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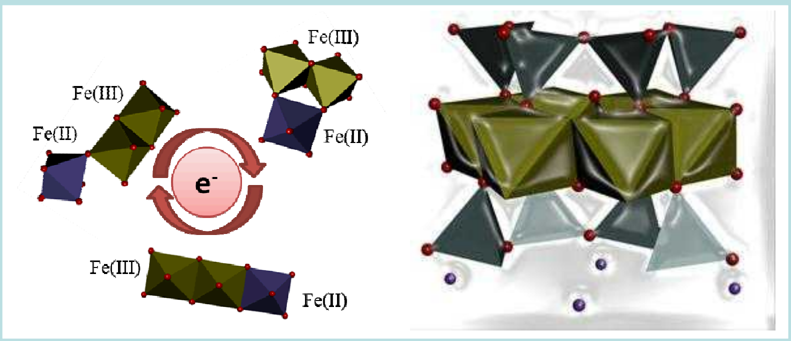

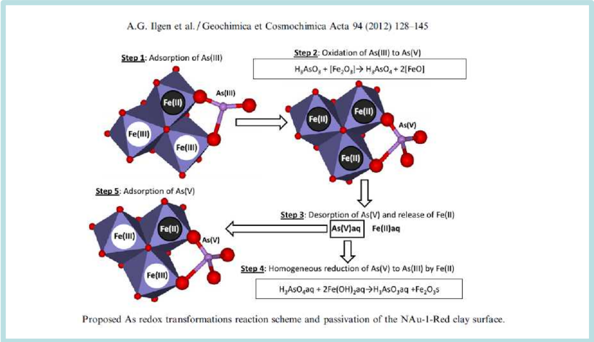

Proposed As redox transformations reaction scheme and passivation of the NAu-1-Red clay surface.

Reactivity of Structural Fe(II)/Fe(III) Redox Couple in Fe-rich Clay Minerals

Anastasia Ilgen

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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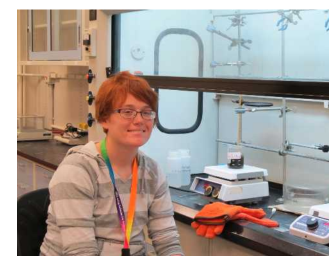


Sorption and redox on clay surfaces

- 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]

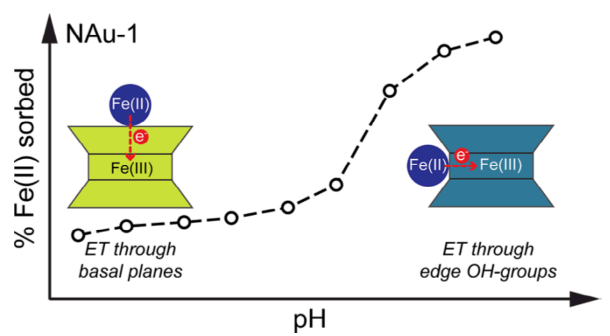
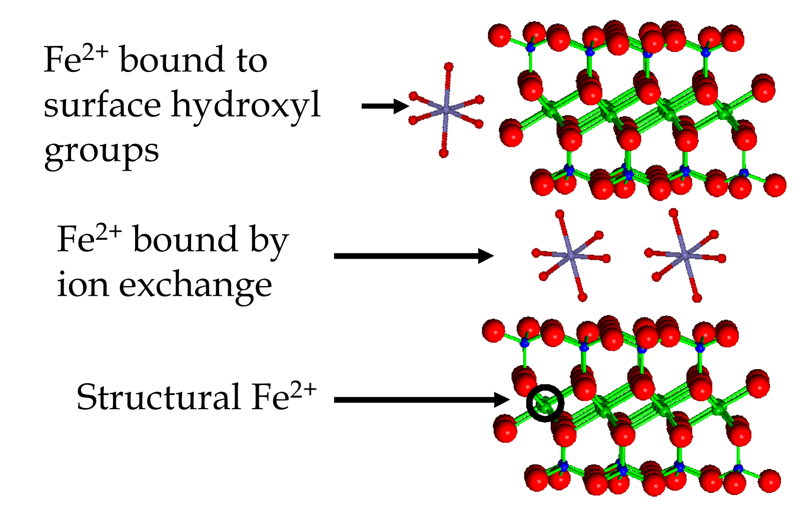


Figure from: Neumann et al., 2013



Fe(II) species associated with 2:1 clay

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

[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]

* 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

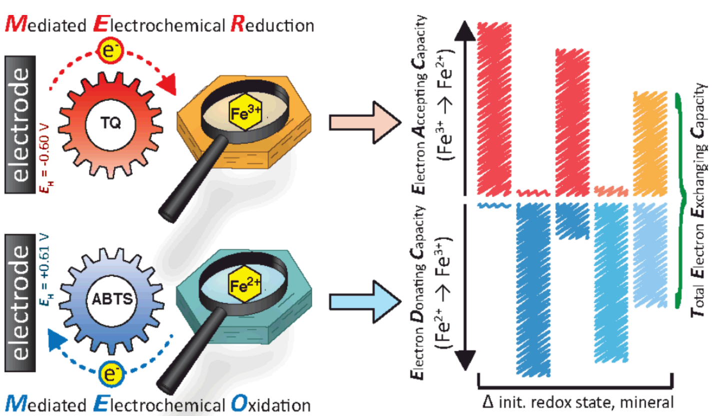


Figure from: Gorski et al., 2012

Redox reactions between Arsenic/ Antimony and NAu-1 nontronite clay

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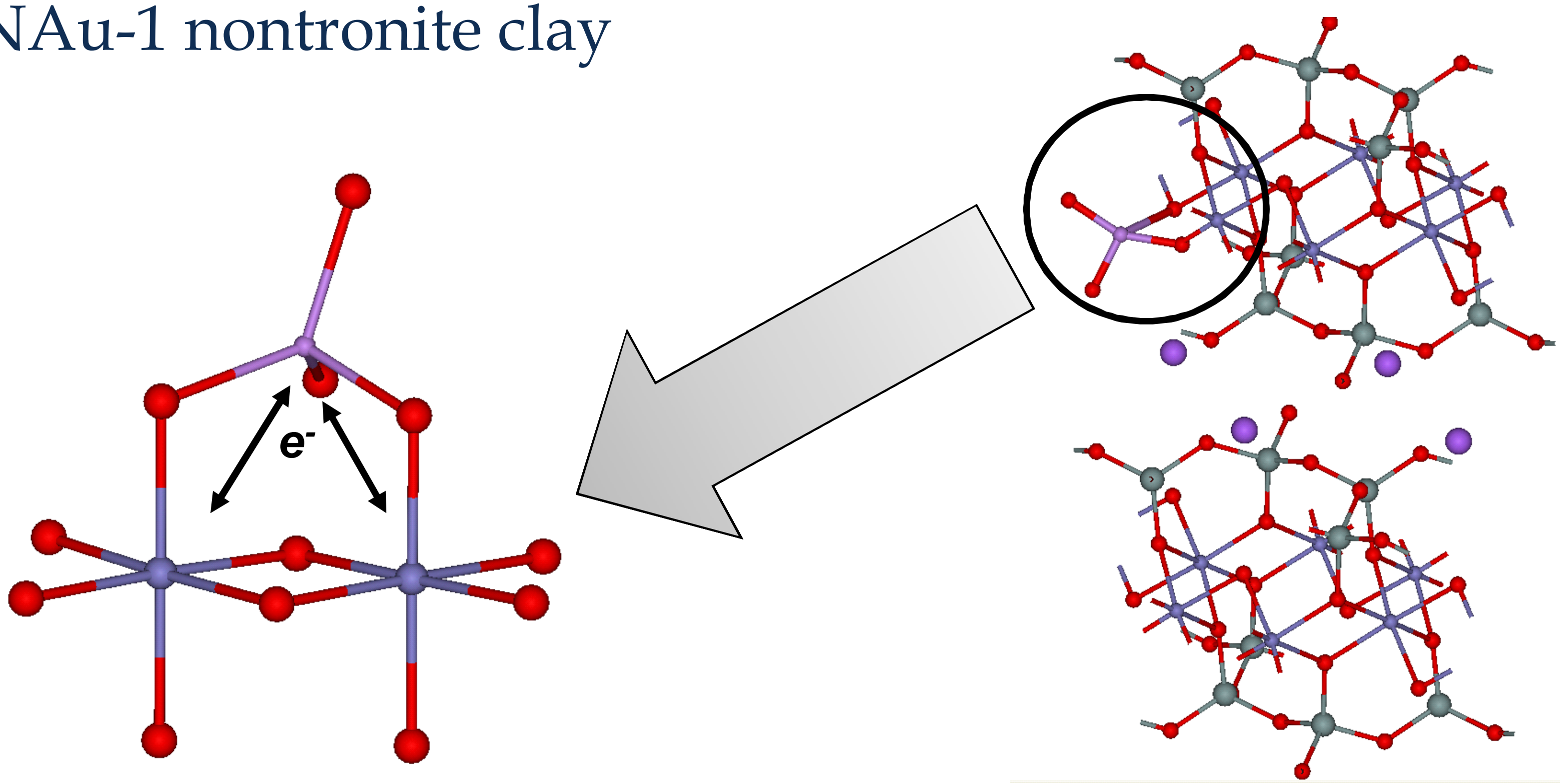

Nontronite with adsorbed As

<u>Goal:</u> To investigate the ability of the structural Fe(II)/Fe(III) to reduce/oxidize As(V)/As(III) and Sb(V)/Sb(III)

Experiment design: substrates

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Source clay kaolinite KGa-1b*

Special clay nontronite NAu-1*

Carbonates removed CH_3COONH_4/CH_3COOH buffer

Synthetic hydrous aluminium oxide $Al(OH)_3$ CONTROL

12.82 mM $Al(NO_3)_3$ titrated with 1 M NaOH to pH 8.9

Background electrolyte 0.01 M NaCl

NAu-1 reduced/re-oxidized

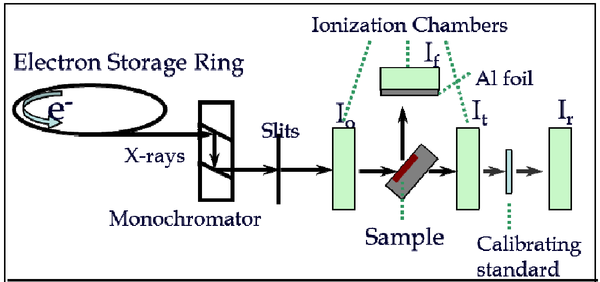
Procedure from Stucki et al., 1984 [1]

* Natural clay from Clay Mineral Society Repository

[1] Stucki, J. et al. (1984) Clays and Clay Minerals 32, 191

As/Sb speciation analysis

APS, Argonne National Lab.



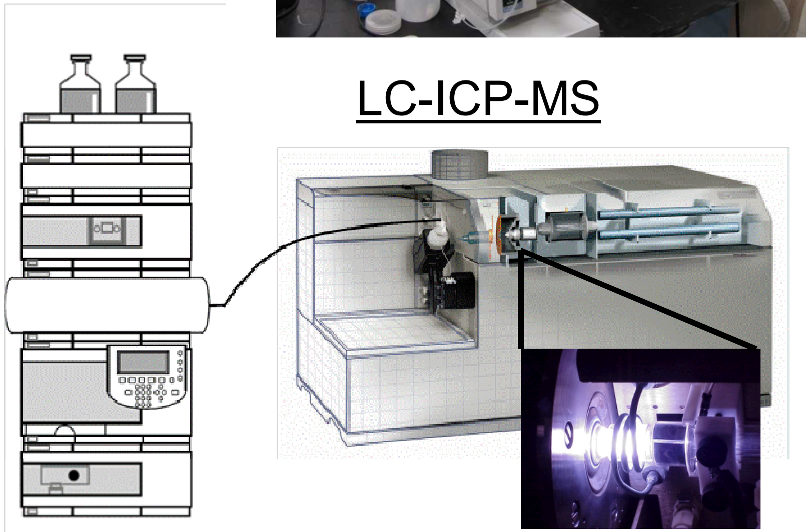
EXAFS spectroscopy instrumental setup [1]

XAS:

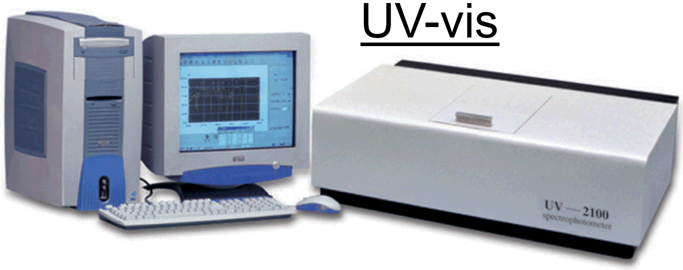
- Element specific
- Oxidation state measurement
- Local atomic structure information
- Low detection limit (~100 ppm)

AAS

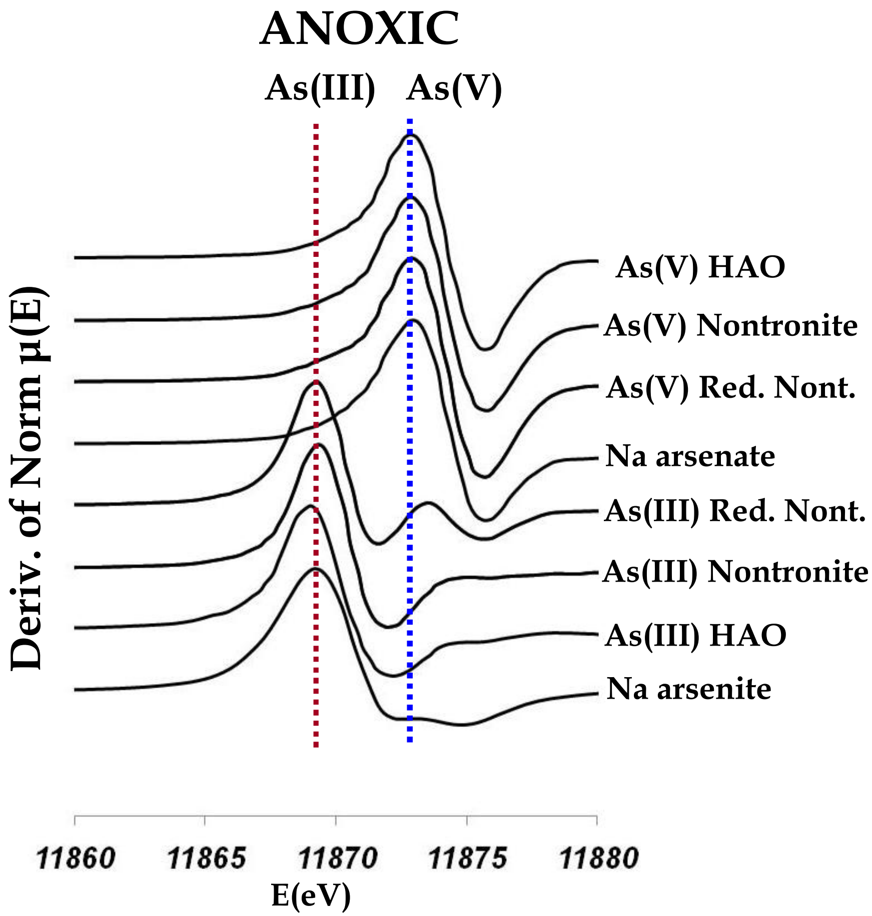
LC-ICP-MS

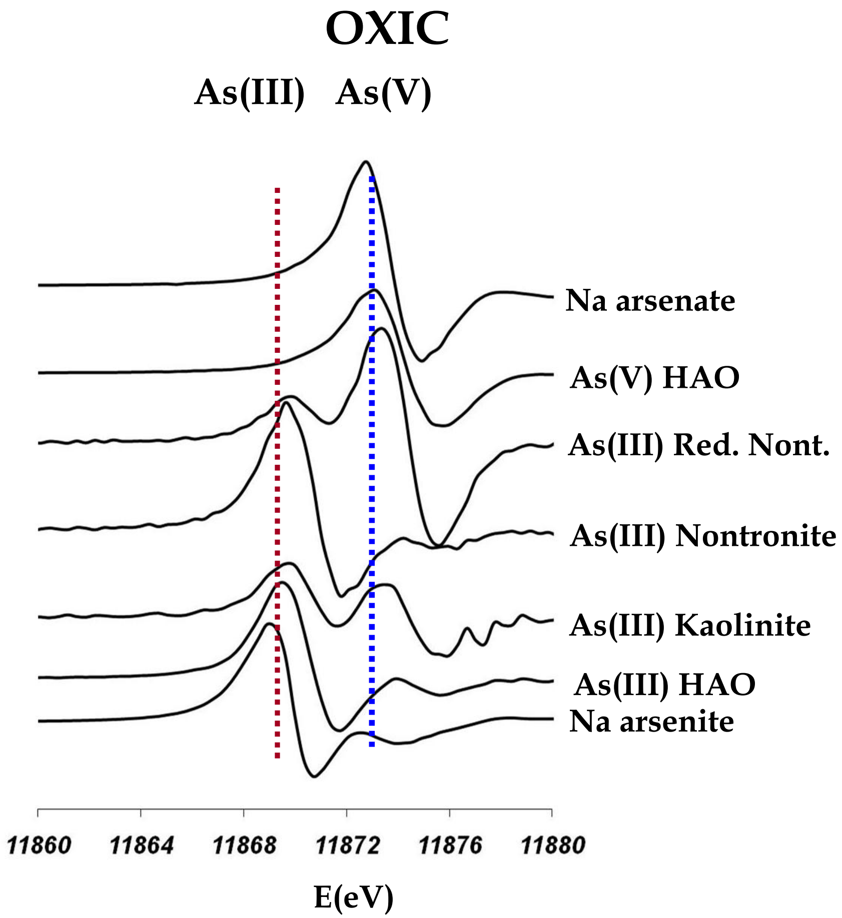


UV-vis



Results: XAS study

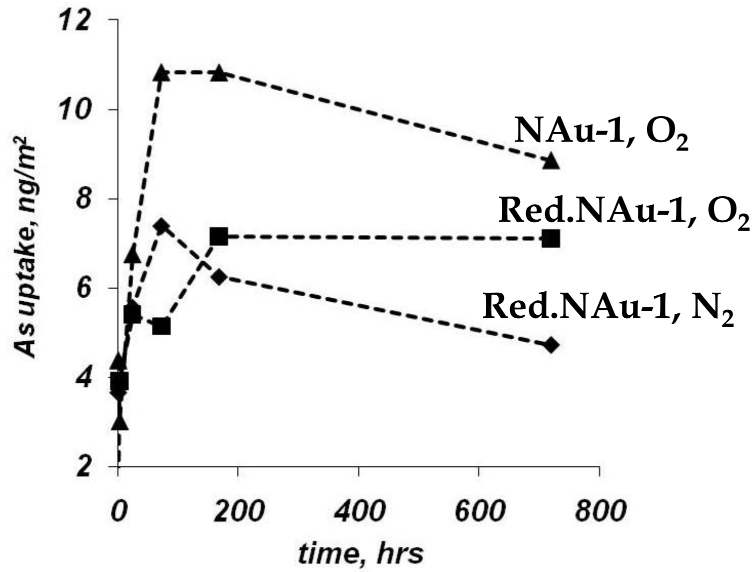




- ✓ <u>As(III)</u> no oxidation by the str. Fe(III)
- ✓ Minor oxidation in reduced NAu-1 system
- ✓ <u>As (V)</u> no reduction by reduced NAu-1

- ✓ <u>As(III)</u> oxidation in reduced, but not in oxidized NAu-1 systems!
- ✓ <u>As(III)</u> oxidation in KGa-1b system

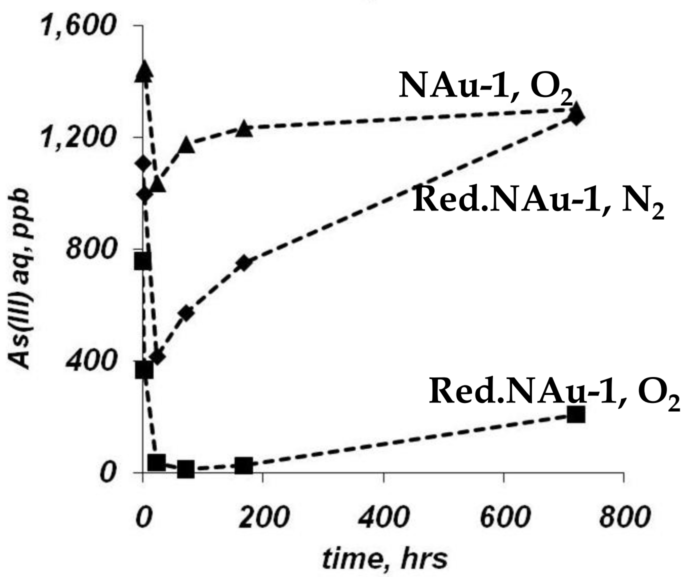
As(III) oxidation, low concentration study

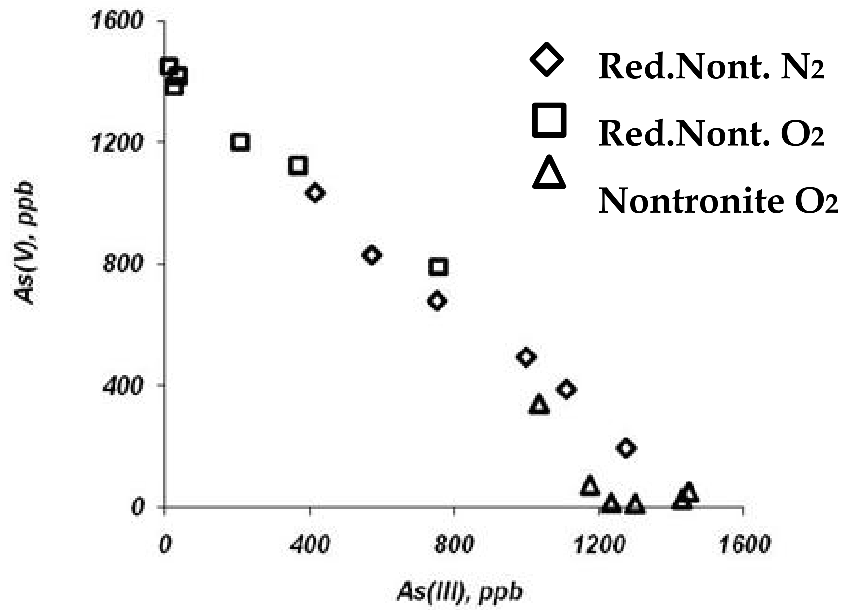


- As(III) + oxidized and reduced nontronite (oxic and anoxic conditions)
- At ~ 24 hours max oxidation & uptake

~100% oxidation in RN+O_2
~70% oxidation in RN+N_2

- Sorption is not the rate limiting step





Summary: O_2 is not the only oxidant

- maximum O_2 in the anaerobic chamber = 1 ppm
- aqueous O_2 < 1.3 nM
- maximum [As(V)] = 13.8 μM

⇨ Dissolved oxygen could not be the primary oxidant

NAu-1: $M^{+}_{1.05}[Si_{6.98}Al_{1.02}][Al_{0.29}Fe_{3.68}Mg_{0.04}]O_{20}(OH)_4$ **[2]**

# of moles of Fe(III) ~$1.7 \cdot 10^{-3}$

# of moles of As $21 \cdot 10^{-6}$

no other likely oxidants in the system

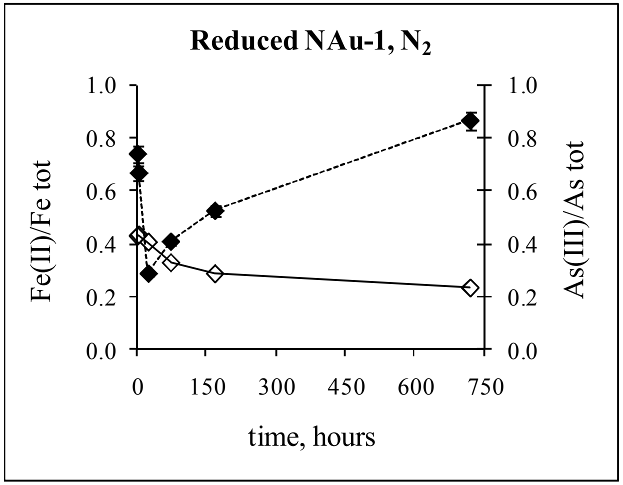
⇨ As(III) was oxidized by the structural Fe(III) in reduced NAu-1

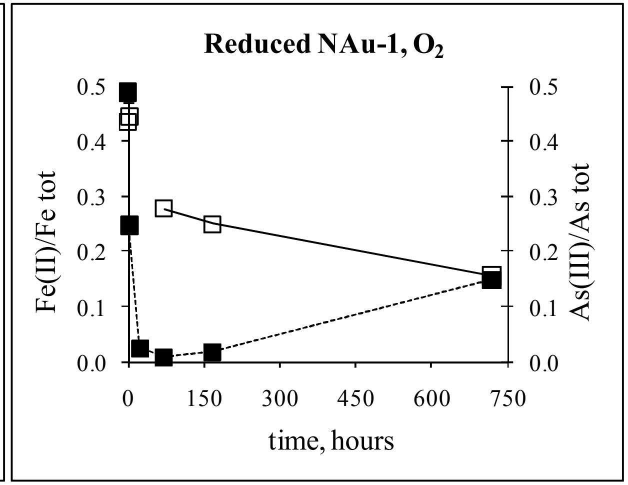
⇨ As(III) was not oxidized by oxidized NAu-1

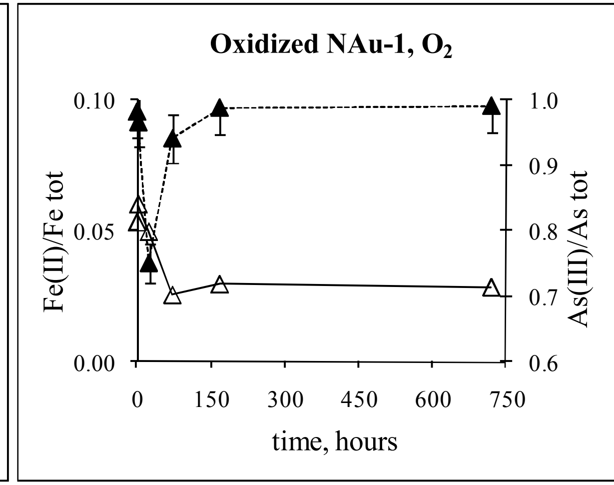
Some Fe(II) is required for this reaction

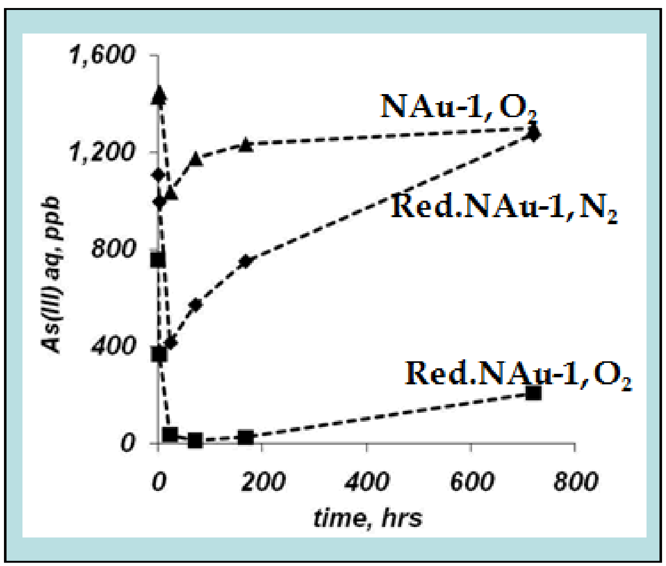
[1] Linstrom, P. and W. Mallard , 2005; [2] Keeling, J., M. Raven, and W. Gates, 2000

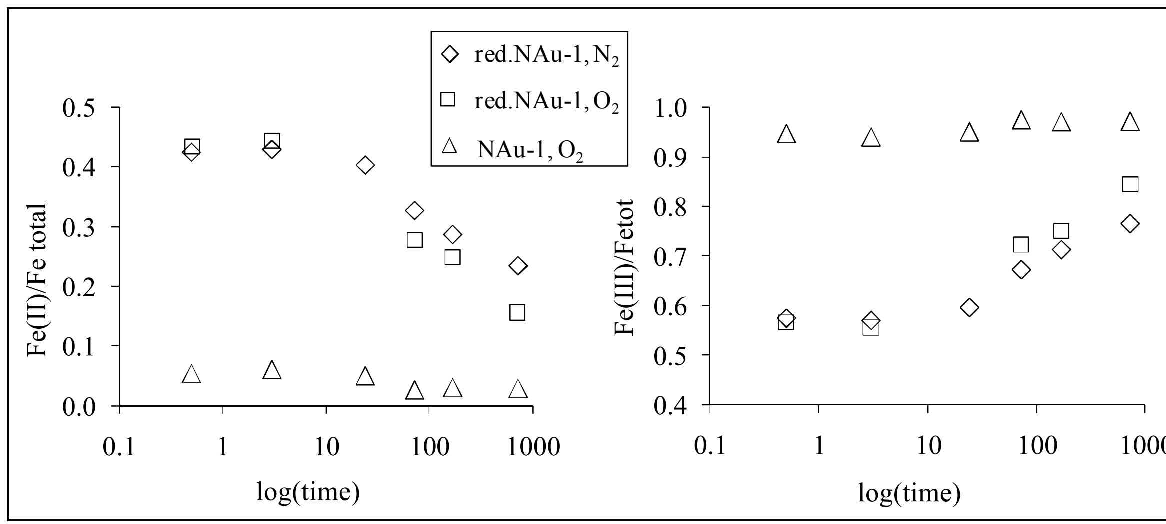
Results: re-reduction of As(V), As(III)/Fe(II) correlation



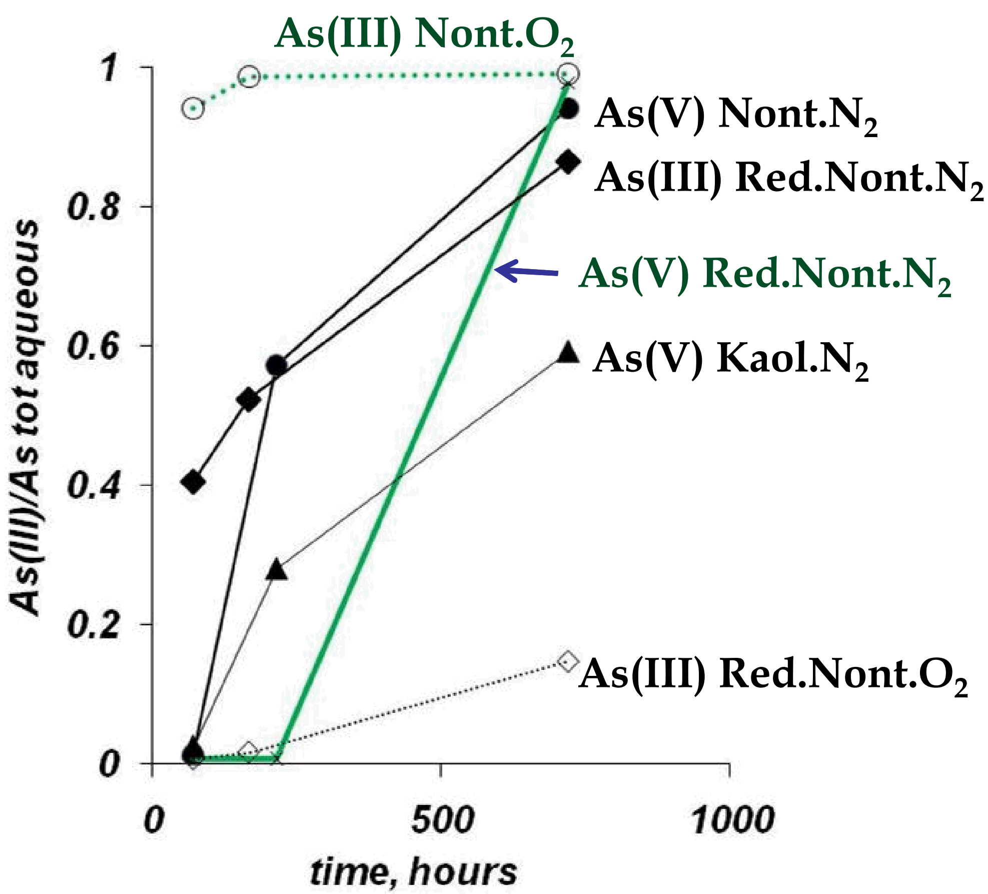








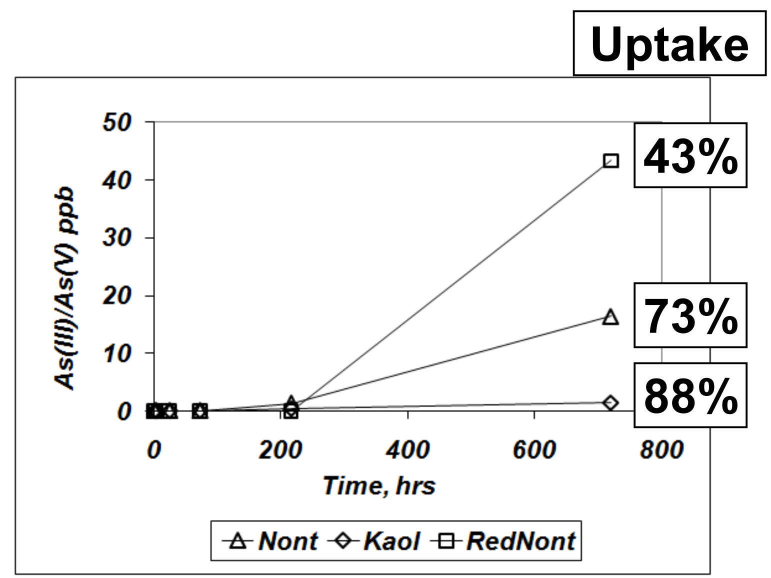
Results: reduction of As(V) by Fe(II)



Reduction rate is slow and is similar to homogeneous reduction rate [1]

- Slow reduction
- As increase over time is similar for 4 systems

- 2 exceptions:
  - -low initial As(V)
  - -high initial Fe(II)



[1] Bose and Sharma, 2002

Results: Sb redox in low concentration experiments

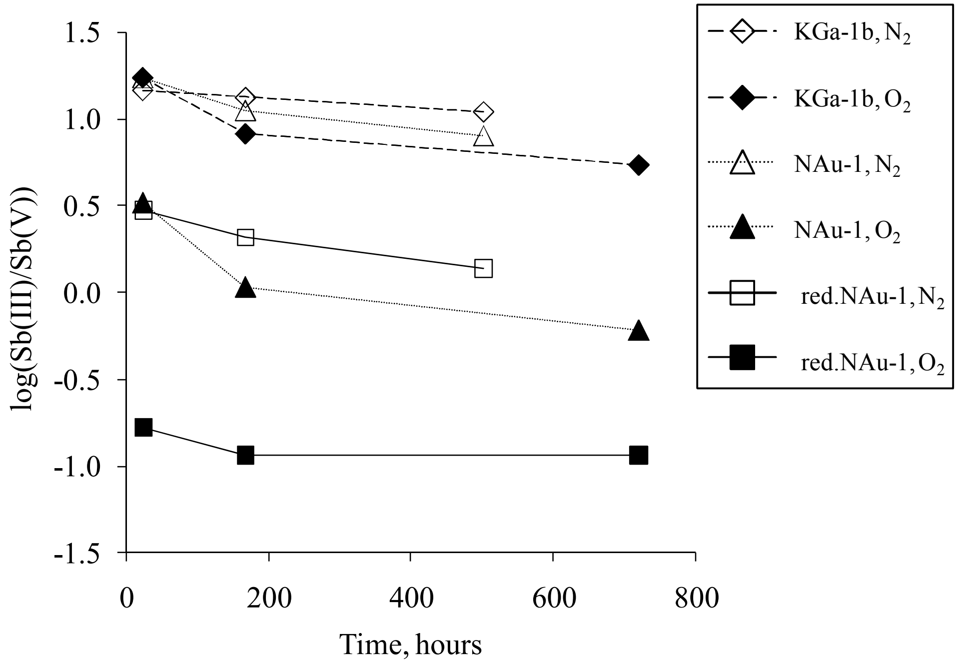
- **O_2 atm**

significant oxidation of Sb(III)=>Sb(V) in the presence of kaolinite, reduced and oxidized nontronite. Reduced nontronite was the most reactive. Overall trend: Reduced nontronite pH 5.5>nontronite pH 5.5>kaolinite pH 8> kaolinite pH 5.5

- No evidence of re-reduction reaction

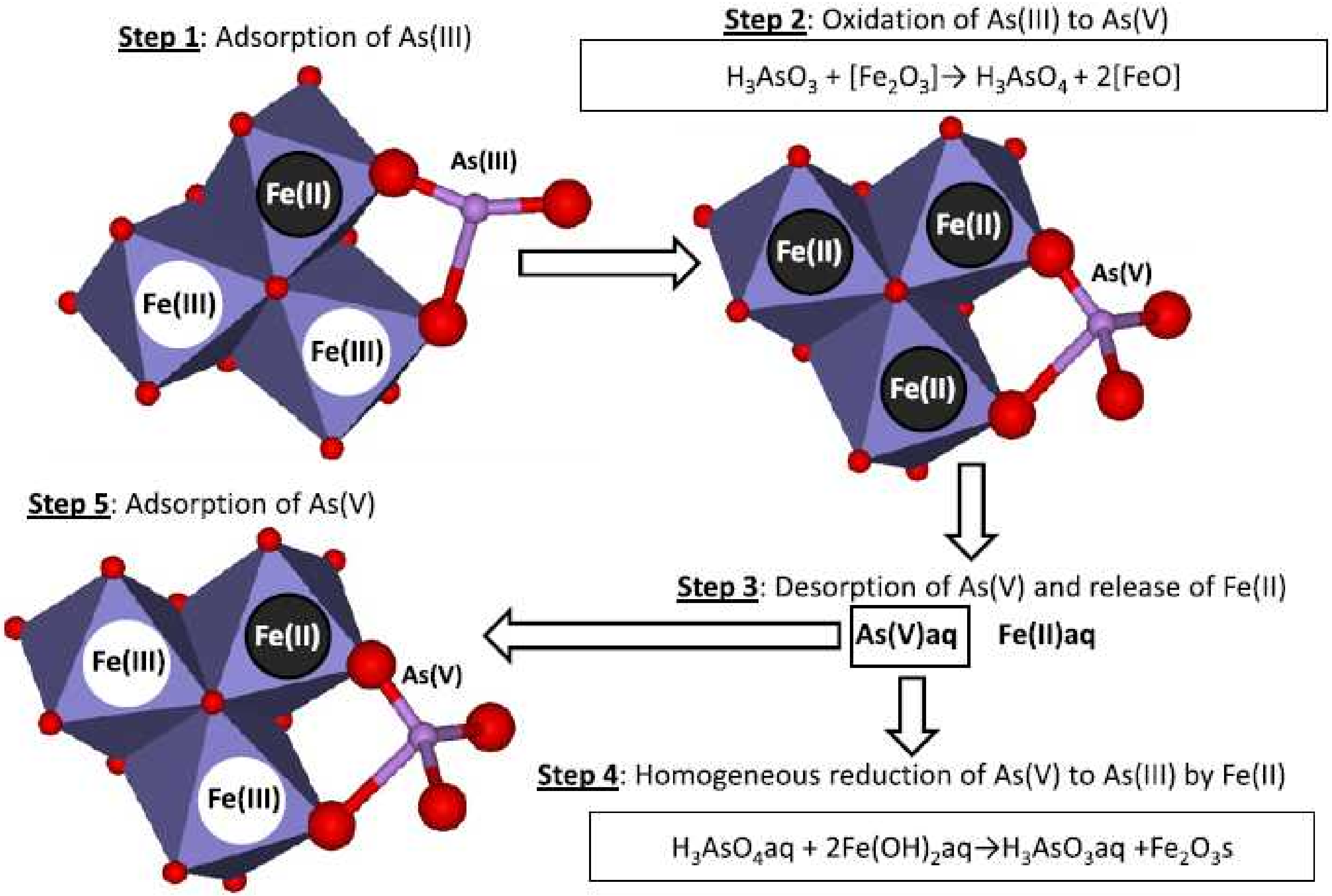
- **N_2 atm**

Relatively low oxidation, most advanced in the presence of reduced nontronite.



Proposed model

A.G. Ilgen et al. / Geochimica et Cosmochimica Acta 94 (2012) 128–145



- As(V) is reduced back to As(III) by aqueous/adsorbed Fe(II)
- Sb(V) remains in oxidized form [no Sb(V) reduction by Fe(II)]

Similar observations

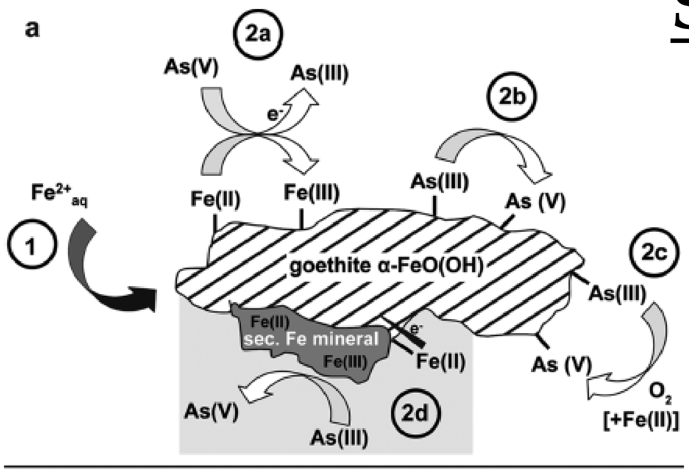
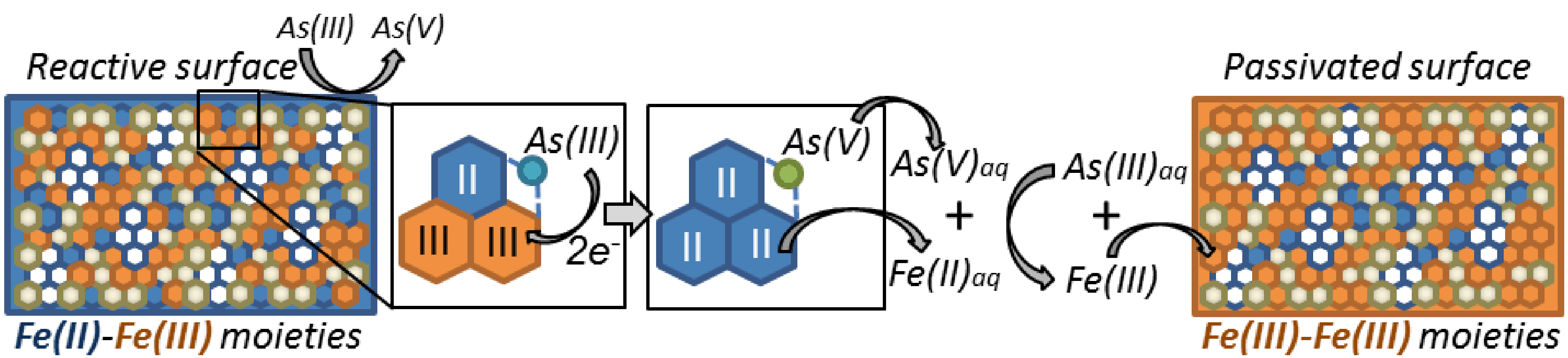


Figure from Amstaetter et al., 2010
Environ. Sci. Technol. 2010, 44, 102–108

- <u>Mechanism not fully understood</u>:
  - Amstaetter et al., 2010:

Fe(II) added to **<u>anoxic</u>** system with **<u>goethite</u>** initiates As(III) oxidation by unknown Fe(III) phase.

Our study: some structural Fe(II) is required for oxidation of As(III)/Sb(III), but surface is passivated with time.



Unknowns

What is the mechanism of Fe(III) activation in two different systems:

(1) In **goethite** system with added **aqueous Fe(II)**

(2) In **partially reduced nontronite** system

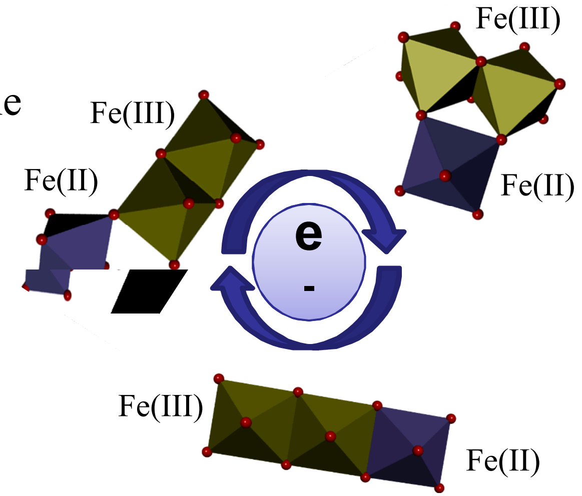
What is the mechanism of surface passivation?

How does reactivity of clay structural iron changes as a function of Fe(II)/Fe(III) ratio?

Fundamentally - what are the differences in the net free energy, and, therefore, in the potential for electron transfer for **Fe** in various molecular environments associated with clay mineral?

Hypotheses

- Fe(III) in Fe(II)-O-Fe(III) moiety is the oxidant, while in the Fe(III)-O-Fe(III) moiety, Fe(III) is not reactive.
- Surface is passivated due to reactive Fe(II)-O-Fe(III) site being blocked by
  - oxidized species of adsorbent, or
  - precipitation of Fe(III) oxide.



Reactivity of synthetic Fe-phyllosilicate

Composition of NAu-1

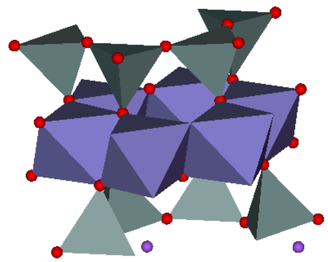
SiO_2 Wt. %	TiO_2 Wt. %	Al_2O_3 Wt. %	Fe_2O_3 Wt. %	MgO Wt. %	CaO Wt. %	Na_2O Wt. %	K_2O Wt. %	Total, %
51.36	0.02	8.15	35.94	0.19	3.57	0.03	0.01	99.5

From Keeling et al., 2000

- Ti impurities catalyze As(III) oxidation by aqueous O_2 [1]

Goals

- Synthesize pure Fe clays;
- Test reactivity of structural Fe(III)/Fe(II);
- Compare to the reactivity of natural Fe-rich clay minerals.



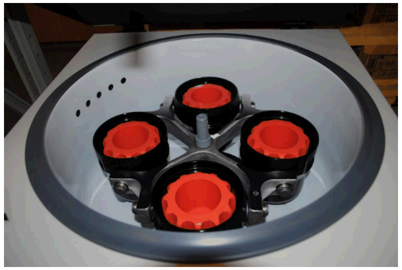
[1] Foster et al., 1998

Hydrothermal Synthesis of Fe Smectite

Suspension made with Sodium Hydroxide, Silicic acid, Ferrous Sulfate, and Sodium Dithionite

Suspension placed in Parr vessels and aged at 150°C for 50 hours

Suspension washed and centrifuged. Clay aged for 24 hours in 1 M NaCl solution



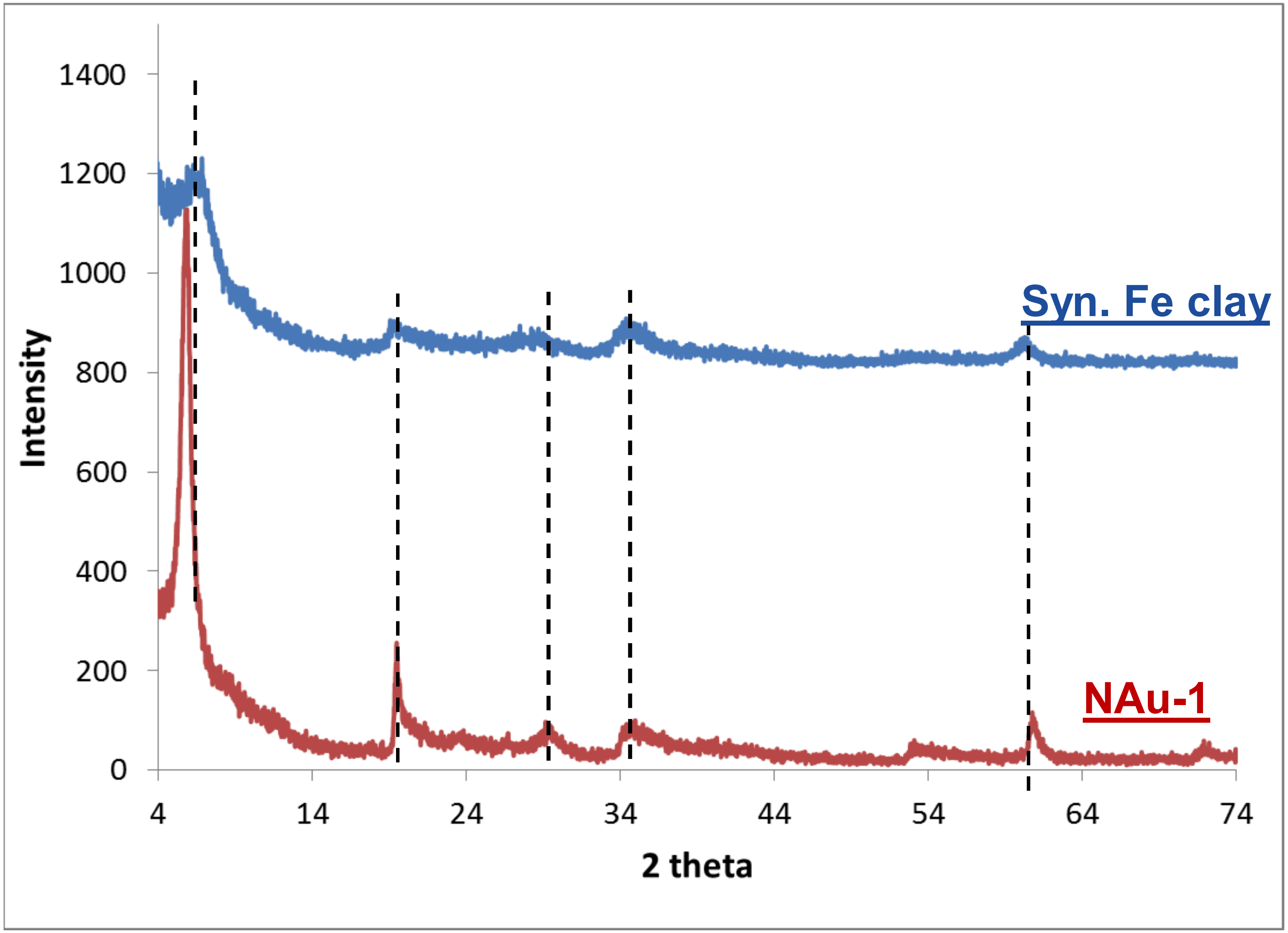
Clay washed, and dialyzed for 96 hours in deionized water

Clay dried and ground

Average yield is 0.6 gram from 200 mL suspension

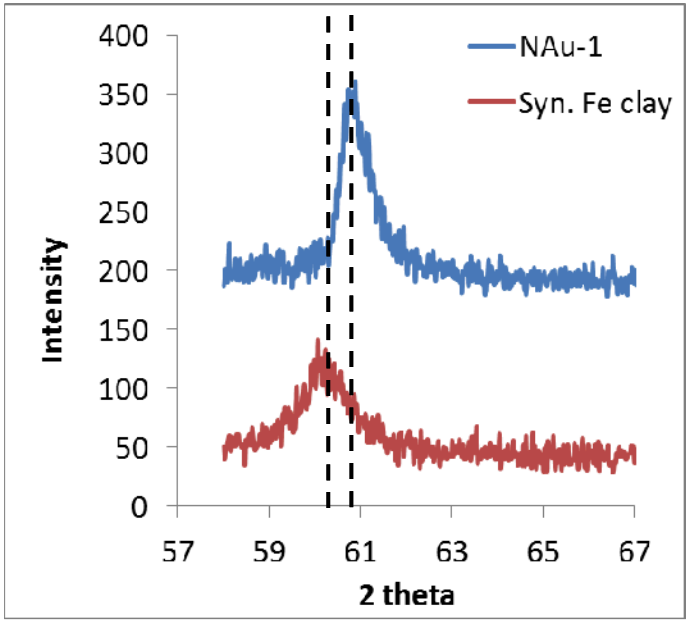
Procedure modified from Xiang and Villemure (1995)

XRD characterization



- Similar structure
- Synthetic clay has lower degree of crystallinity

XRD characterization



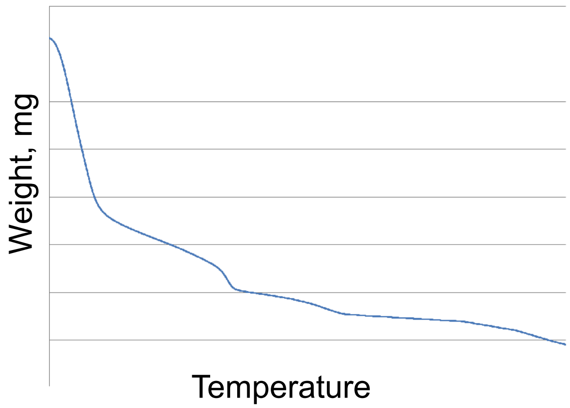
- 060 peak: Scan from 58-78 °2θ

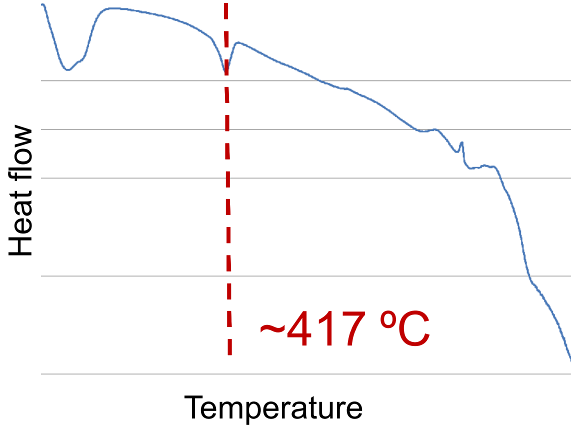
Calculated d-spacing:

- NAu-1 = 1.5226 Å
- Synthetic Clay =1.5414 Å

- Larger d-spacing in synthetic clay indicates **trioctahedral** structure

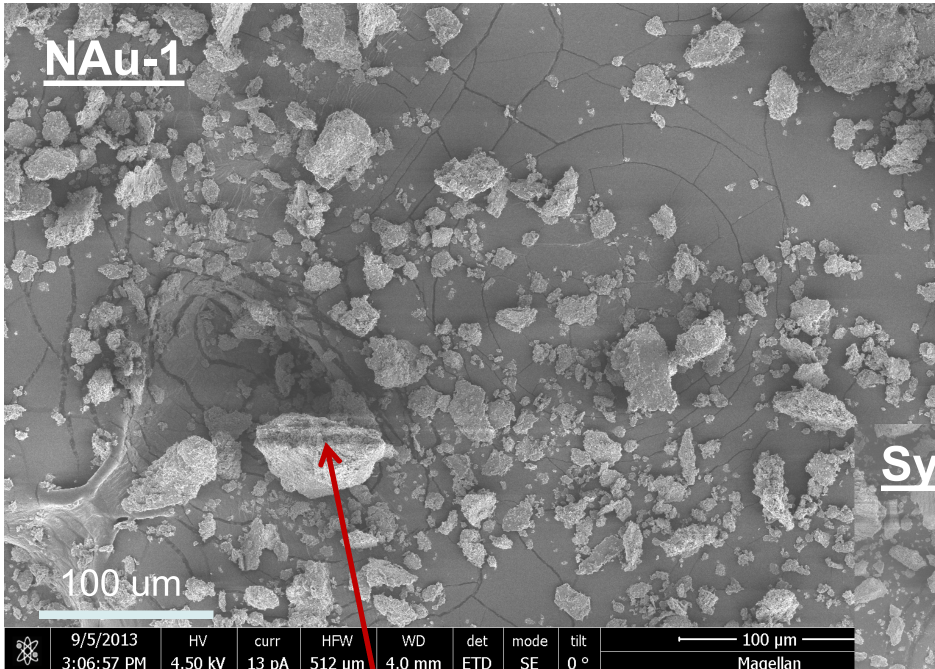
TGA characterization



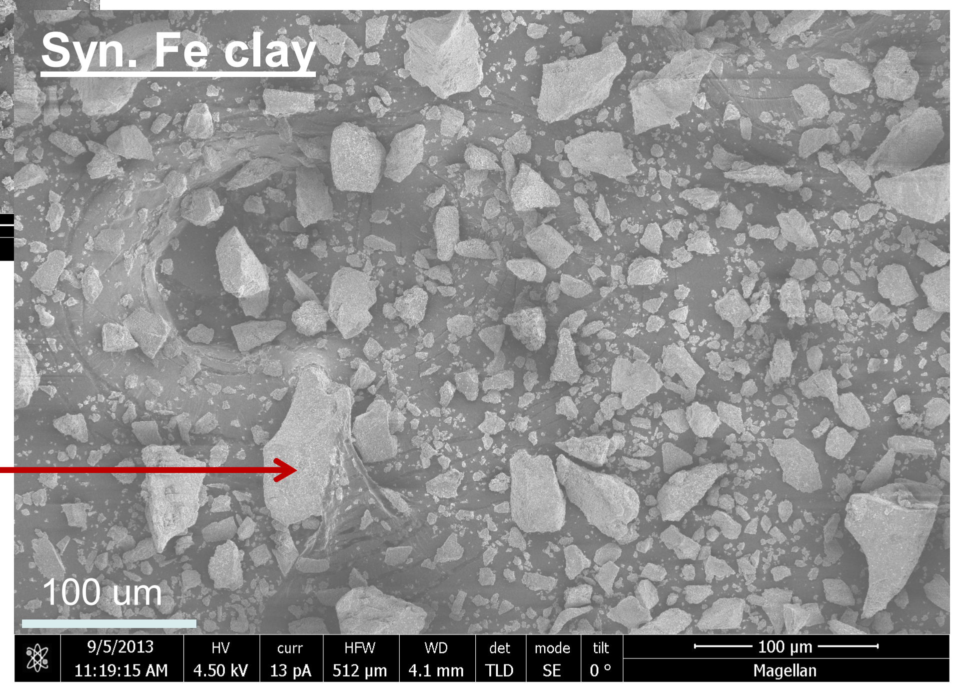


- Temperature of main dehydroxylation peak of 400-500 °C is characteristic for **nontronite**

SEM characterization



- Similar size distribution and morphology



- Agglomeration

SEM characterization

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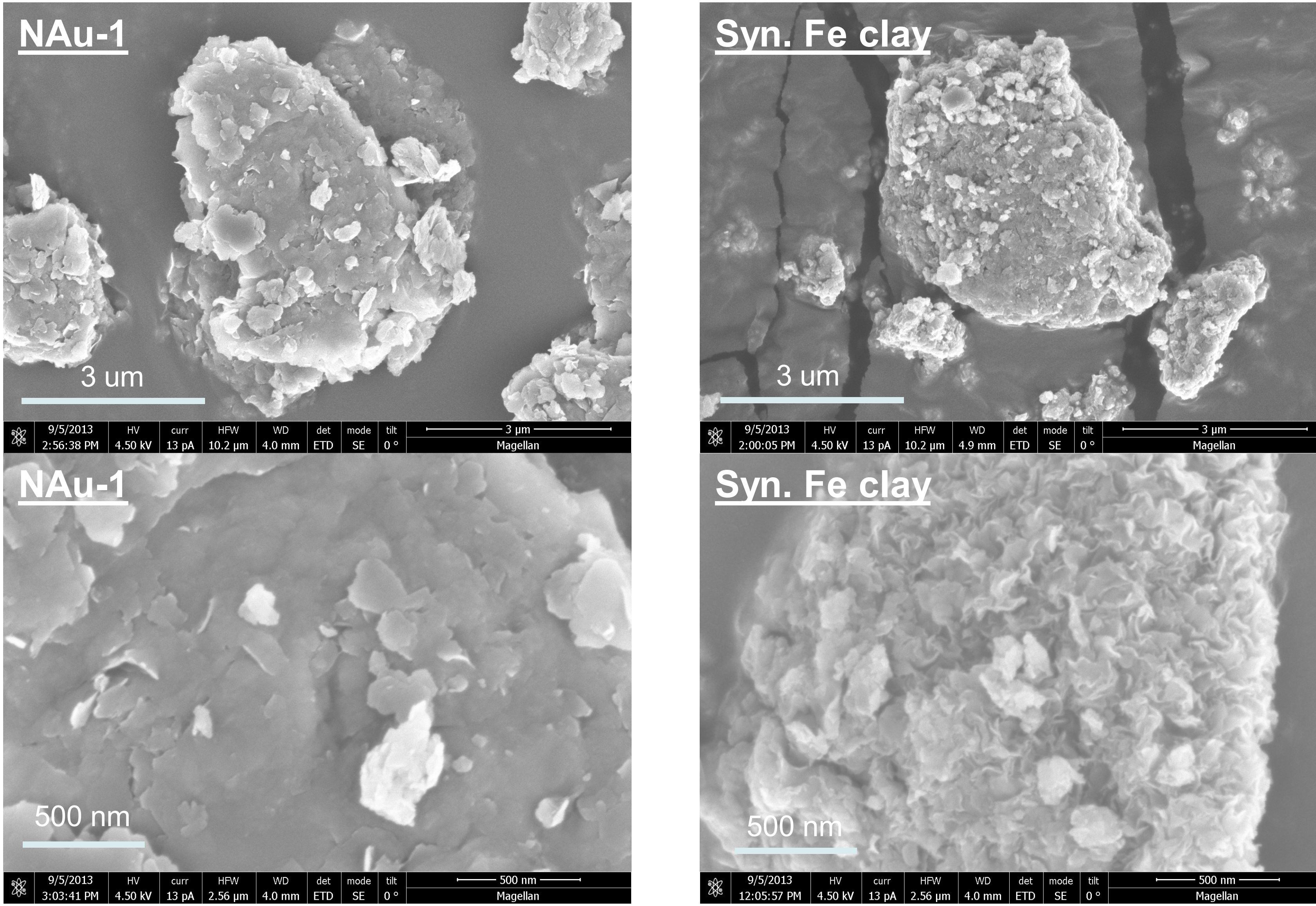
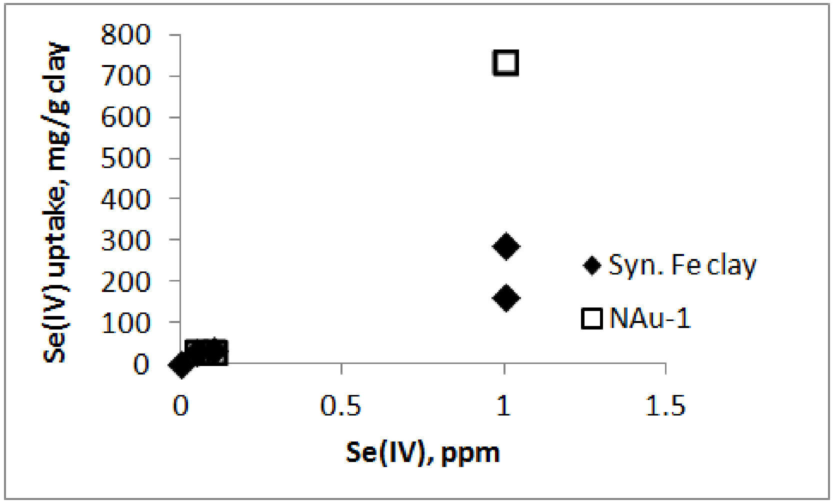
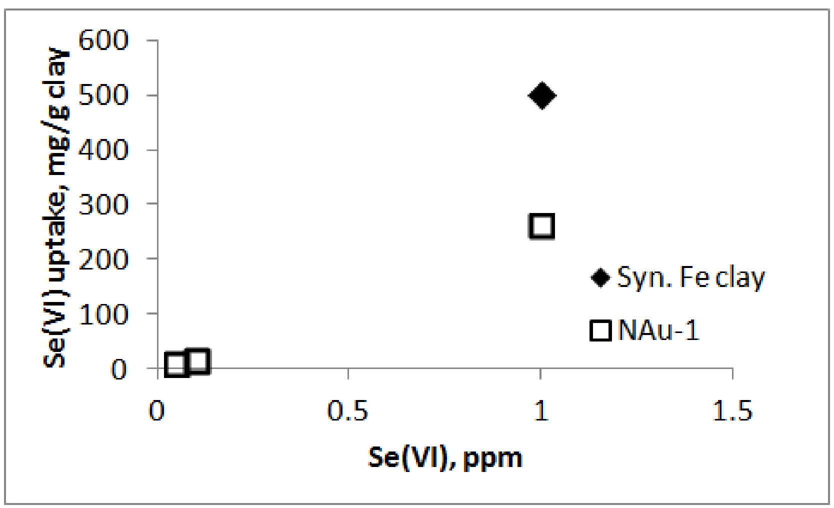


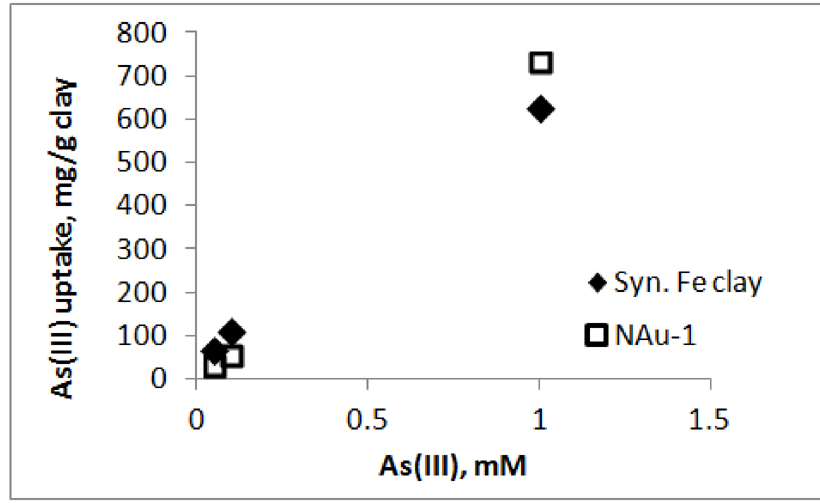
Sorption experiment

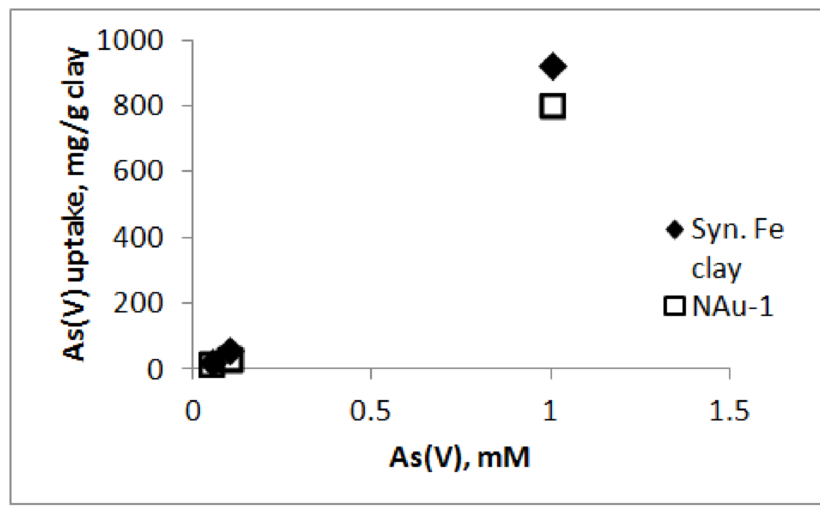
Selenium uptake



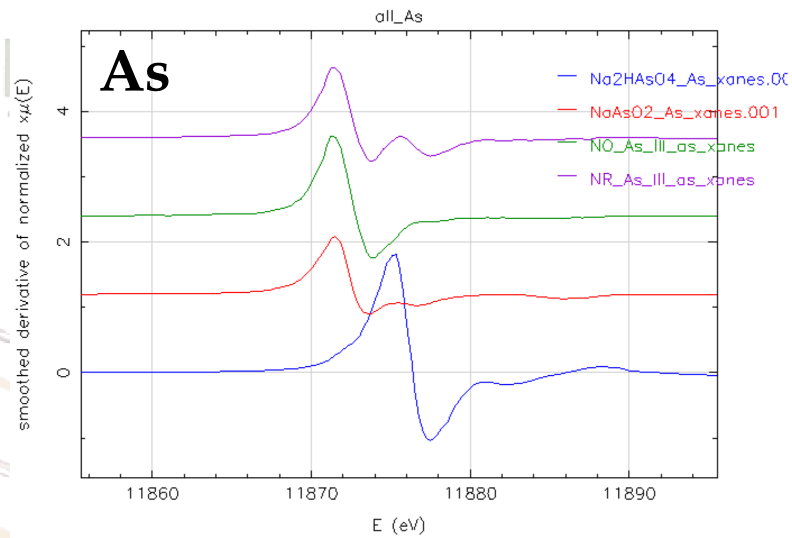


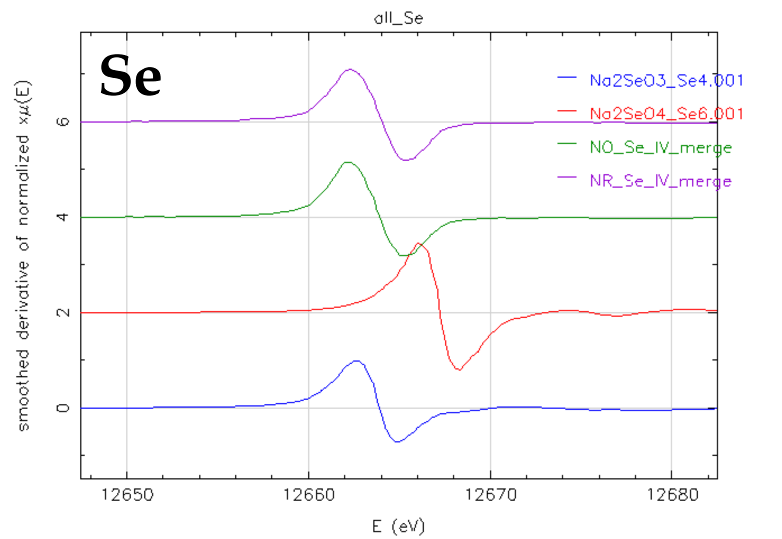
Arsenic uptake

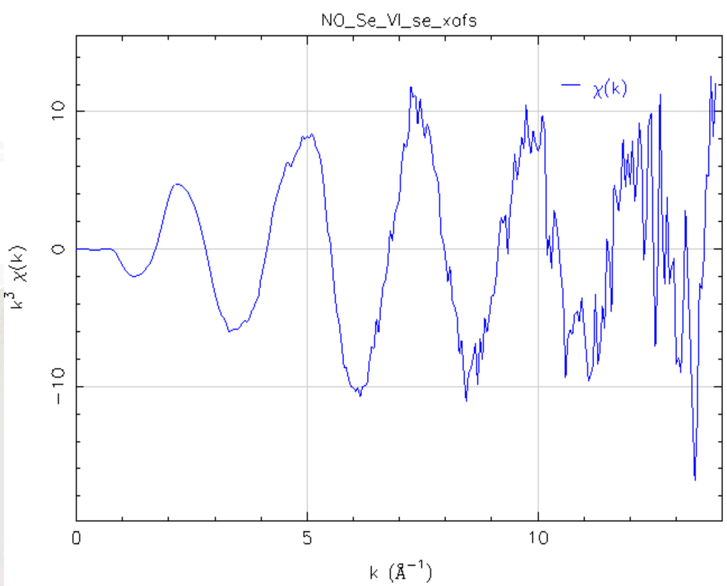


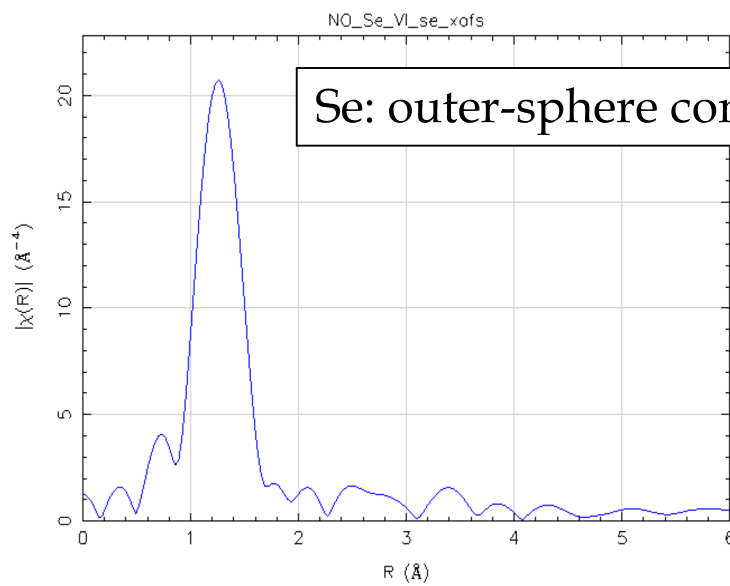


Comparison between As(III) and Se(IV) oxidation in the presence of oxidized and partially reduced NAu-1







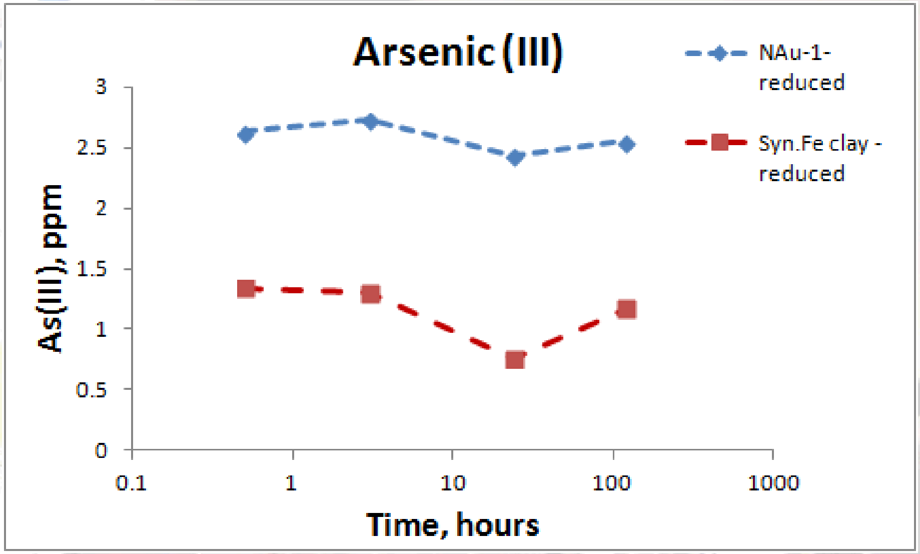


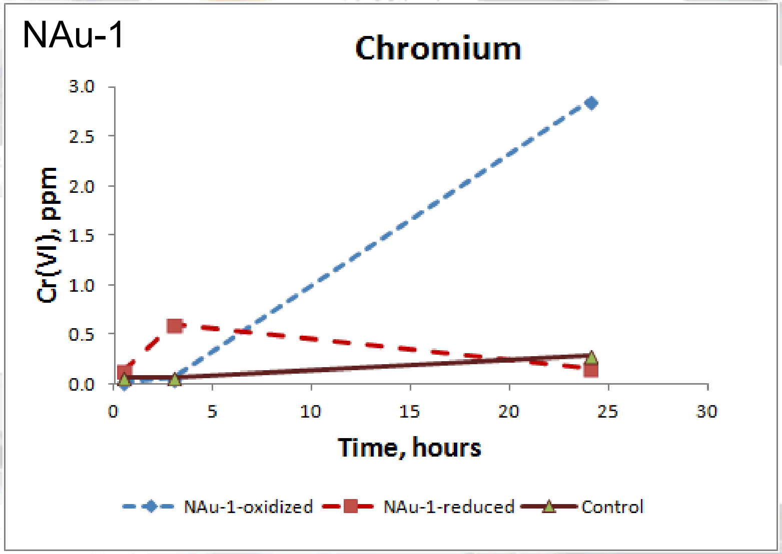
Se: outer-sphere complex

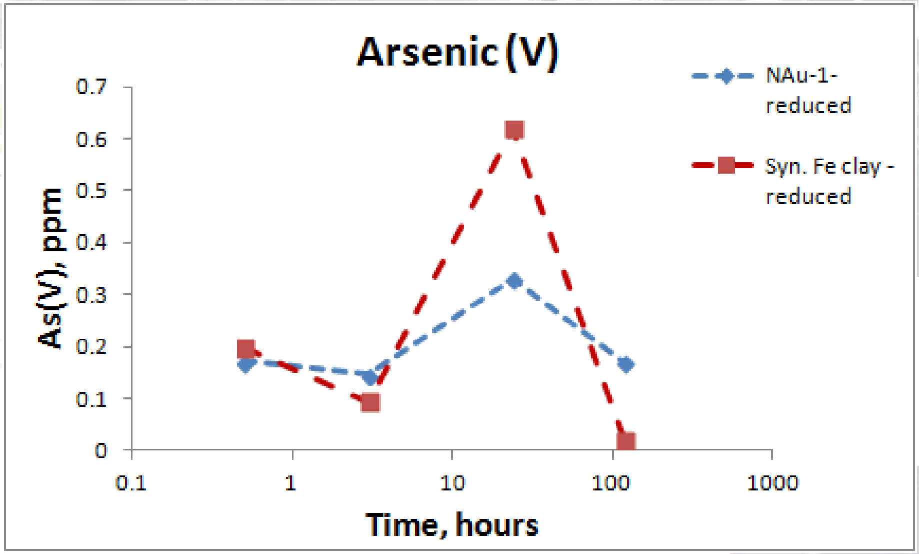
Preliminary results on the reactivity of synthetic Fe clay

Batch reactors:

- 50 g/l clay suspension density
- Partial reduction of both NAu-1 and Synthetic clay
- Oxic conditions
- As(III) initial concentration 3.8 ppm
- Cr(III) initial concentration 3.0 ppm



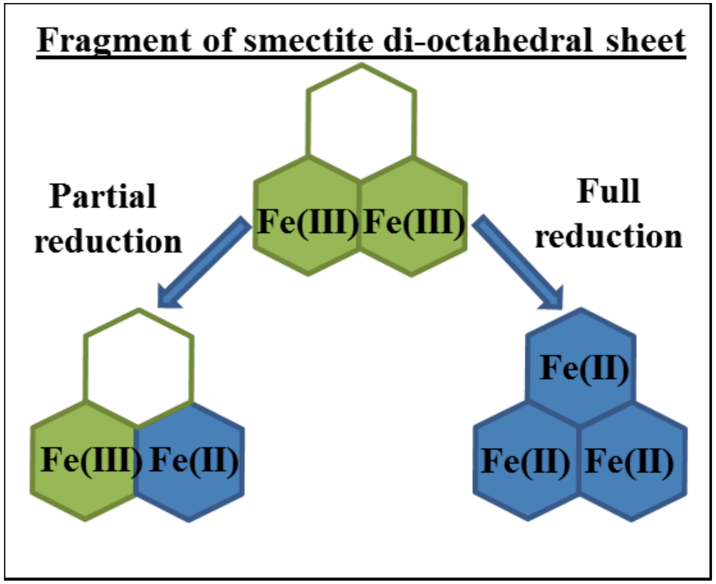




- Synthetic Fe clay: ~60% As uptake NAu-1 clay ~25% As uptake

Future Work

- Continue testing hypothesis: **"Partial reduction of structural Fe(III) to Fe(II) makes nontronite clay an effective oxidant due to formation of reactive Fe(II)-O-Fe(III) moieties within octahedral clay sheet"**.



- Test reactivity of Fe(III) in the Fe(II)-O-Fe(III) moieties using various "probes" – As, Se, Sb, and Cr.
- Quantify the direction and kinetics of electron transfer between clay surface and the "probes".
- Determine how nontronite surface is passivated: does structural Fe dissolve and re-precipitate as Fe-oxide?