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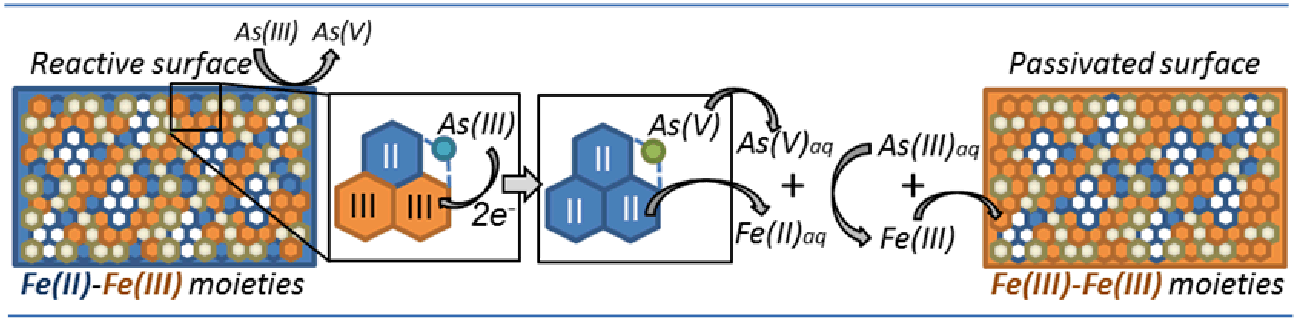

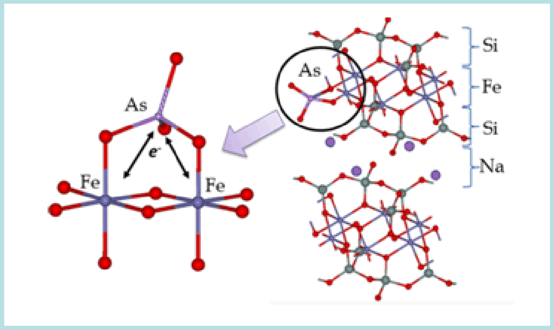

Reactivity of structural Fe(II)/Fe(III) redox couple in natural and synthetic smectite clay

Anastasia Ilgen

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Sorption and redox on clay surfaces

- Some metal oxides and clays facilitate surface redox processes [1-4]
- Iron is a common clay constituent: traces to up to 30 wt.% [5]
- The iron content of a clay affects sorption and redox properties [6]
- Electron transfer at edge sites and through basal surface [7]

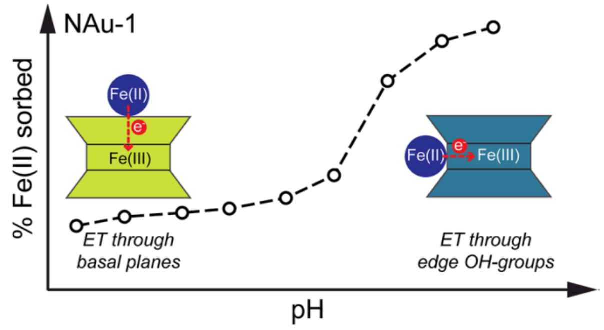
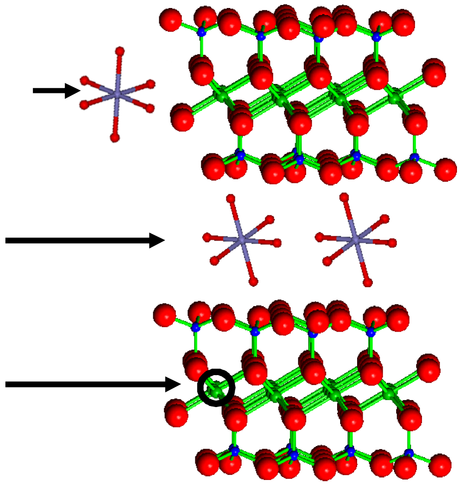


Figure from: Neumann et al., 2013



Fe^{2+} bound to surface hydroxyl groups

Fe^{2+} bound by ion exchange

Structural Fe^{2+}

Fe(II) species associated with 2:1 clay

- Reactivity of iron associated with clays depends on the local molecular environment

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[1] Oscarson, 1991; [2] Manning and Goldberg, 1997; [3] Lin and Puls, 2000; [4] Hofstetter et. al, 2003; [5] Stucki, 1988; [6] Hofstetter et.al, 2006; [7] Neumann et al., 2013.

Redox potential of clay structural Fe

Theory

- Fe(II)/Fe(III) in phyllosilicates* E° = **0.741–0.707 V** (annite), **0.710 V** (nontronite), **0.647–0.653 V** (phlogopite), and **0.460 V** (muscovite) [1]
- Based on E° (Table 1) Fe(III) in am-$Fe(OH)_3$ and goethite <u>should</u> oxidize As(III)/Sb(III) to As(V)/Sb(V)

Observations

- <u>Agree with theory</u>:

  clay str. Fe(II) reduces Cr(VI) to (IV) and Tc(VII) to (IV).
- <u>Disagree with theory</u>:

  (1) clay str. Fe(II) reduces U(VI) to U(IV);

  (2) Fe(III) oxides <u>do not directly oxidize</u> As(III)/Sb(III).
- <u>Homogeneous catalysis</u>:

  aq. Fe(II) catalyzes oxidation of As(III)/Sb(III) by aq O_2.
- <u>Fe content and history-dependent redox behavior</u> [5]

Table 1

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	E° =1.232 V	[2]
$SeO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SeO_3 + 2OH^-$	E° =1.151 V	[2]
$Fe(OH)_3$ (am) + $3H^+ + e^- \rightarrow Fe^{2+}$(aq) + $3H_2O$	**E° =0.98 V**	[3]
$TcO_4^- + 4H^+ + 3e^- \rightarrow TcO_2 + 2H_2O$	E° =0.782 V	[2]
Fe^{3+}(aq) + $e^- \rightarrow Fe^{2+}$(aq)	**E° =0.771V**	[2]
α-FeOOH (goethite) + $3H^+ + e^- \rightarrow Fe^{2+}$(aq) + $2H_2O$	**E° =0.77 V**	[3]
$Sb(OH)_6^- + 3H^+ + 2e^- \rightarrow Sb(OH)_3 + 3H_2O$	E° =0.76 V	[3]
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2H_2O$	E° =0.560 V	[2]
$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$	E° =0.327 V	[2]

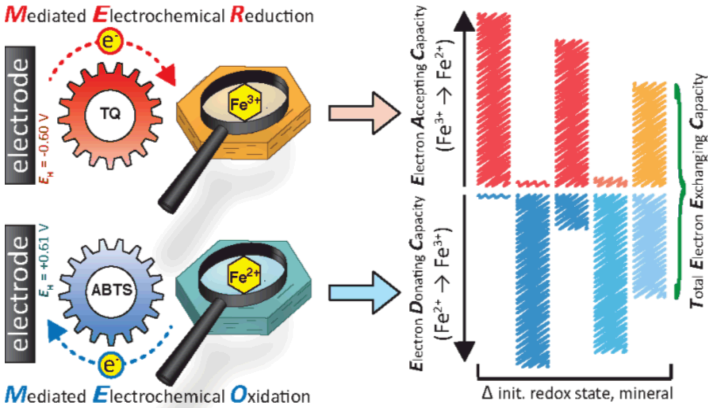

Figure from: Gorski et al., 2012

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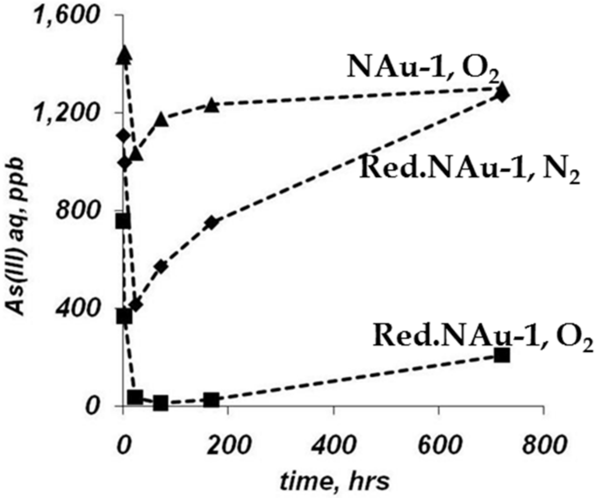
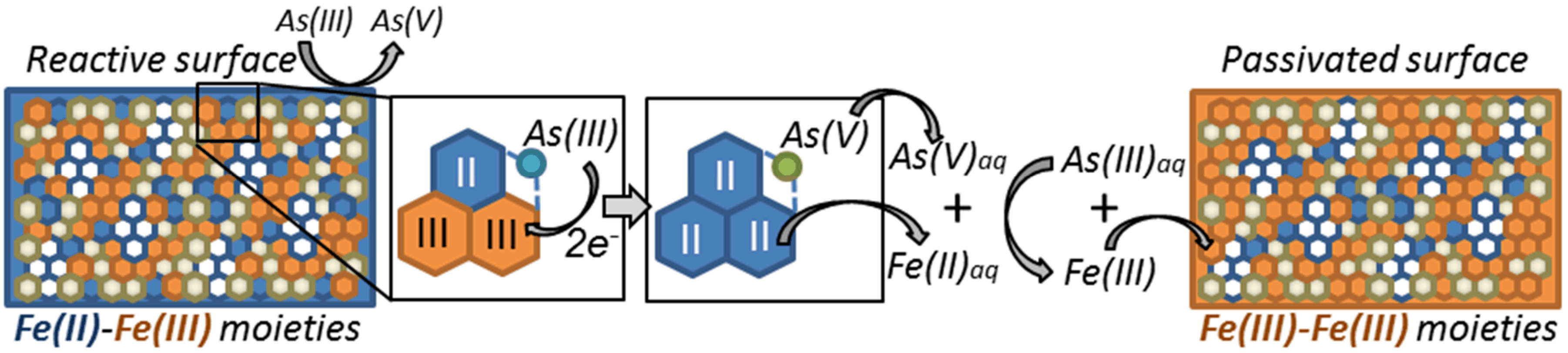
* estimated using crystal field theory;
[1] Amonette, 2002; [2] Lide, 2006; [3] Wilson et al., 2010; [4] Amstaetter et al., 2010; [5] Gorski et al., 2012

Goal: To develop a mechanistic model of the clay structural iron reactivity wrt As, Cr, Se, and Sb and further characterize redox properties of Fe-rich phyllosilicates.

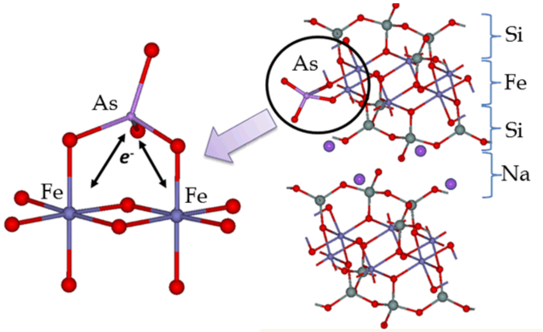
Our previous findings: Fe(III) in nontronite NAu-1 is not redox active, BUT if some structural iron is reduced to **Fe(II)** then As(III) or Sb(III) are oxidized by remaining structural Fe(III). Surface is passivated with time.





Remaining unknowns

- Mechanisms of Fe-rich clay surface activation/passivation
- How does Fe(II)/Fe(III) in octahedral lattice sites control the reactivity of clay structural iron
- Under what conditions structural Fe in nontronite is reactive towards other redox-active elements



Nontronite with adsorbed As

Current work

- Reactivity of nontronite towards Se(IV) oxidation
- Synthesis and characterization of pure Fe phyllosilicate
- Comparison of the natural nontronite and synthetic Fe phyllosilicate reactivity

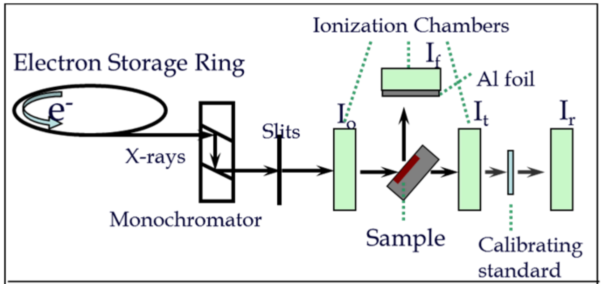
Composition of NAu-1

SiO_2 Wt. %	TiO_2 Wt. %	Al_2O_3 Wt. %	Fe_2O_3 Wt. %	MgO Wt. %	CaO Wt. %	Na_2O Wt. %	K_2O Wt. %	Total, %
51.36	0.02	8.15	35.94	0.19	3.57	0.03	0.01	99.5

From Keeling et al., 2000

As/Sb speciation analysis

APS, Argonne National Lab.



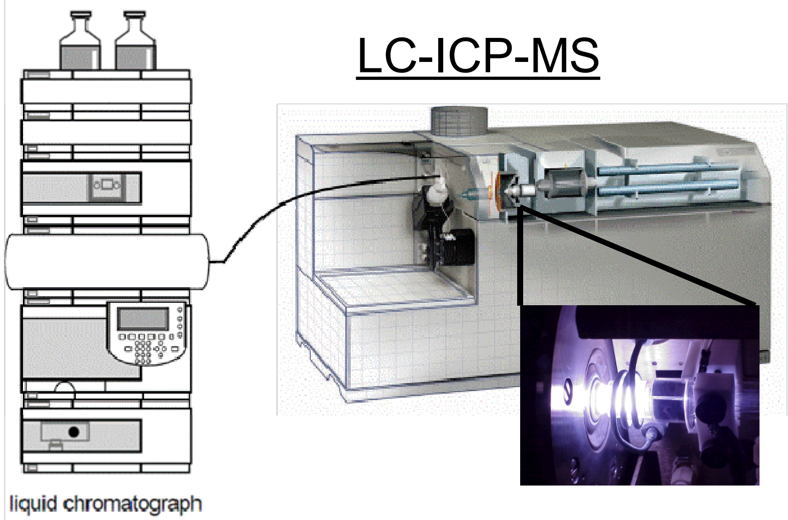
EXAFS spectroscopy instrumental setup [1]

XAS:

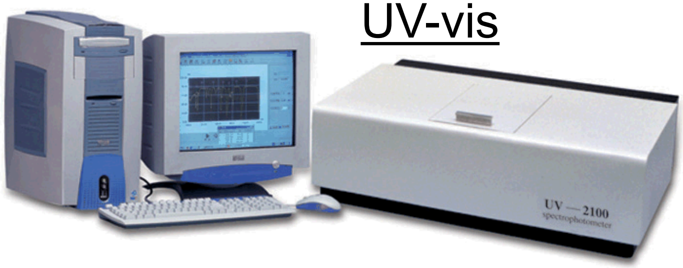
- Element specific
- Oxidation state measurement
- Local atomic structure information
- Low detection limit (~100 ppm)

AAS

LC-ICP-MS



UV-vis



Special clay nontronite NAu-1*

< 2 um size fraction

CH_3COONH_4/CH_3COOH buffer to remove carbonates

Citrate-Bicarbonate-Dithionite treatment [1]

Saturate with Na+

NAu-1 reduced/re-oxidized

~24 wt.% Fe(III)

~19 wt.% Fe(III)
~5 wt.% Fe(II)

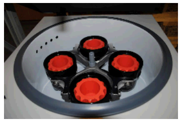
* Natural clay from Clay Mineral Society Repository
[1] Stucki, J. et al. (1984) Clays and Clay Minerals 32, 191

Synthetic Fe phyllosilicate

Sodium Hydroxide, Silicic acid, Ferrous Sulfate, and Sodium Dithionite*

Aged in Parr vessels, 150°C for 50 hours

Washed, centrifuged, aged for 24 hours in 1 M NaCl



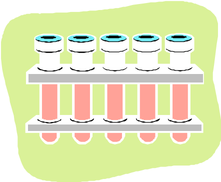
Clay washed, and dialyzed for 96 hours in deionized water

* Procedure modified from Xiang and Villemure (1995)

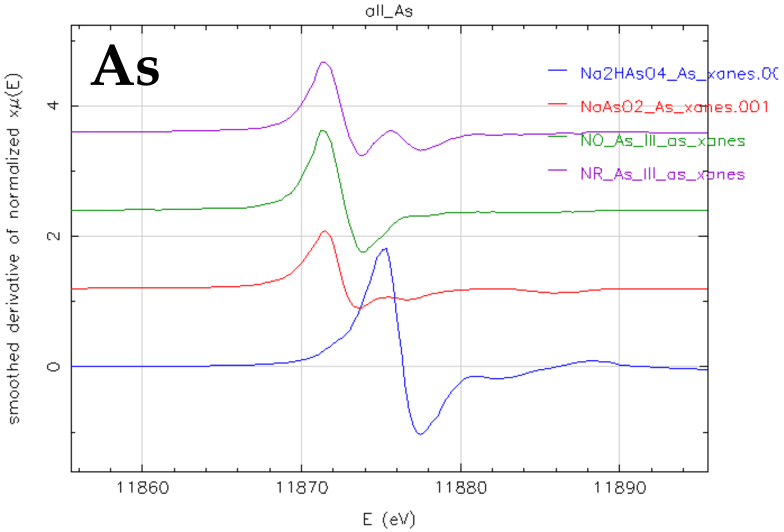
Batch experiments with As, Se, Cr, and Sb

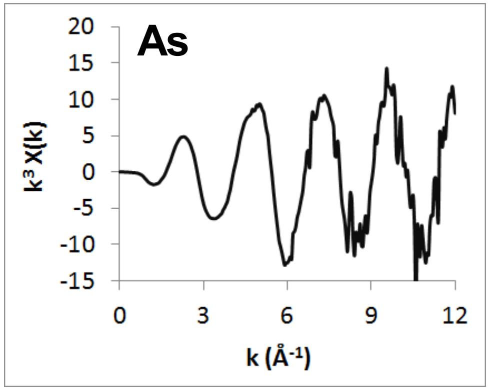
Anoxic/Oxic

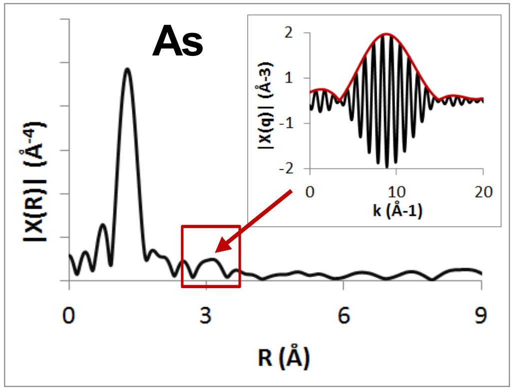
Background electrolyte 0.01 M NaCl

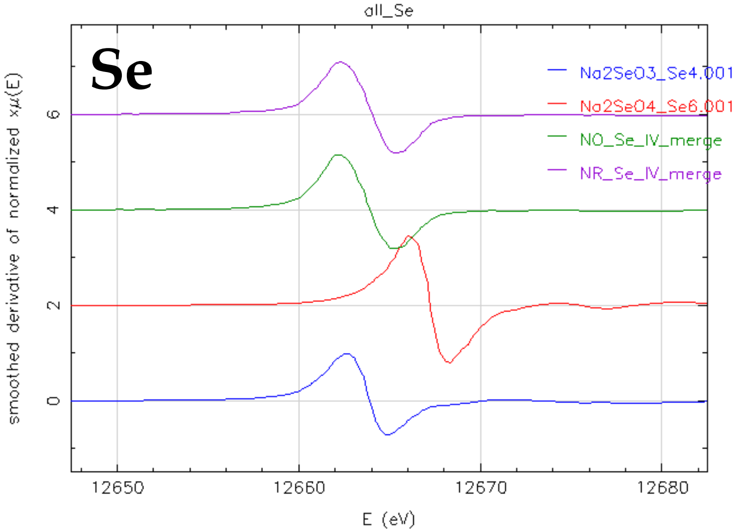


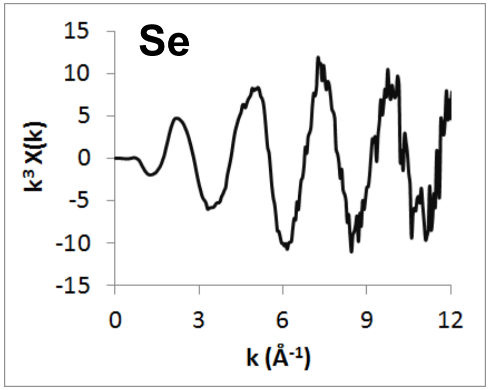
Comparison between As(III) and Se(IV) oxidation in the presence of oxidized and partially reduced NAu-1

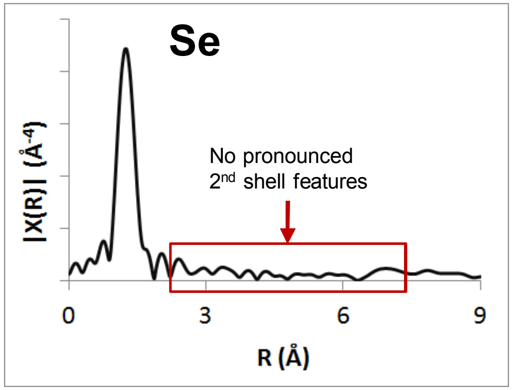






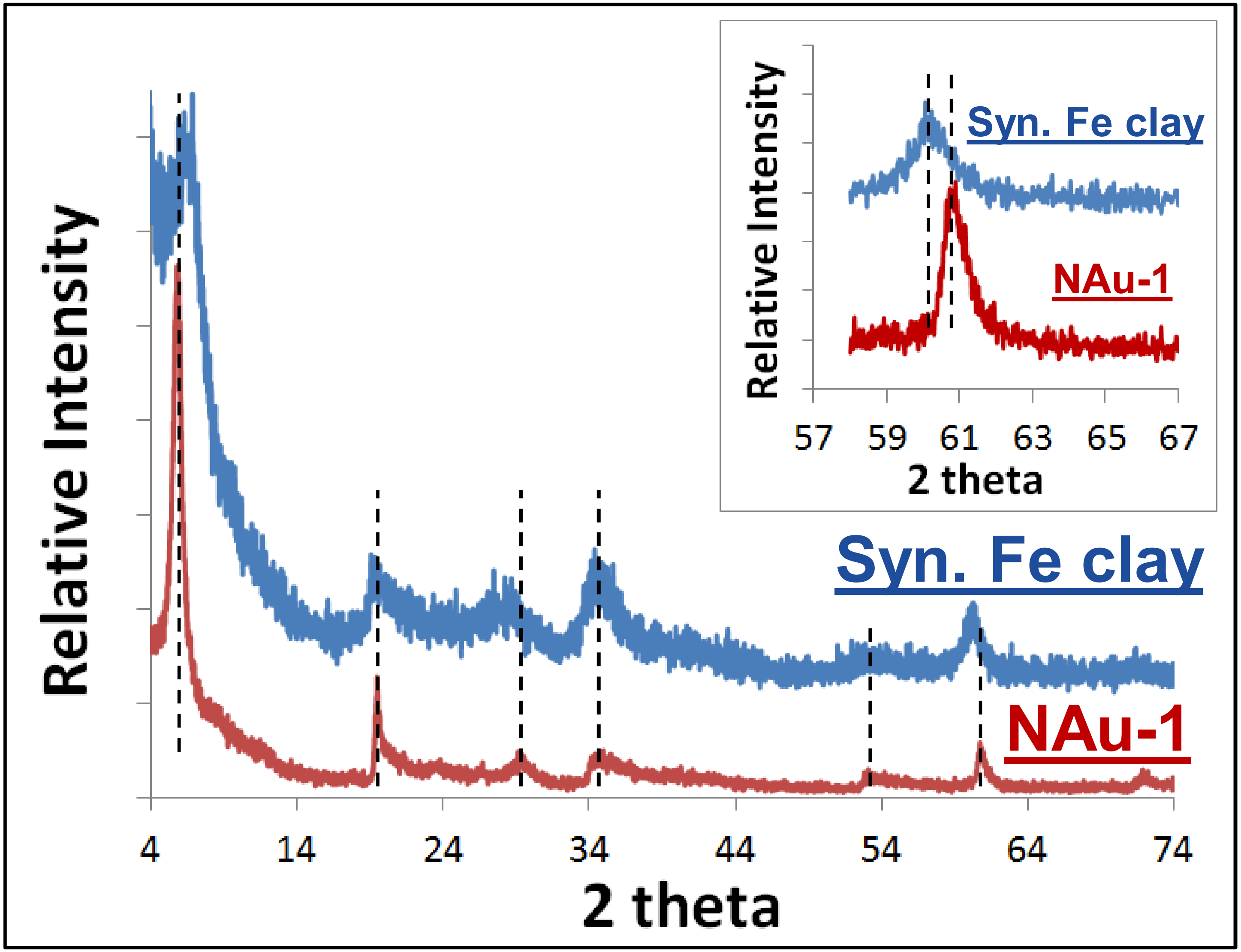






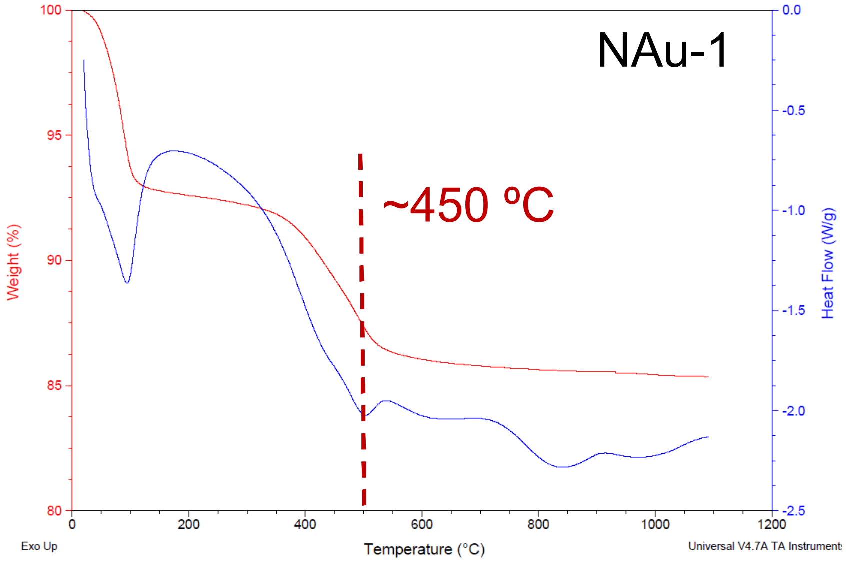
No pronounced 2nd shell features

XRD characterization of synthetic Fe phyllosilicate



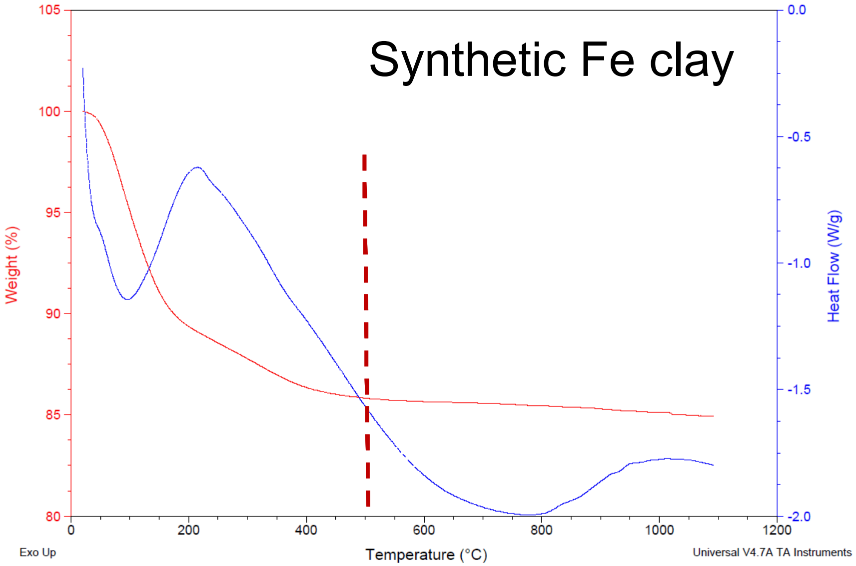
- ➢XRD patterns of NAu-1 and synthetic Fe clay show similar crystalline structure
- ➢Synthetic clay has more tri-octahedral domains compared to NAu-1 (insert)

TGA characterization

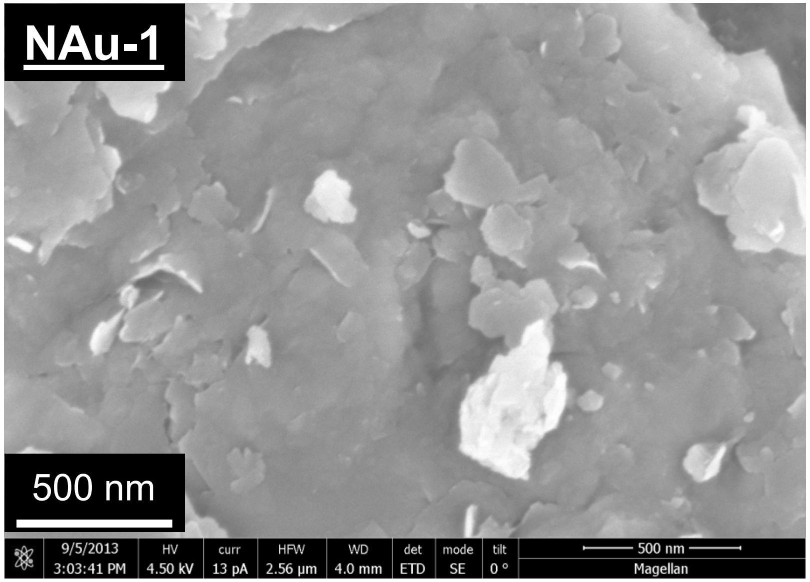


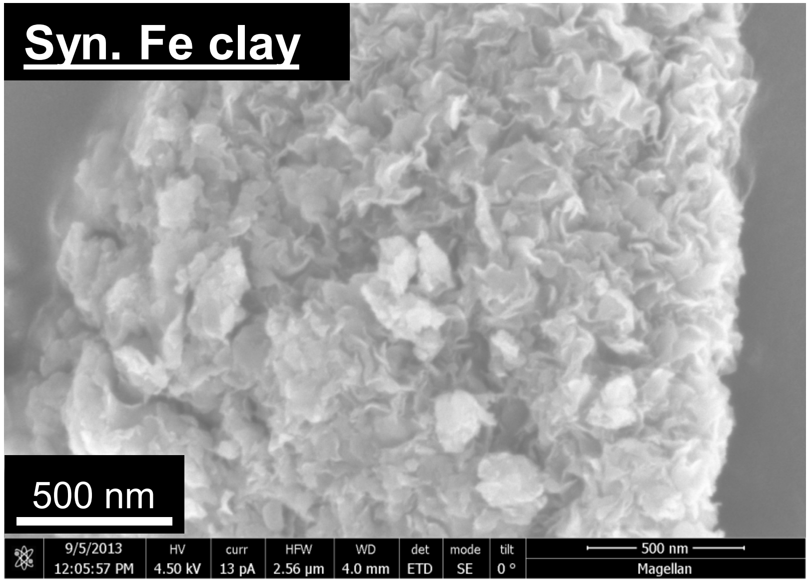
- Temperature of main dehydroxylation peak of 400-500 °C is characteristic for **nontronite**

- No corresponding peak: more trioctahedral domains, less hydroxyls in the structure.



SEM characterization

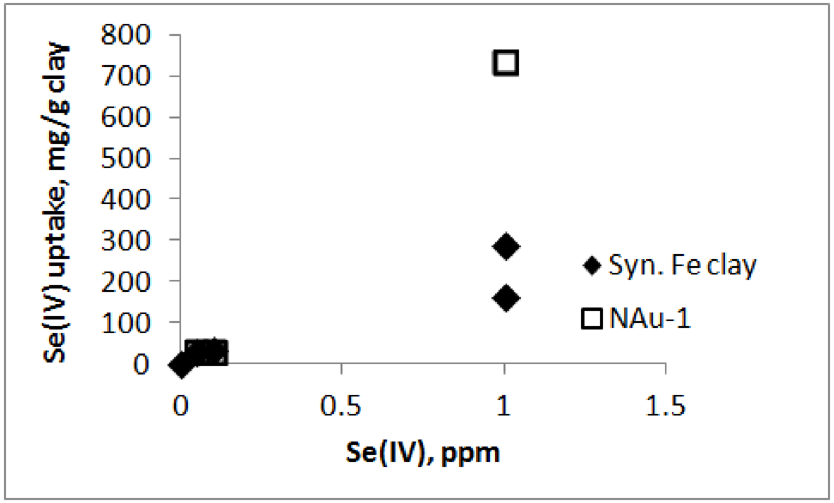


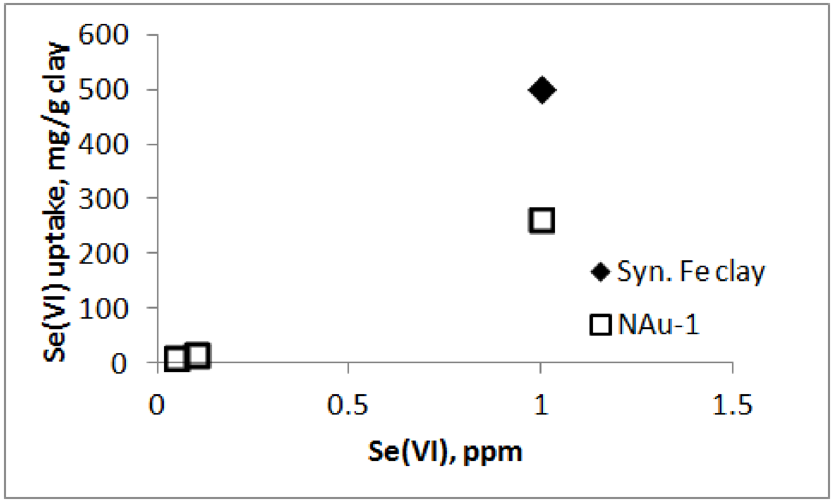


- Individual particles have typical platelet geometry, and synthetic clay particles are smaller, compared to NAu-1
- Both dried substrates show high agglomeration
- Surface area analysis: 136.6 m^2/g for synthetic clay, vs. 46.5 m^2/g for NAu-1

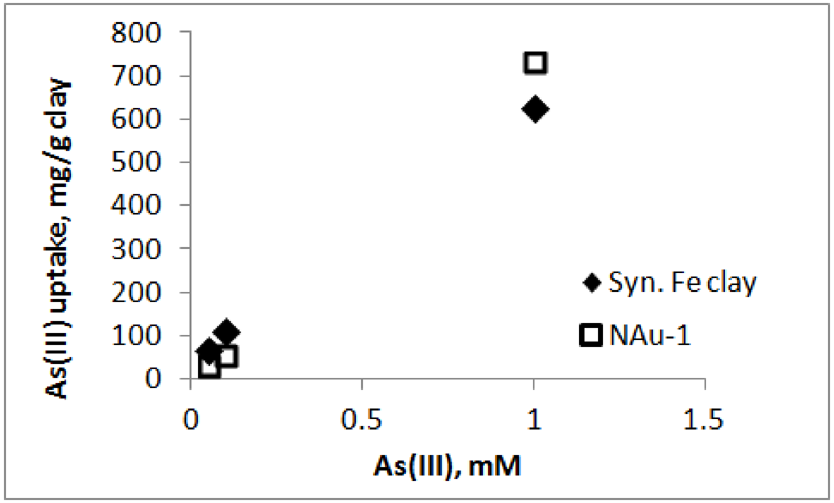
Sorption experiment

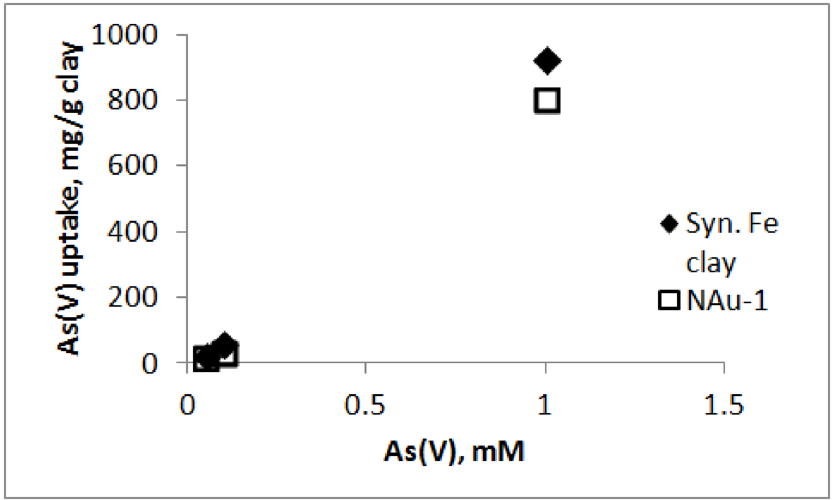
Selenium uptake





Arsenic uptake



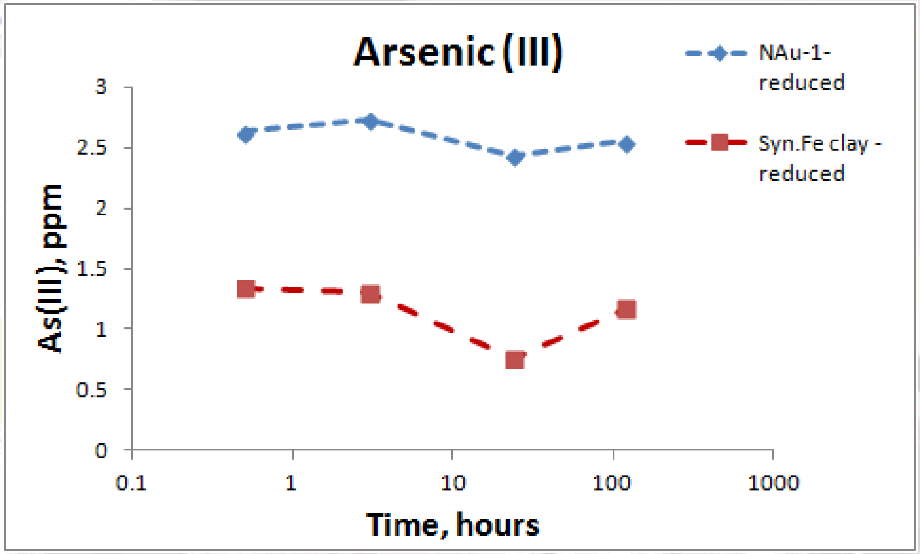


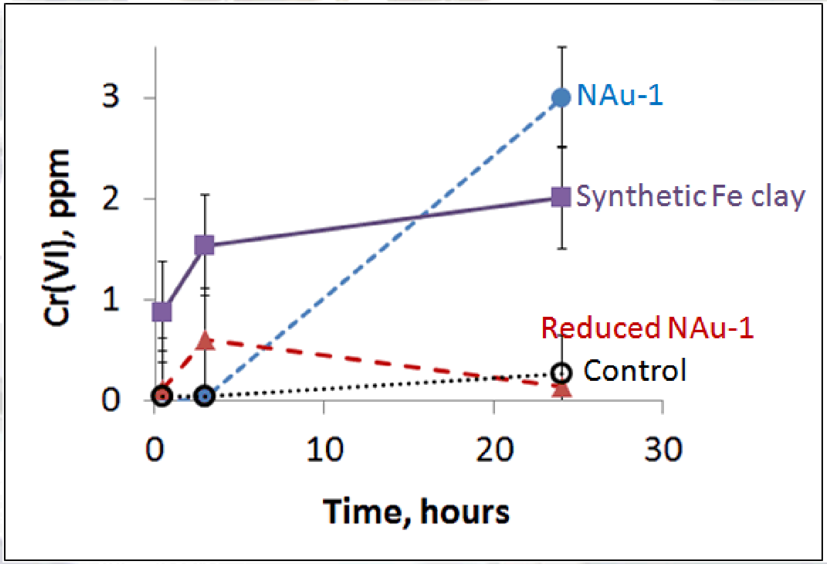
Preliminary results on the reactivity of synthetic Fe clay

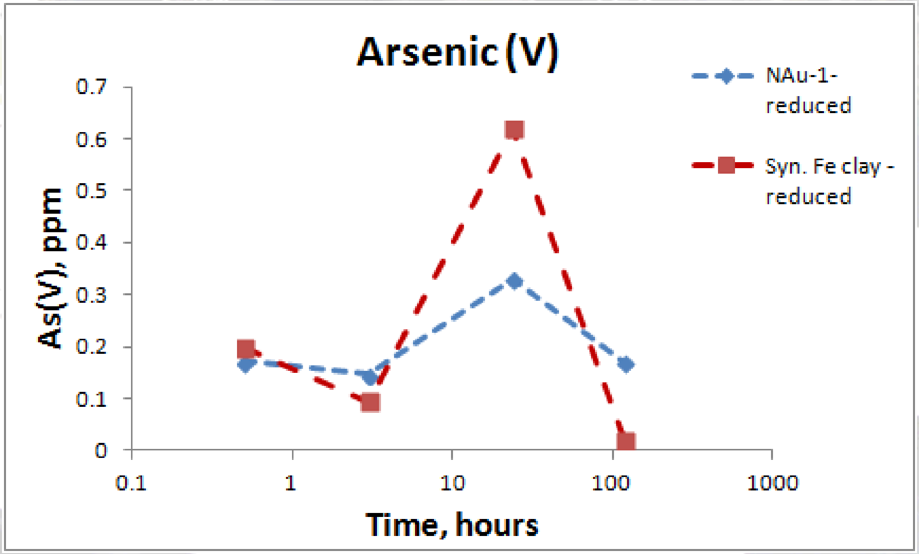
Batch reactors:

- ➢ 50 g/l clay suspension density
- ➢ CBD treatment of NAu-1 and Synthetic clay
- ➢ Oxic conditions
- ➢ As(III) initial concentration 3.8 ppm
- ➢ Cr(III) initial concentration 3.0 ppm
- ➢ Synthetic Fe clay: ~60% As uptake

NAu-1 clay ~25% As uptake







Future Work

- Determine whether Cr(III) is oxidized directly by structural Fe(III), or if structural Fe(III) catalyzes oxidation of Cr(III) by dissolved oxygen
- Determine how Fe(II)/Fe(III) ratio in the octahedral clay sheet controls the reactivity of nontronite clay
- Characterize the kinetics of electron transfer by collecting time resolved measurements of the changes in the UV-visible absorption band at 730 nm - the Fe(II)-O-Fe(III) intervalence transfer band, and corresponding aqueous speciation of the "probe" element
- Determine how nontronite surface is passivated: does structural Fe dissolve and re-precipitate as Fe-oxide?