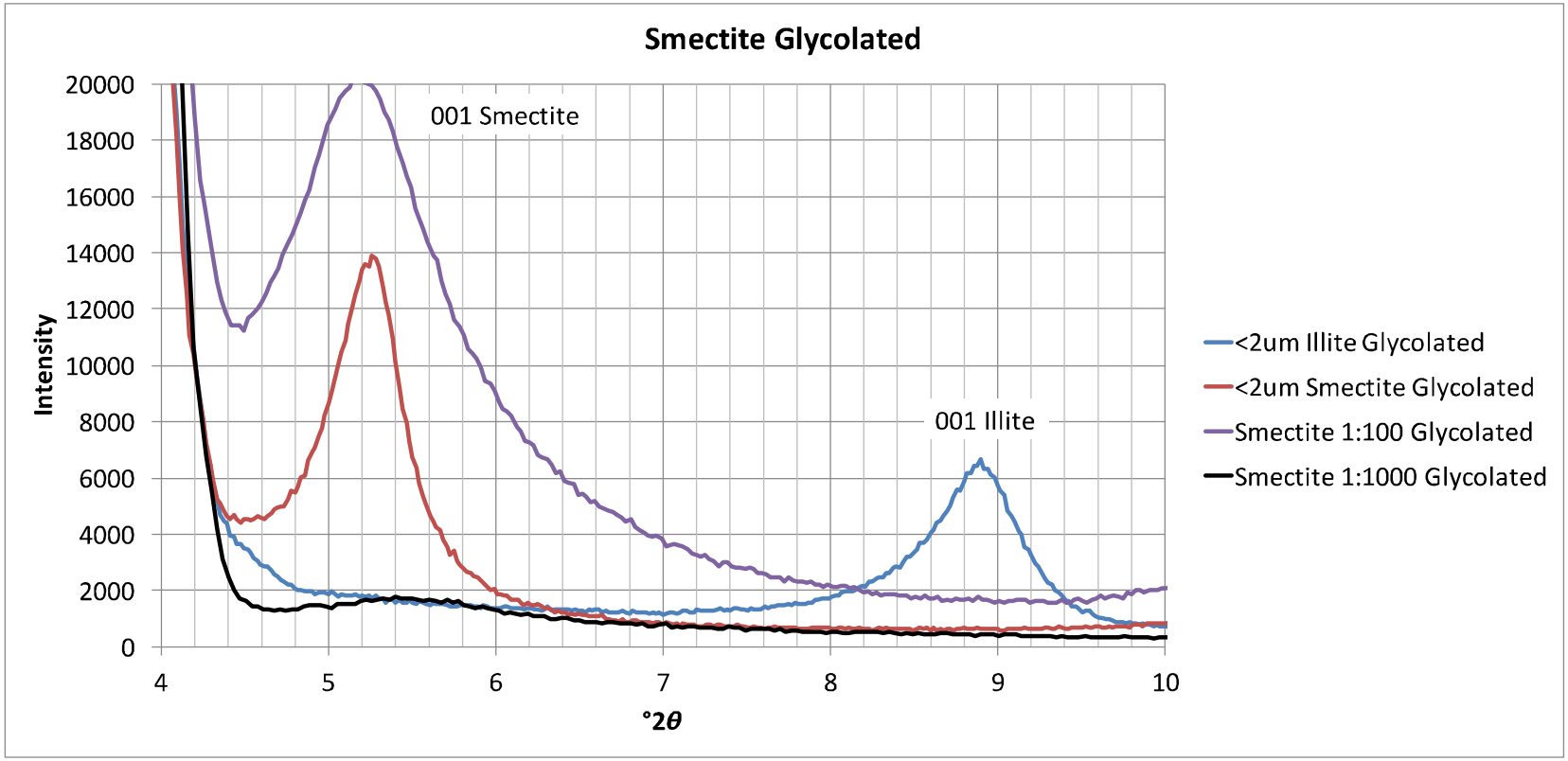
Sample Conditions

- **All samples subject to T=200ºC for 1 week within Parr Vessel**

Sample	Loading
K-Exchanged Smectite	1:20
	1:100
	1:500
	1:1000
Cs-Exchanged Smectite	1:500
	1:1000
NH4-Exchanged Smectite	1:100
	1:500
<2μm Smectite	1:100
	1:1000

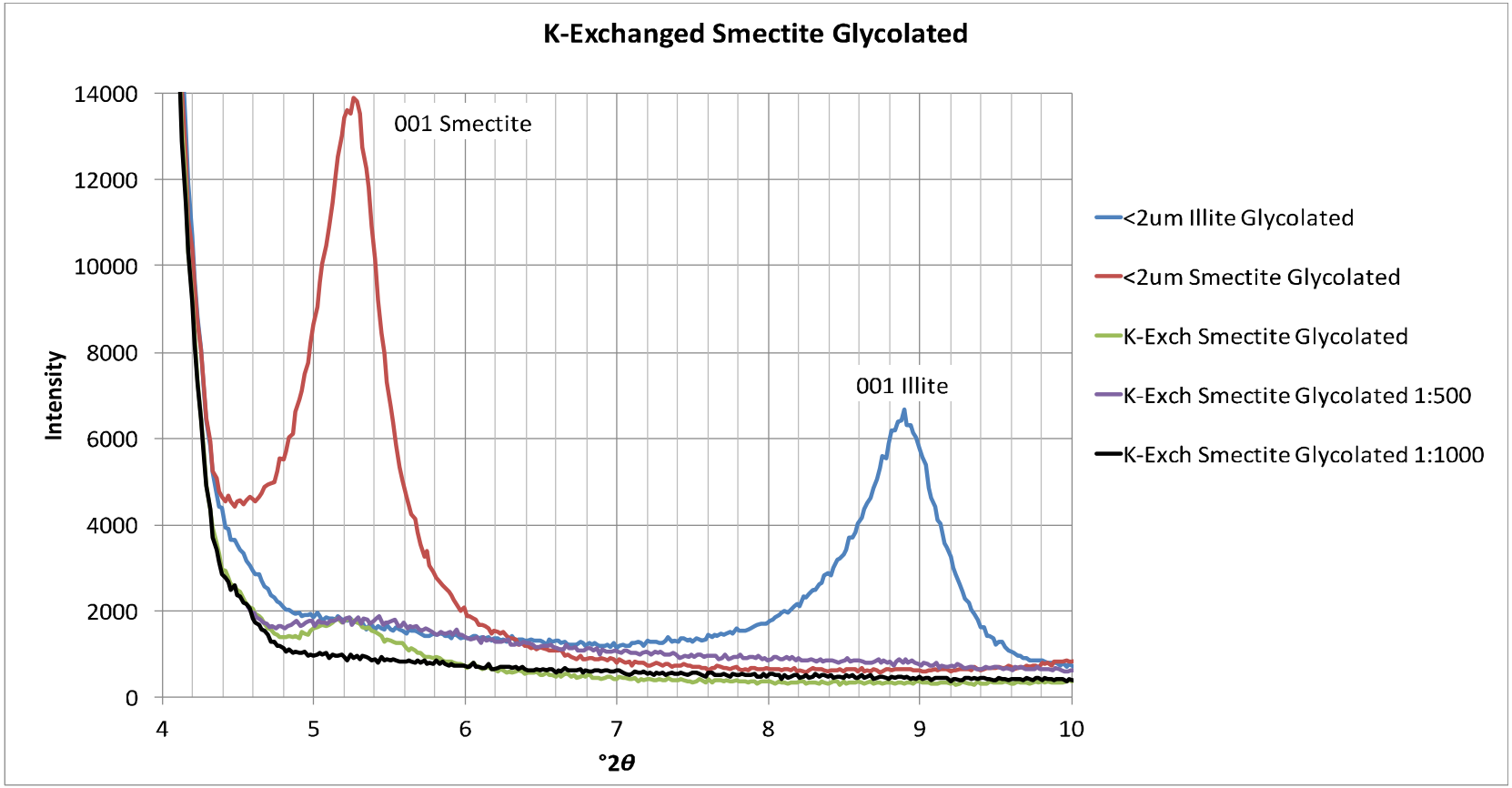


Results: XRD



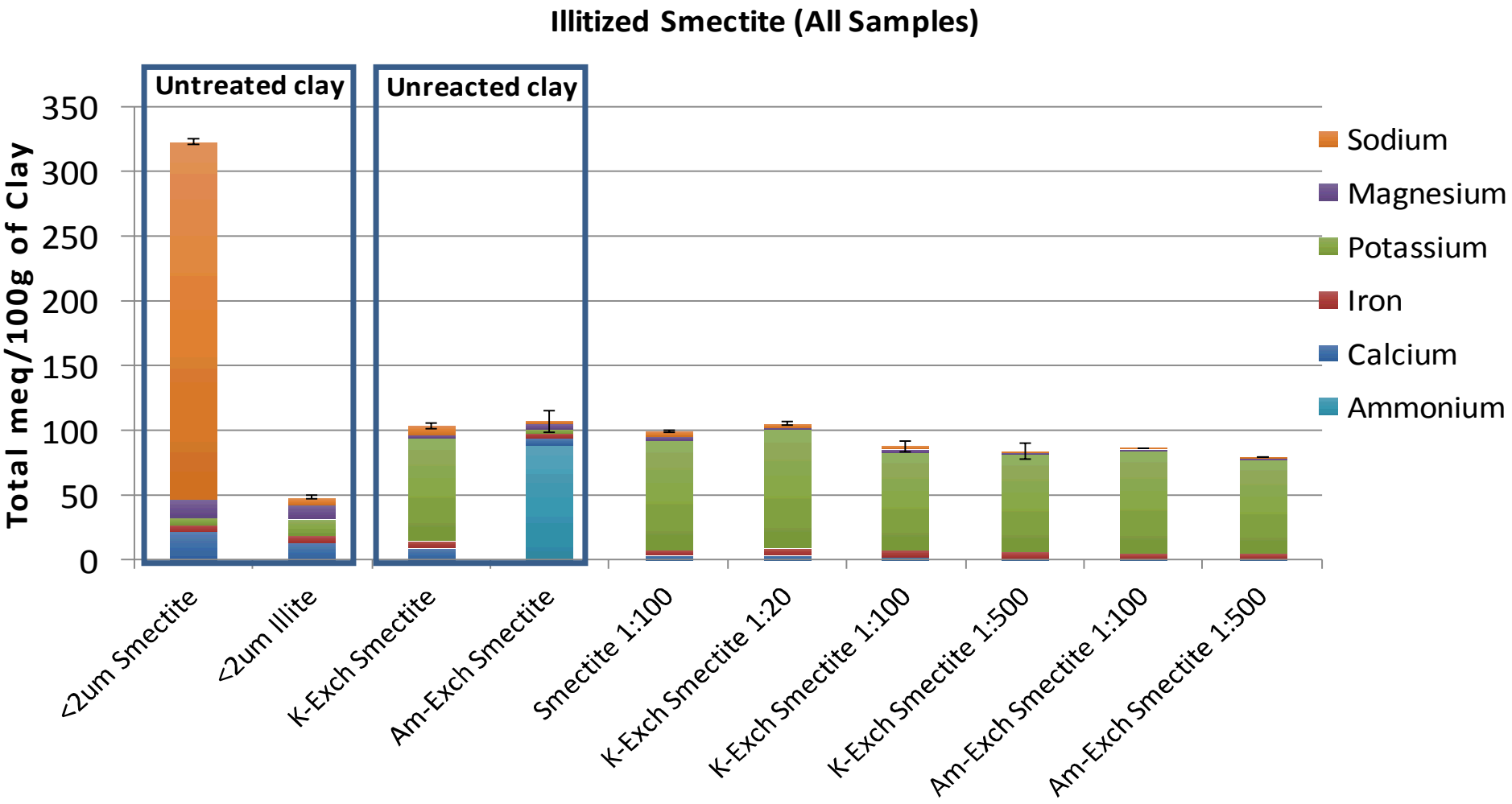
- 1:1000 loading shows no prominent 001 peak for smectite or illite.

Results: XRD

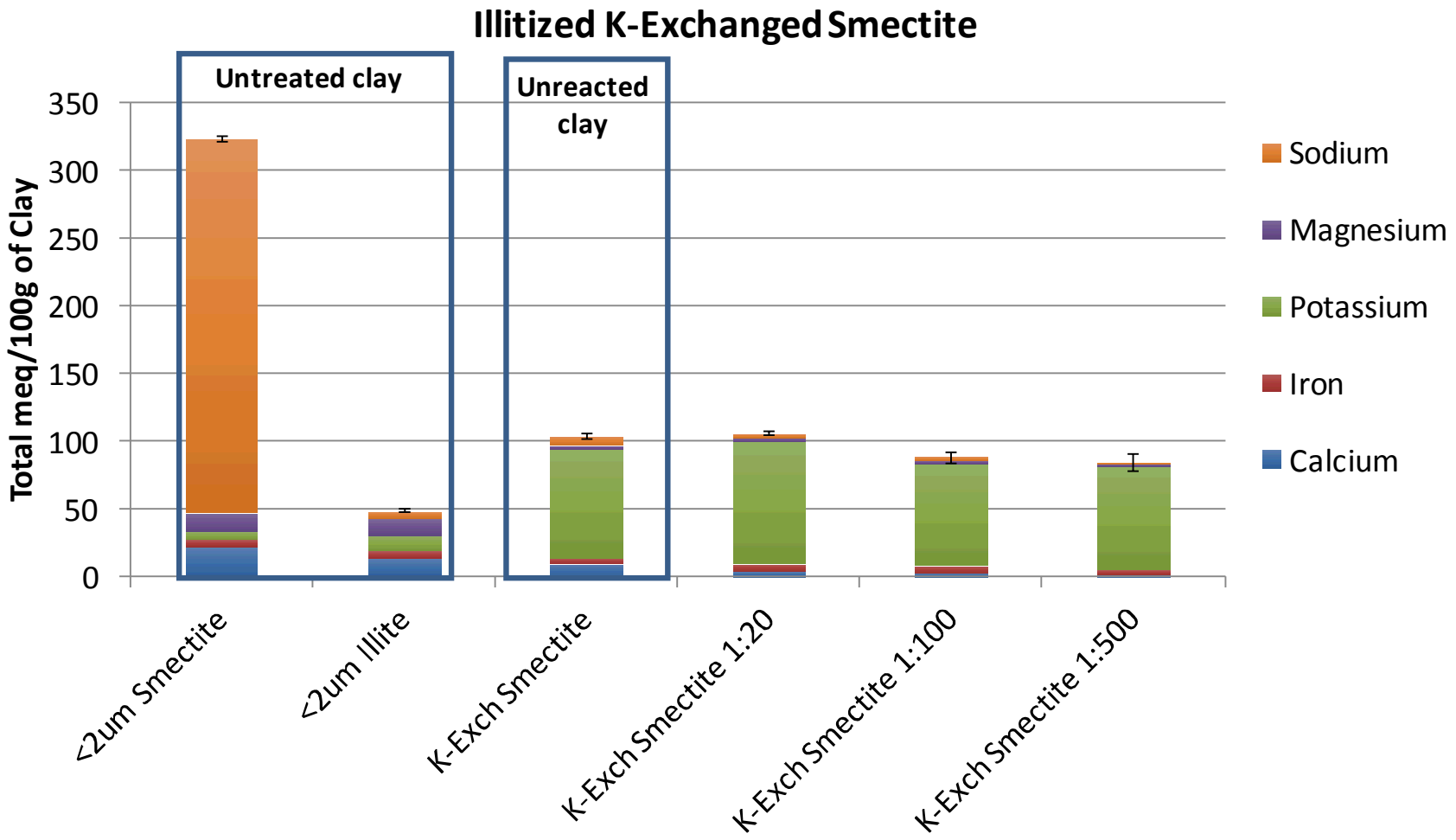


- Only exchanging smectite with K^+ decreases 001 smectite reflection
- Again, 1:1000 loading shows no prominent peaks

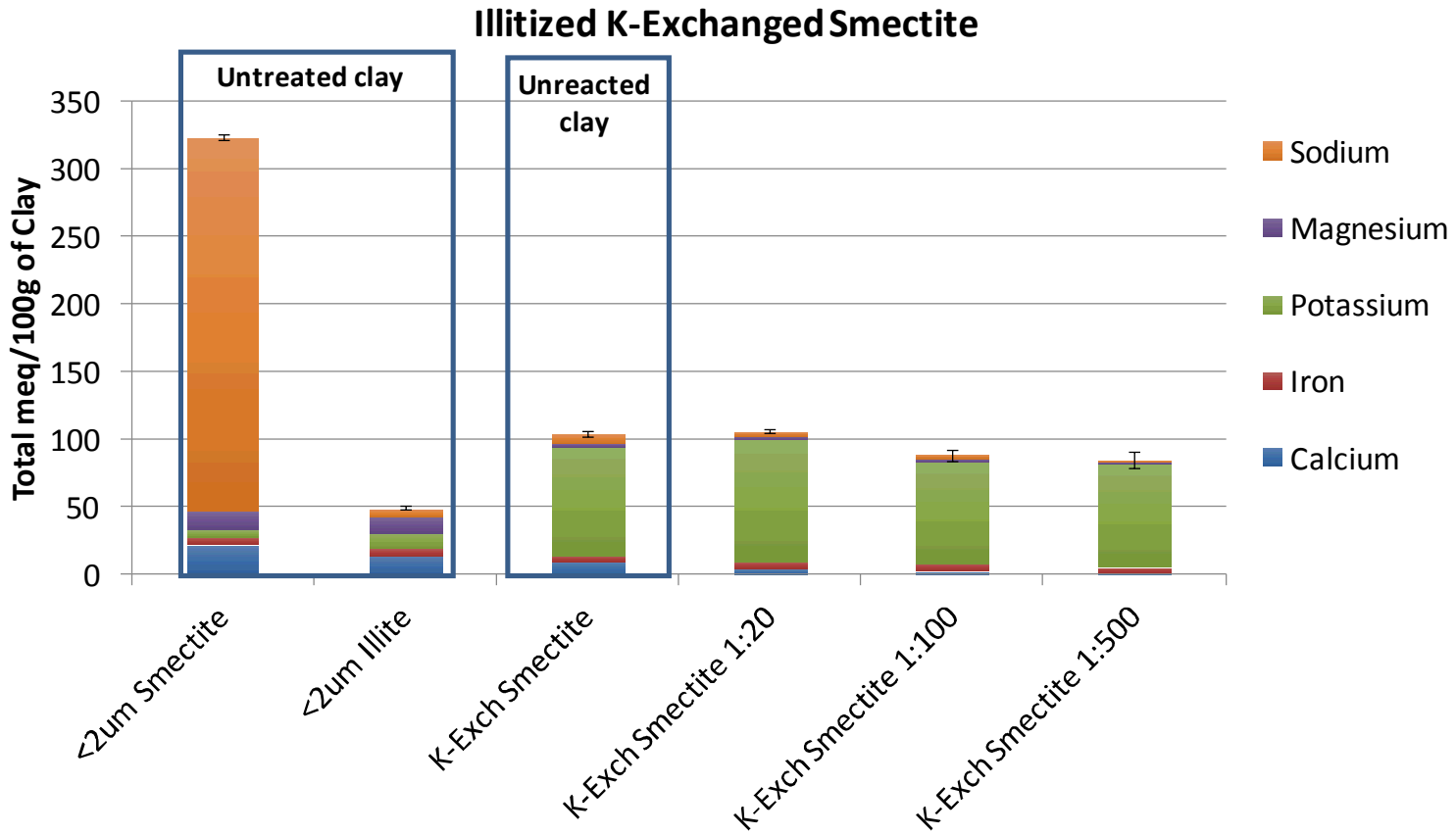
Results: Cation Exchange Capacity



Results: Cation Exchange Capacity Cont.



Results: Cation Exchange Capacity Cont.



Future Endeavors

- Further XRD analysis of glycolated starting material
- Addition measurements of CEC
- Evaluation of mixed-layer illite/smectite
- Determination of %Smectite from XRD
- Addition of mica to possibly escalate conversion
- Addition of quartz to inhibit conversion

Sources

- Roaldset, E., Wei, H., and Grimstad, S., 1998. Smectite to Illite Conversion by hydrous pyrolysis. Clay Minerals 33, 147-158
- Moore, D.M., and Reynolds, R.C., 1997. X-Ray Diffraction and Identification and Analysis of Clay Minerals. 2nd Ed, Oxford University Press
- Huang, W.L., Longo, J.M., and Pevear, D.R., 1993. An Experimentally Derived Kinetic Model for Smectite-to-Illite Conversion and its Use as a Geothermometer. Clays and Clay Minerals, Vol. 41, No. 2, 162-177.
- Hendershot, W.H., and Duquette, M., 1986. A Simple Barium Chloride Method for Determining Cation Exchange Capacity and Exchangeable Cations
- Chipera, S.J., and Bish, D.L., 2001. Baseline Studies of the Clay Minerals Society Source Clays: Powder X-Ray Diffraction Analyses. Clays and Clay Minerals, Vol. 49, No. 5 398-409

Questions?