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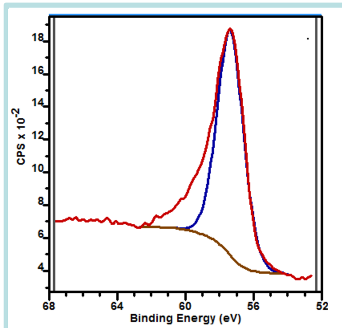

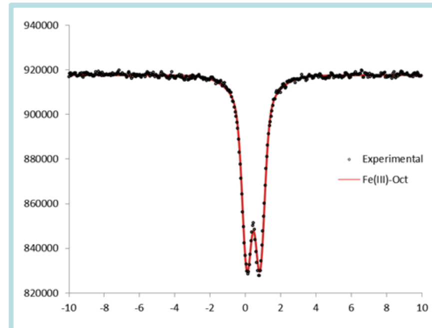

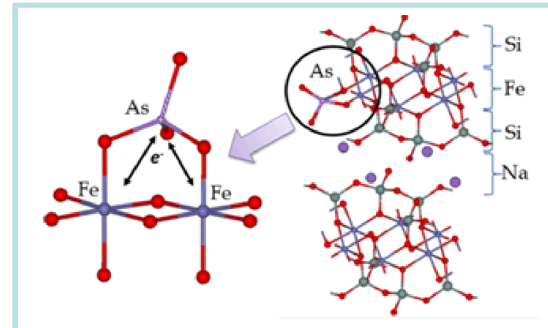

Controls on the reactivity of clay structural Fe(II)/Fe(III) redox couple

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Redox on clay mineral surfaces

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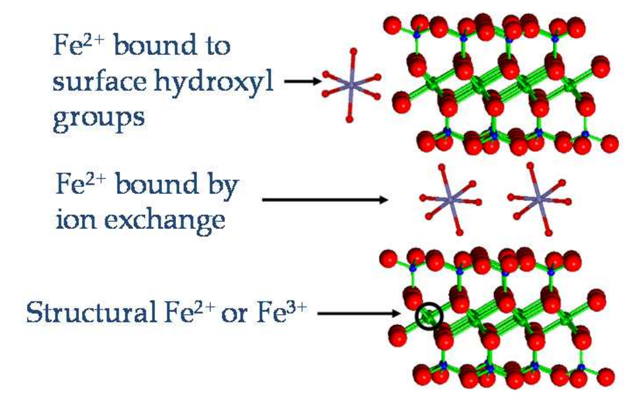
- Redox on clay mineral surfaces: catalysis and direct e⁻ transfer.[1-4]
- Iron in clay minerals: traces to up to 30 wt.%.[5]
- Structural iron is redox-active. [6,7]
- *Experiments*: e⁻ transfer at edge sites and through basal surface.[7]
- *Computation*: e⁻ transfer at edge sites only, no evidence for e⁻ transfer through basal surface.[8]
- Unique Fe^{2+}/Fe_{total} – Eh relationships. Structural parameters (Fe_{total}, layer charge, and quadrupole splitting values) control the reactivity of clay structural Fe.[9]



Fe species associated with 2:1 clay

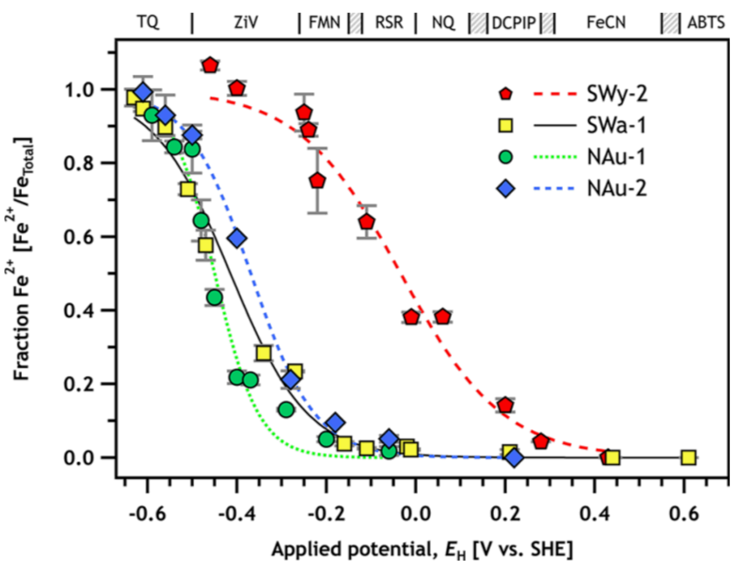


Figure from Gorski et al., ES&T, 2013

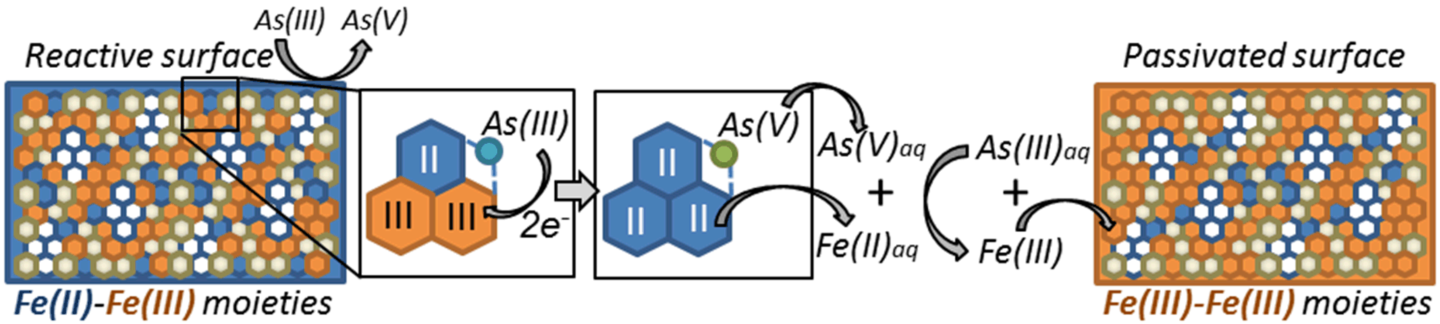
[1] Oscarson et al., 1991
[2] Manning and Goldberg, 1997
[3] Lin and Puls, 2000
[4] Hofstetter et. al, 2003
[5] Stucki, 2006
[6] Hofstetter et.al, 2006
[7] Neumann et al., 2013
[8] Alexandrov and Rosso 2013
[9] Gorski et al., 2013

Objective

- Mechanistic model of the clay structural iron (Fe) reactivity

Our previous findings

- Non-reactive Fe(III)-nontronite is activated (becomes an oxidant) when <20% of structural Fe(III) is reduced to Fe(II). Surface is passivated after reacting.



Remaining unknowns

- Does this "activated" nontronite react with other redox-active elements?
- Reactivity as a function of Fe(II)/Fe(III) ratio in the octahedral clay sheet.
- **Do impurities in the natural nontronite affect the reactivity?**
- What is the surface passivation mechanism?

Experimental approach

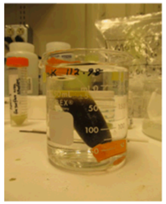
- **Synthesis and characterization of pure Fe-phyllosilicate**
- **Compare the reactivity of synthetic Fe-phyllosilicate to the natural and "activated" nontronites, using As, Cr, and Se species as "probes"**

Synthesis of Fe-phyllosilicate (SIP)

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

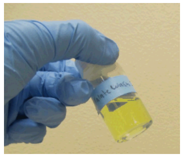
Aged in Parr vessels, 150°C for 50 hours

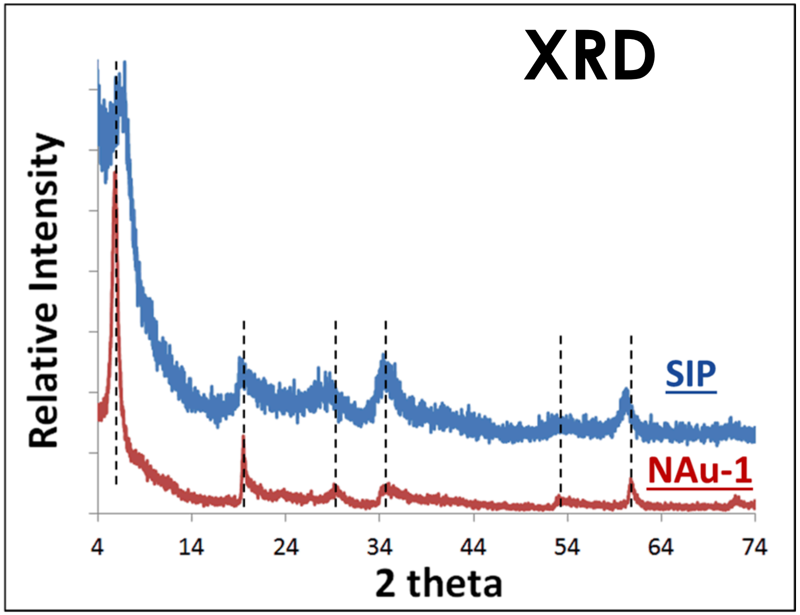
Washed, centrifuged, aged for 24 hours in 1 M NaCl



Dialyzed for 96 hours in deionized water

Oxalate treatment to remove iron oxides





- NAu-1 and SIP show similar crystalline structure;
- SIP has more tri-octahedral domains compared to NAu-1

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

Characterization of SIP

XRD SIP crystalline structure matching nontronite NAu-1

SIP has lower degree of crystallinity and more tri-octahedral domains compared to NAu-1

SAXS Similar geometry (platelets) for the NAu-1and SIP, and liquid crystalline ordering

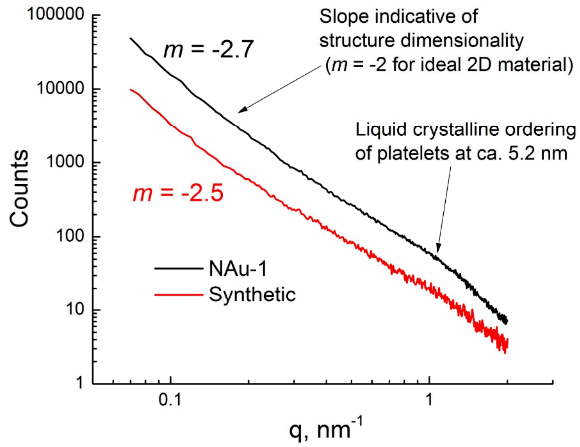
FTIR Matching Si-O bands at 1100 cm^{-1}: similar silicate framework

SEM Typical platelet geometry, smaller size in SIP

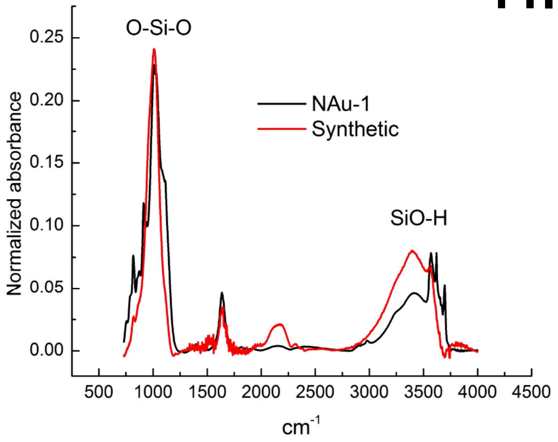
BET SIP - 136.6 m^2/g, and

NAu-1 - 46.5 m^2/g.

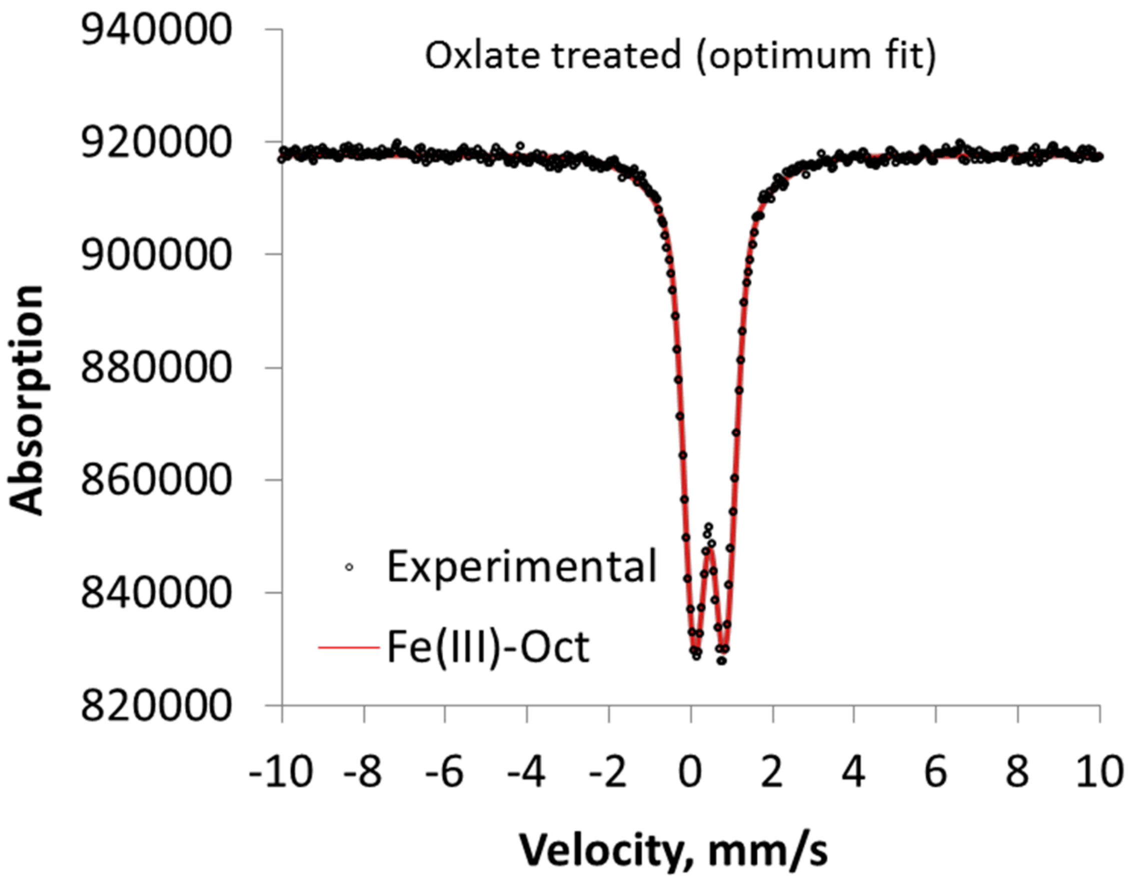
SAXS



FTIR



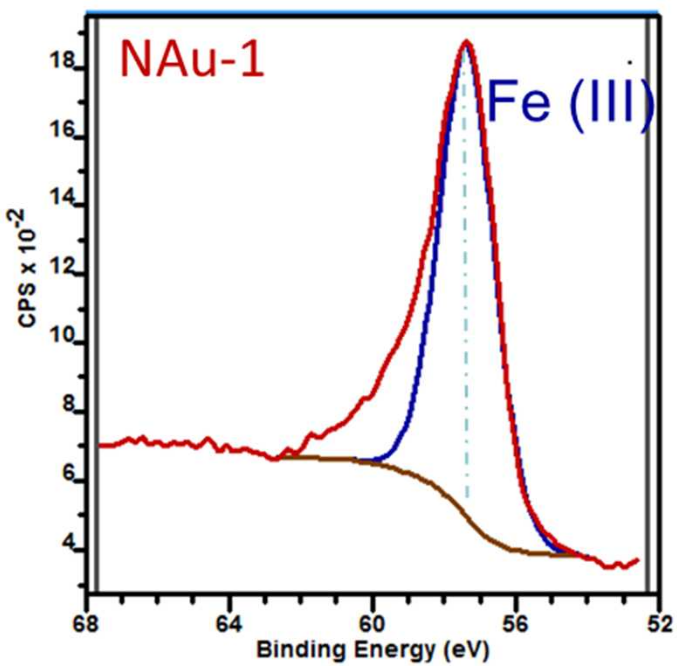
Mössbauer Spectroscopy

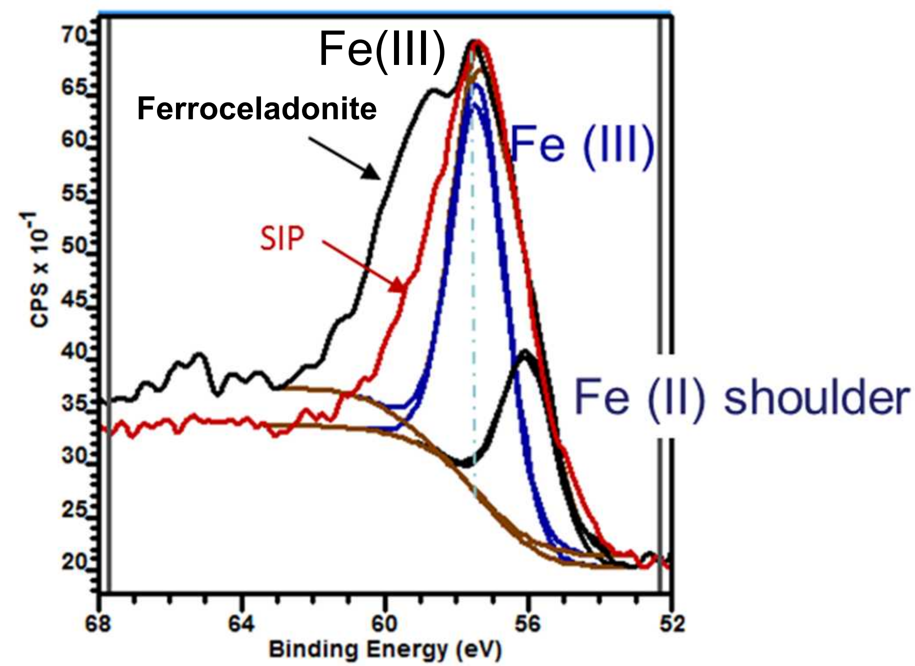


- Fe(II) content in the SIP is on the order of 1-3% of total Fe;
- Free of Fe-oxide impurities;
- Fe(III) in the phyllosilicate is predominantly (or completely) octahedral.

X-ray Photoelectron Spectroscopy

High resolution Fe 3p spectra





- NAu-1 – exclusively Fe(III);
- Ferroceladonite – Fe(II) – preliminary (not accounting for the shoulder on the left) – 37% in Black shoulder – another Fe(III) in a different structural position;
- SIP – minor Fe(II).

Reactivity experiments

Hypothesis:

Partial reduction of synthetic Fe-phyllosilicate will activate the surface and promote oxidation of As(III) to As(V)

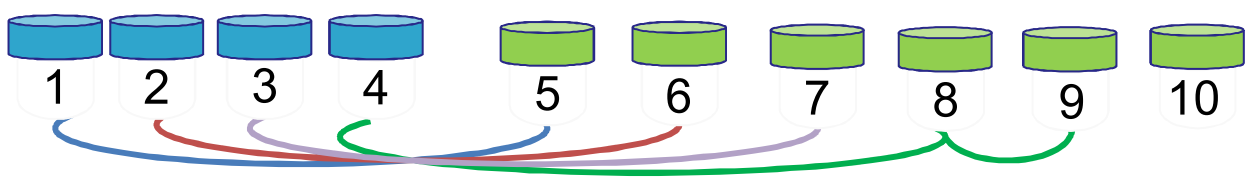
Methods:

- Batch reactors to track the oxidation of As(III);
- Prepare passive and activated natural nontronite (NAu-1) and synthetic Fe-phyllosilicate (SIP);
- XRD for phase ID;
- Liquid Chromatography coupled to the ICP-MS for arsenic speciation.

1	N-Nont	NAu-1
2	N-Nont-Red	NAu-1, activated
3	N-SIP	SIP
4	N-SIP-Red	SIP, activated

5	O-Nont	NAu-1
6	O-Nont-Red	NAu-1, activated
7	O-SIP	SIP
8	O-SIP-Red	SIP activated
9	O-SIP-Red	SIP activated, duplicate
10	O-control	No solids

Anoxic (glove box) **Oxic (bench top)**



Structural Fe(III) reduction

< 2 um size fraction

CH_3COONH_4/CH_3COOH buffer to remove carbonates

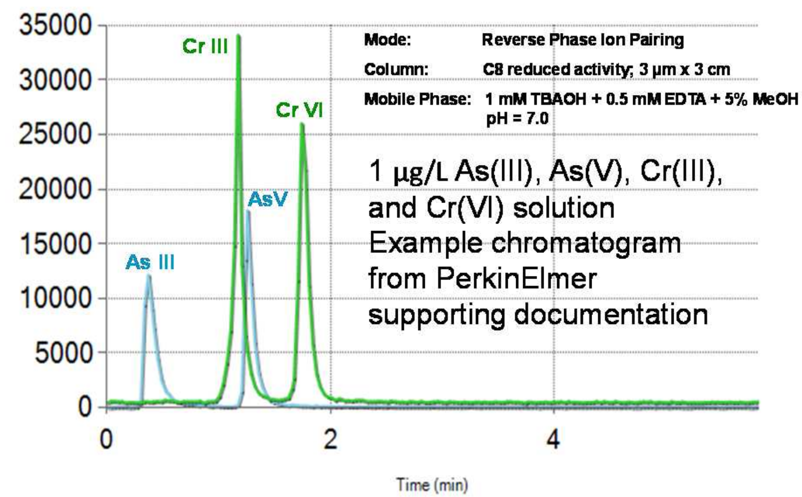
Citrate-Bicarbonate-Dithionite treatment [1]

Saturate with Na^+

NAu-1 reduced/re-oxidized

As Speciation Analysis

LC-ICP-MS

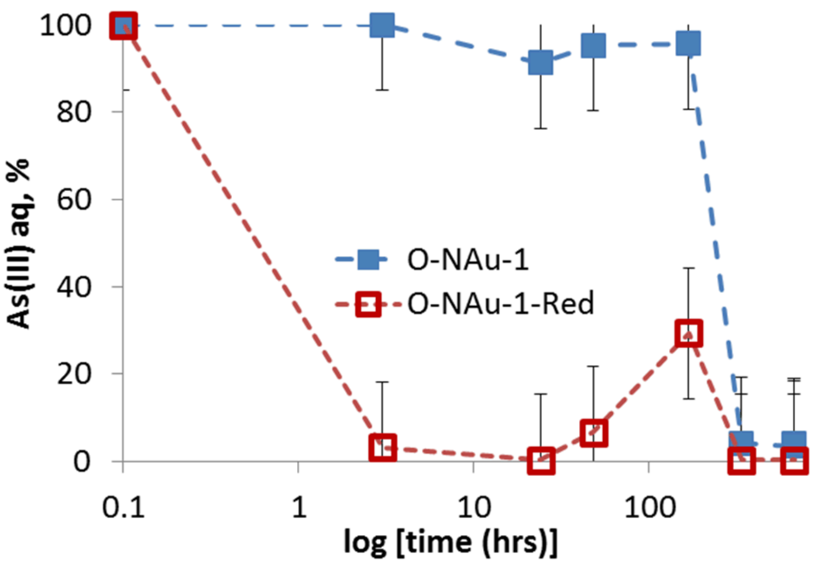


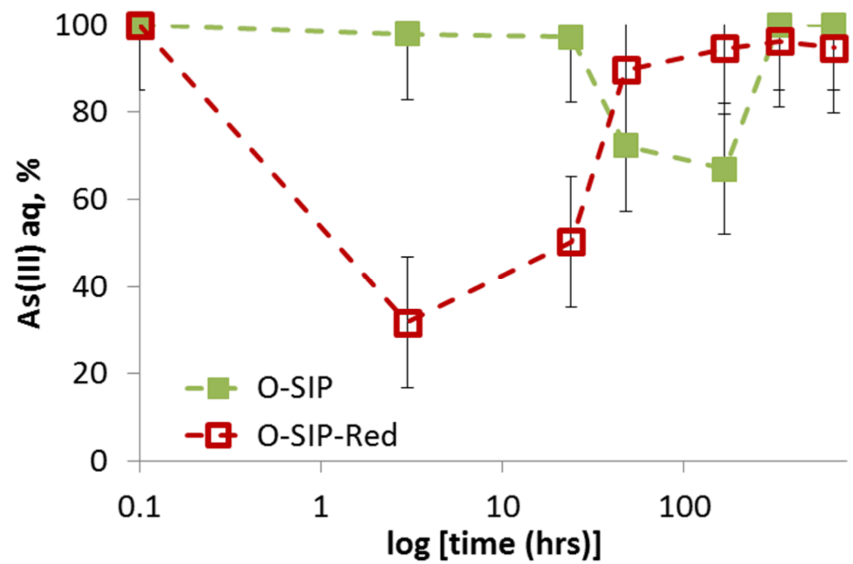
* Natural clay from Clay Mineral Society Repository

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

Reactivity of SIP and NAu-1

OXIC

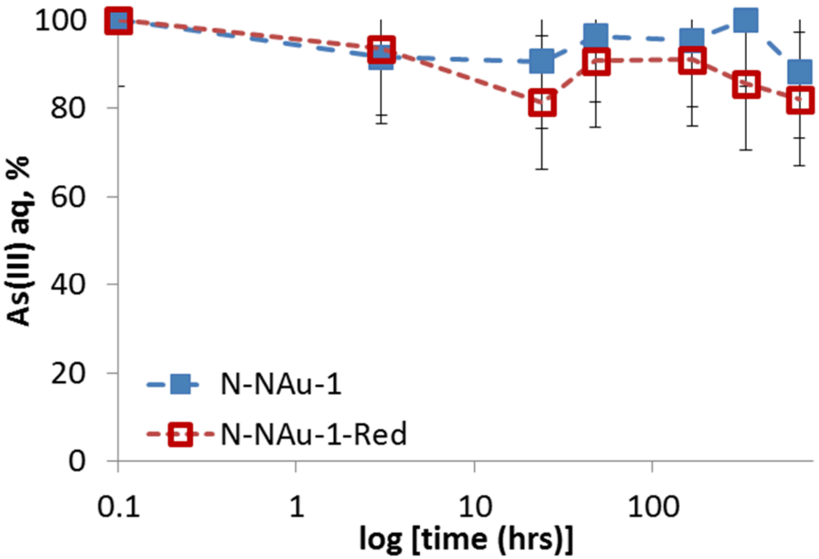


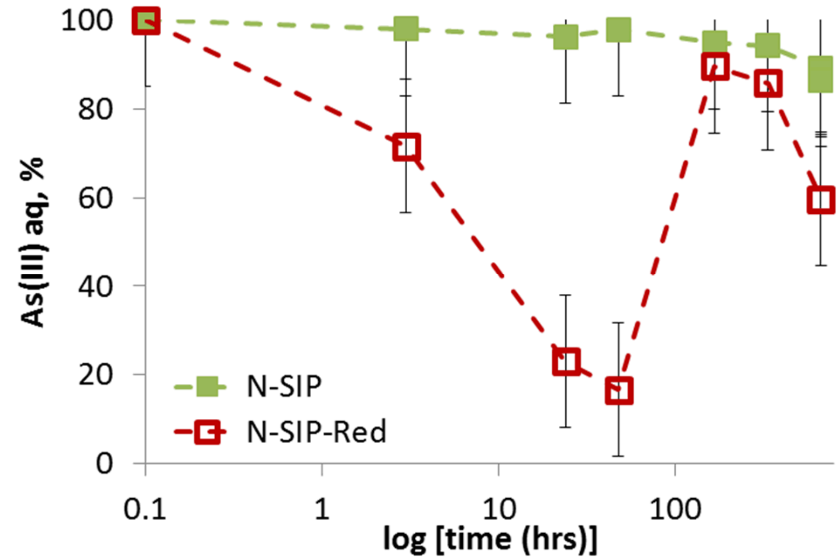


- Surfaces are inactive if no Fe(II) in the octahedral sheet;
- Surfaces are activated by partial reduction:
  - Catalyze oxidation of As(III) by dissolved O_2;
- Surfaces passivate with reaction progress.

Reactivity of SIP and NAu-1

ANOXIC





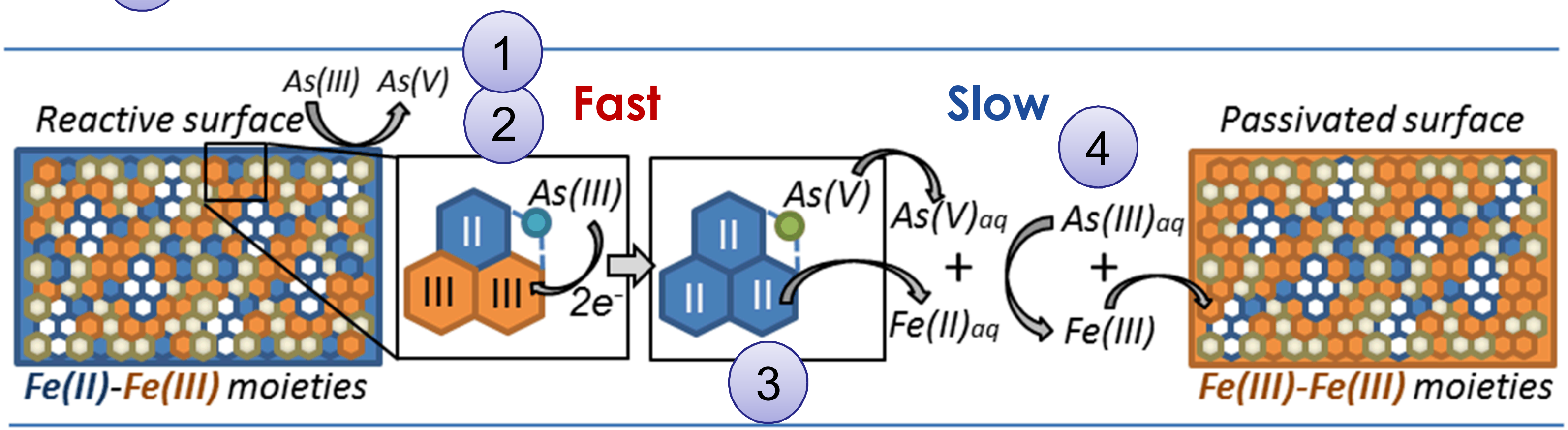
- Surfaces are activated by partial reduction:
    - Direct oxidation of As(III) by octahedral Fe(III);
    - Higher degree of oxidation for SIP vs NAu-1;

- Surfaces passivate with reaction progress.

Summary

- SIP and NAu-1 have similar structure;
- Surfaces are inactive if no Fe(II) in the octahedral sheet;
- Surfaces are activated by partial reduction:
    - Catalyze oxidation of As(III) by dissolved O_2;
    - Direct oxidation of As(III) by octahedral Fe(III);
- Surfaces passivate with reaction progress.

1. $H_3AsO_3 + {}^1/_2 O_2(aq) \longrightarrow H_2AsO_4^- + H^+$
2. $H_3AsO_3 + [Fe_2O_3] \longrightarrow H_2AsO_4^- + H^+ + 2[FeO]$
3. $[FeO] + H_2O \longrightarrow Fe^{2+} + 2OH^-$
4. $H_2AsO_4^- + 2Fe^{2+} + 3OH^- \longrightarrow H_3AsO_3 + 2Fe_2O_3 + 2H_2O$



Planned Work

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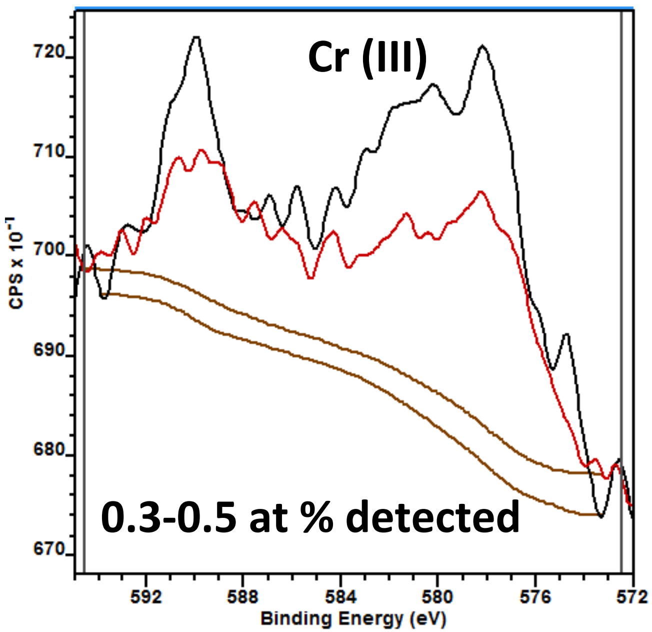
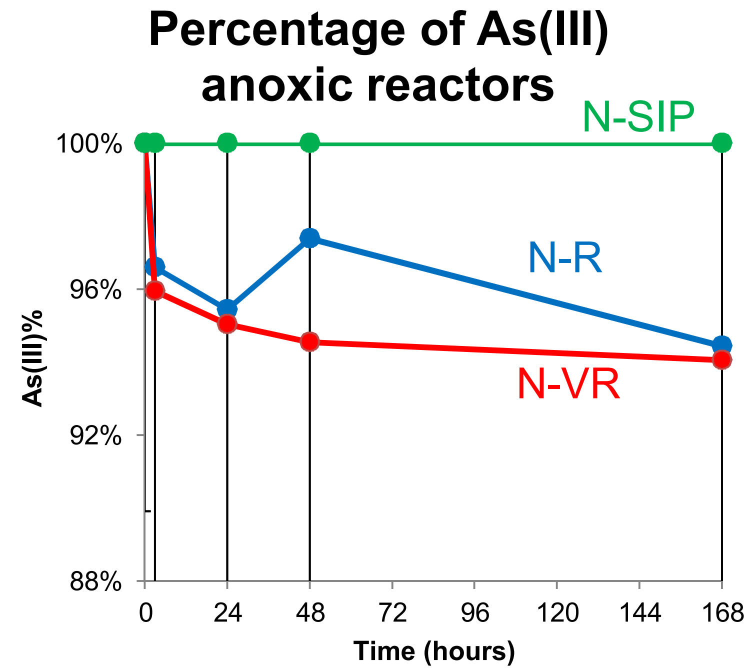
- **Determine whether Cr(III) is oxidized directly by the structural Fe(III)**
- **Probe the reactivity while varying initial Fe(II)/Fe(III) ratio**

High resolution Cr 2p spectra





- Kinetics of e⁻ transfer using time-resolved diffuse reflectance of the UV-vis absorption band at 730 nm - the Fe(II)-O-Fe(III) intervalence transfer band.
- Determine how nontronite surface is passivated: does structural Fe dissolve and re-precipitate as Fe-oxide?