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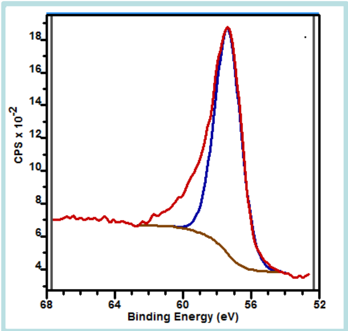

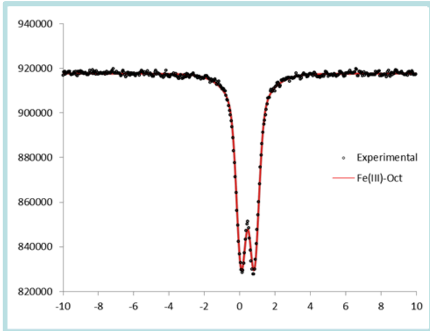

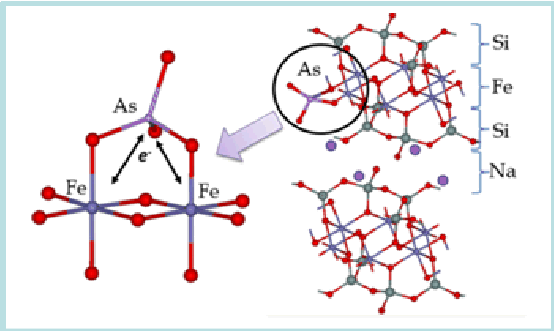

Reactivity of Fe(III) in the Octahedral Sheet of Natural and Synthetic Fe-phyllosilicates

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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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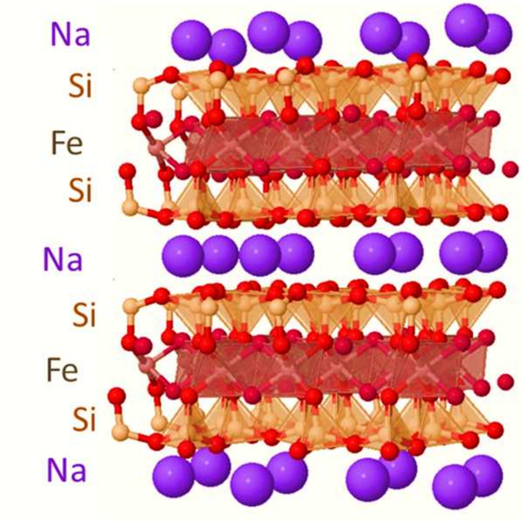
- Redox on clay mineral surfaces: catalysis and direct e^- transfer.[1-4]
- Iron in clay minerals: traces to up to 30 wt.%.[5]
- Structural iron is redox-active. [6,7]
- *Experiments*: e^- transfer at edge sites and through basal surface.[7]
- *Computation*: e^- transfer at edge sites only, no evidence 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]



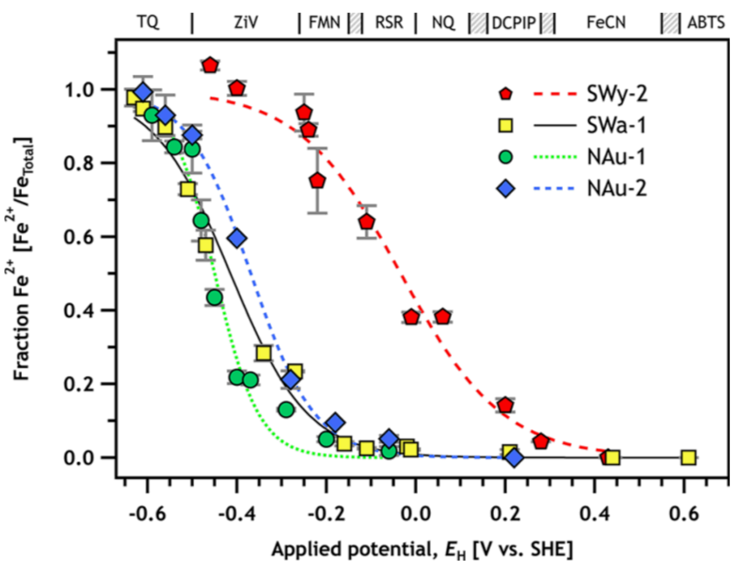
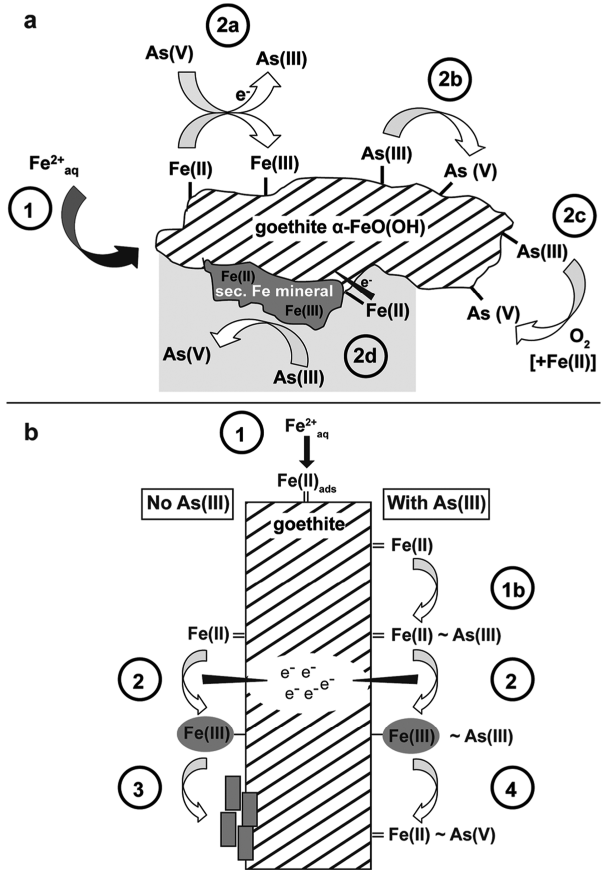


Figure from Gorski et al., ES&T, 2013

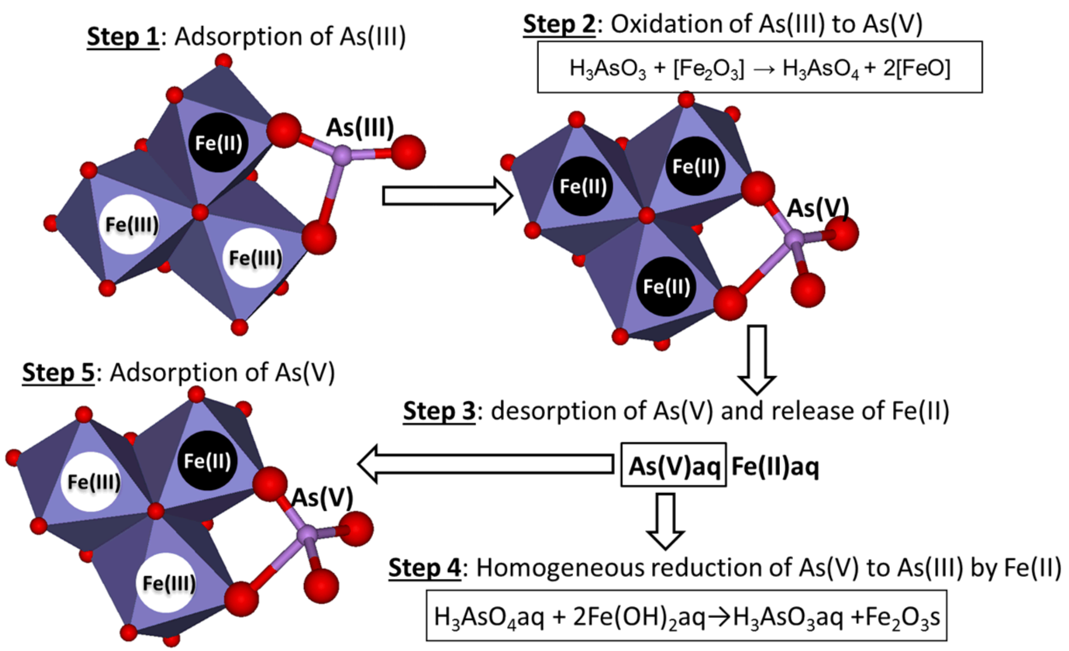
[1] Oscarson et al., 1991
[2] Manning and Goldberg, 1997
[3] Lin and Puls, 2000
[4] Hofstetter et. al, 2003
[5] Stucki, 2006
[6] Hofstetter et.al, 2006
[7] Neumann et al., 2013
[8] Alexandrov and Rosso 2013
[9] Gorski et al., 2013

Fe(II)-activated goethite

Nontronite activated by partial reduction



Amstaetter et al., 2010



Ilgen et al., 2012

Adsorbed Fe(II) oxidizes to Fe(III) on the goethite surface and resulting intermediate Fe(III) phase (unidentified) is oxidizes As(III) to As(V).

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.

Objective

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

Our previous findings

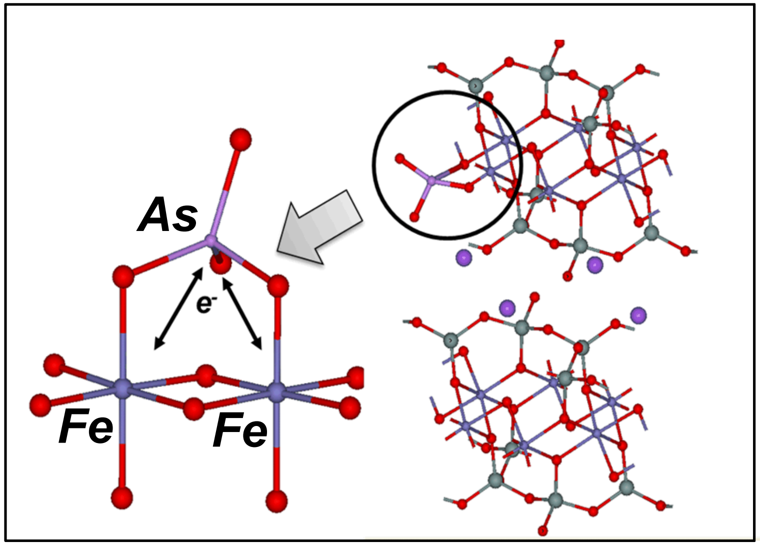
- Non-reactive Fe(III)-nontronite is activated (becomes an oxidant) when <20% of structural Fe(III) is reduced to Fe(II). Surface is passivated after reacting.

Remaining unknowns

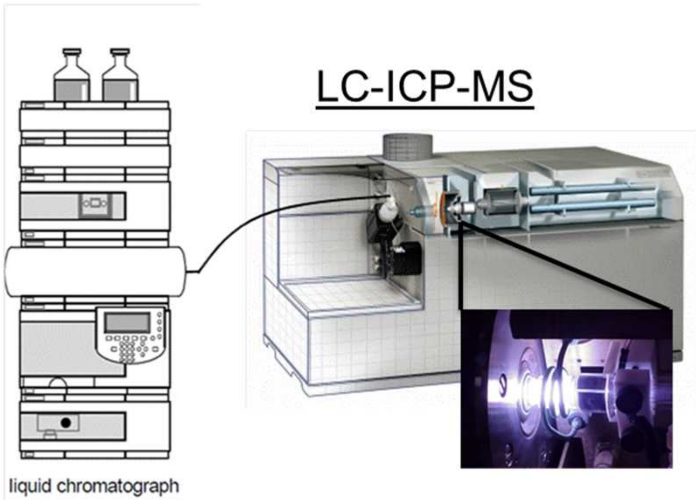
- **Does this "activated" nontronite react with other redox-active elements?**
- Reactivity as a function of Fe(II)/Fe(III) ratio in the octahedral clay sheet.
- **Do impurities in the natural nontronite affect the reactivity?**
- What is the surface passivation mechanism?

Experimental approach

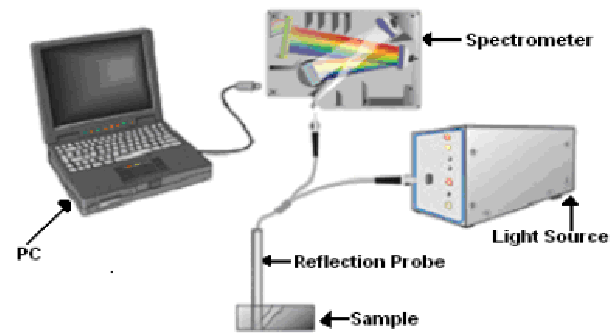
- Synthesis and characterization of pure Fe-phyllosilicate
- Reactivity of synthetic Fe-phyllosilicate compared to the natural and "activated" nontronites, using As(III) as a "probe"
- *in situ* diffuse reflectance coupled to the aqueous speciation analysis for As and Fe.

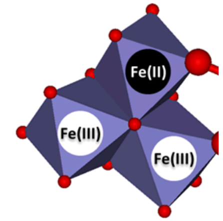


Aqueous and solid phase speciation



Diffuse Reflectance

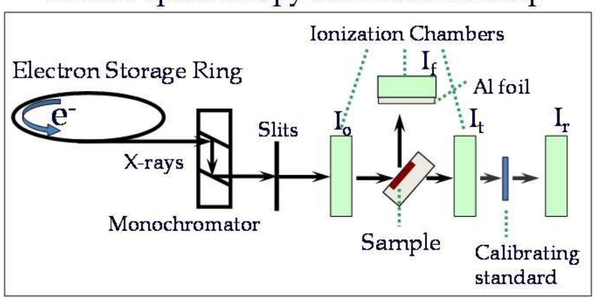




Typical Reflection Setup

Ocean Optics Manual Spectra Suite Operating Manual (2009)

EXAFS spectroscopy instrumental setup



APS, Argonne National Lab.

- Aqueous speciation: liquid chromatography coupled to an inductively coupled plasma mass spectrometer (LC-ICP-MS) (As), UV-vis (Fe).
- Solid phase speciation of arsenic and selenium: X-ray Absorption Spectroscopy (XAS) at Advanced Photon Source, Argonne National Lab.

Synthesis and characterization of Fe-phyllosilicates

Synthesis route 1 (R1)

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

Synthesis route 2 (R2)

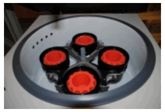
Tetraethyl orthosilicate, Aluminum Chloride, Ferrous Chloride, and Hydrazine (or Sodium Dithionite)

pH adjusted to 8 using Calcium Hydroxide

Added 160 mg of Calcium Carbonate as pH buffer

Aged at 89°C for 8 weeks

Purged with CO_2 for 12 hours, centrifuged, washed with de-ionized water, then freeze-dried.



Characterization

XRD, XRF, Raman, SAXS, FTIR, SEM, BET, Mössbauer, XAS

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

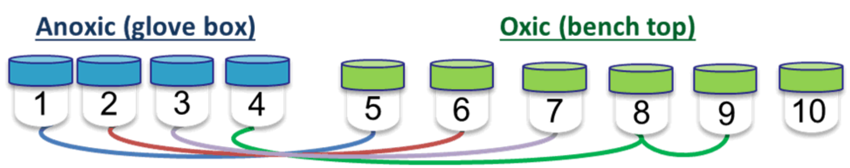
From Keeling et al., 2000

Reactivity experiments

Batch reactors:

	Anoxic
1	NAu-1
2	NAu-1, activated
3	SIP
4	SIP, activated

	Oxic
5	NAu-1
6	NAu-1, activated
7	SIP
8	SIP activated
9	SIP activated, dup
10	Aqueous control



- Batch reactors to track the oxidation of As(III);
- Passive and activated natural nontronite (NAu-1) and synthetic Fe-phyllosilicate (SIP);
- LC-ICP-MS for arsenic speciation.

Activation of structural Fe by partial 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

~24 wt.% Fe(III)

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

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

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

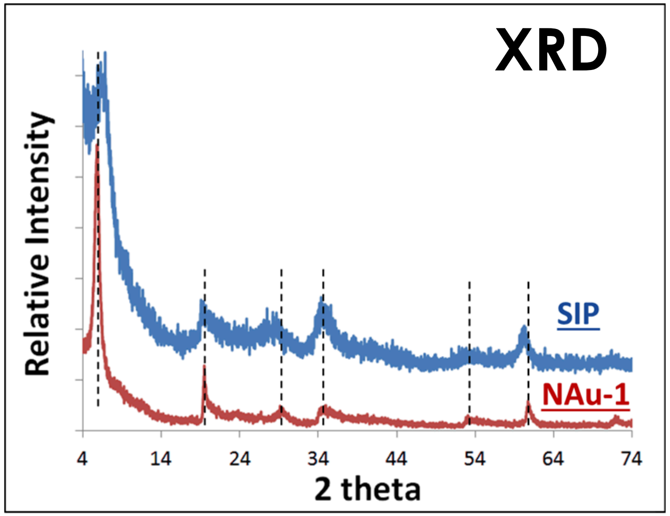
SAXS Similar geometry (platelets) for the NAu-1and SIP, and liquid crystalline ordering

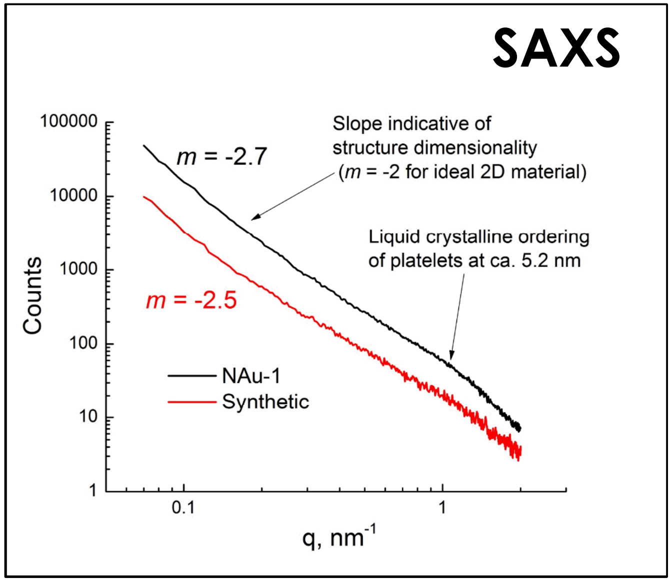
FTIR Matching Si-O bands at 1100 cm^{-1}: similar silicate framework

SEM Typical platelet geometry, smaller size in SIP

BET SIP - 136.6 m^2/g, and

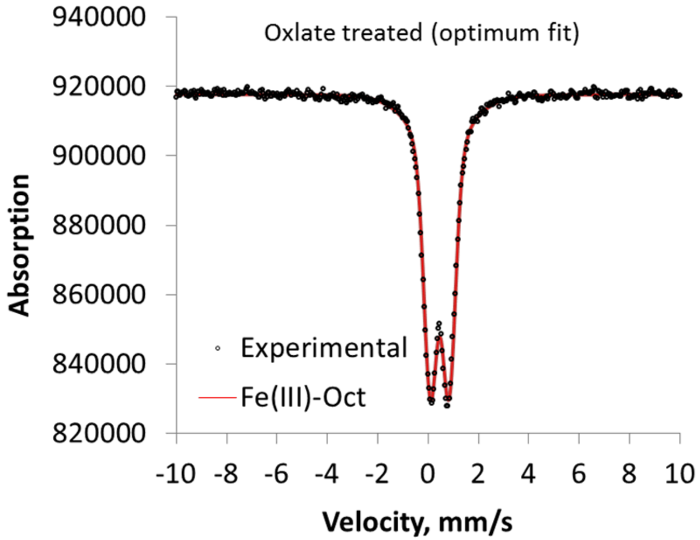
NAu-1 - 46.5 m^2/g.



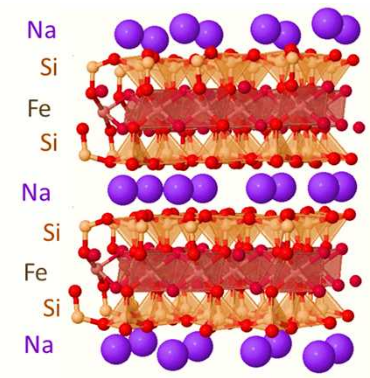


Characterization of SIP

Mössbauer Spectroscopy



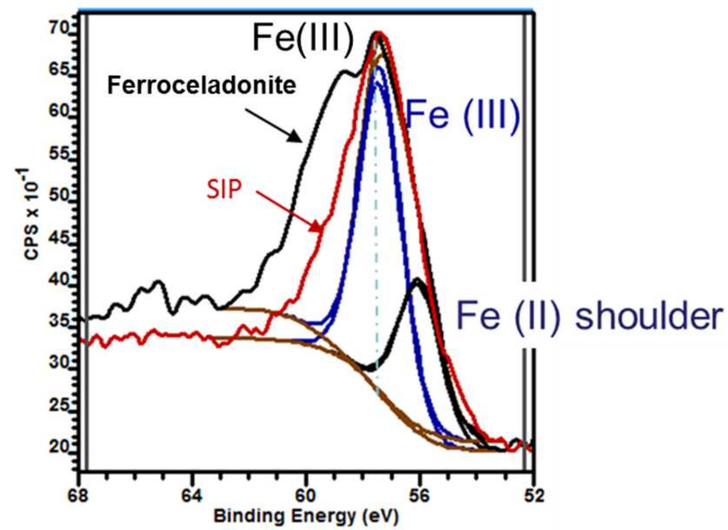
- Fe(II) content in the SIP is on the order of 1-3% of total Fe;
- Free of Fe-oxide impurities;
- Fe(III) in the phyllosilicate is predominantly (or completely) octahedral.



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%; Black shoulder – another Fe(III) in a different structural position;
- SIP – minor Fe(II).



Reactivity of SIP and NAu-1

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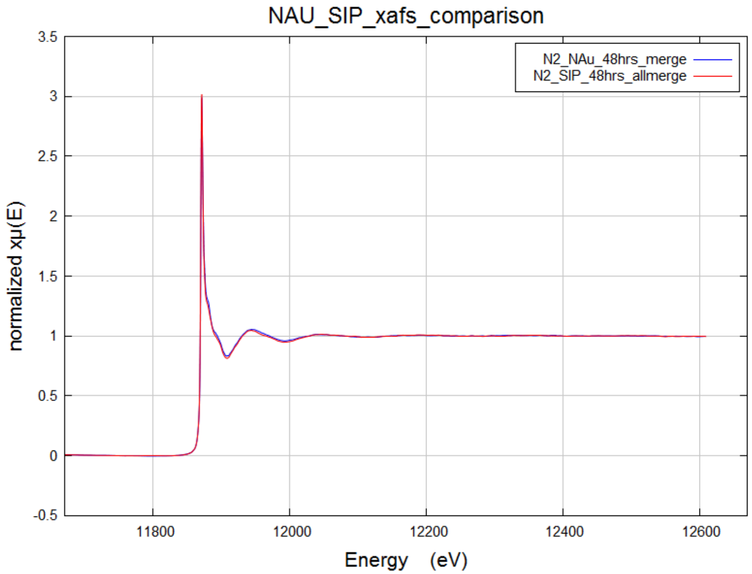
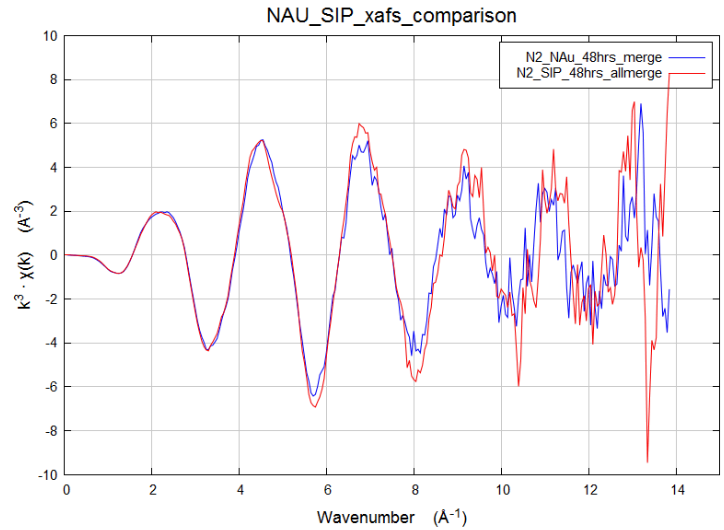
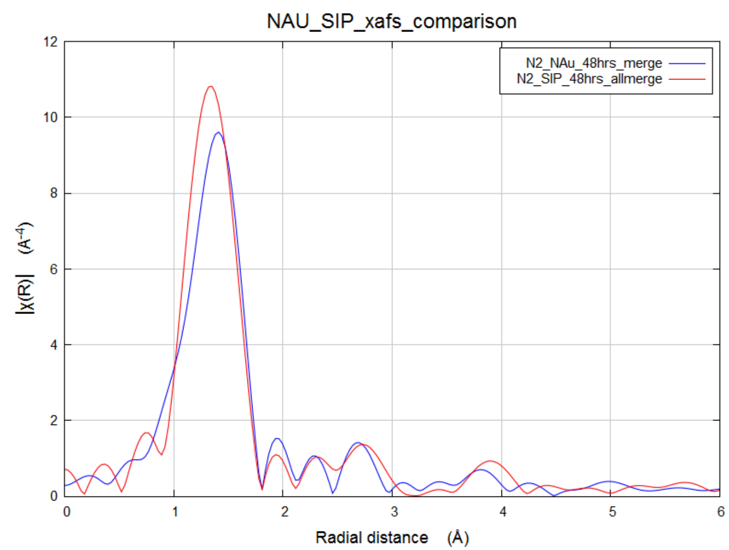
As XAFS



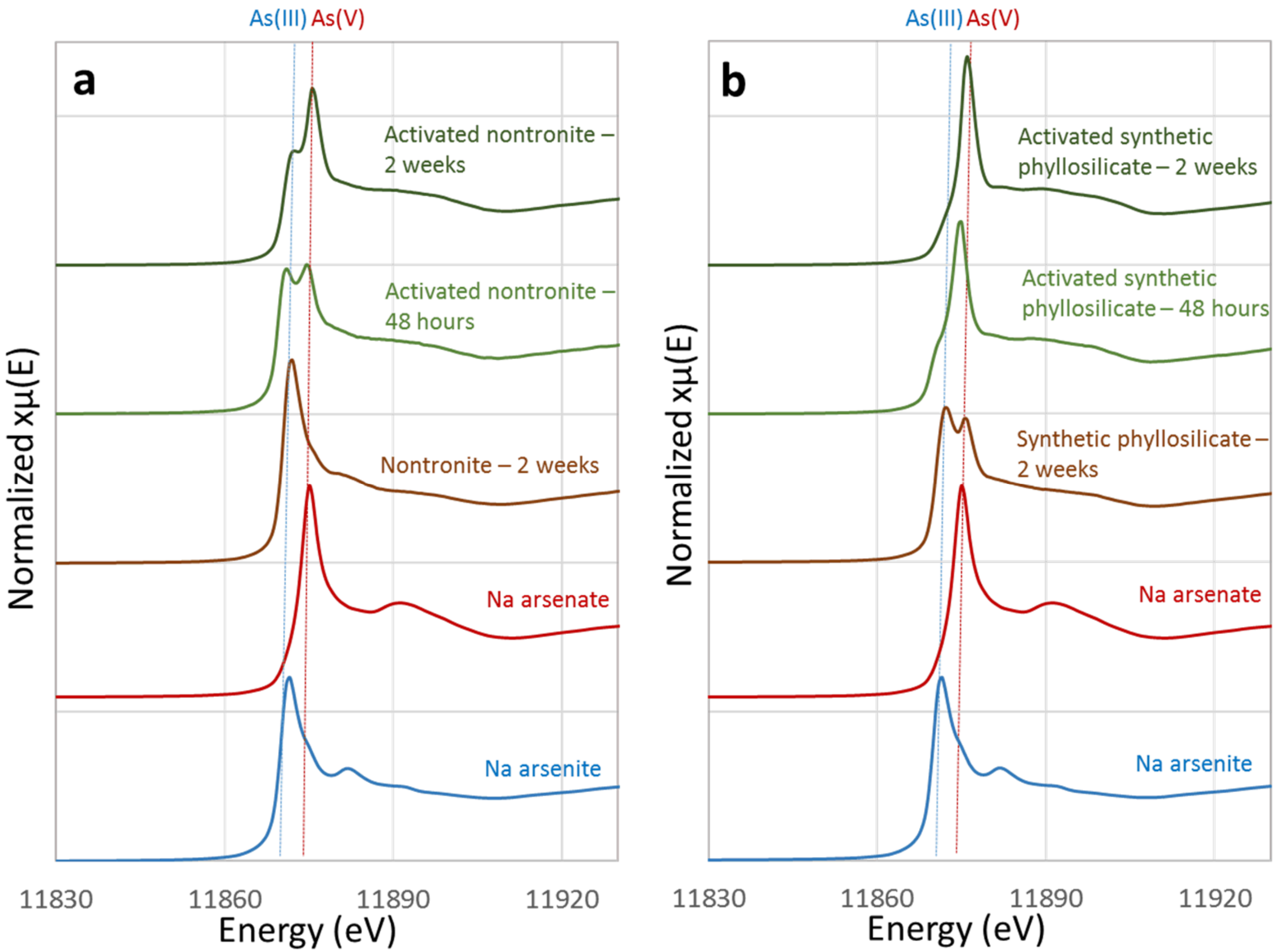




- XAFS data – qualitatively similar.
- As form bi-dentate inner-sphere complex on nontronite NAu-1 surface.

Reactivity of SIP and NAu-1

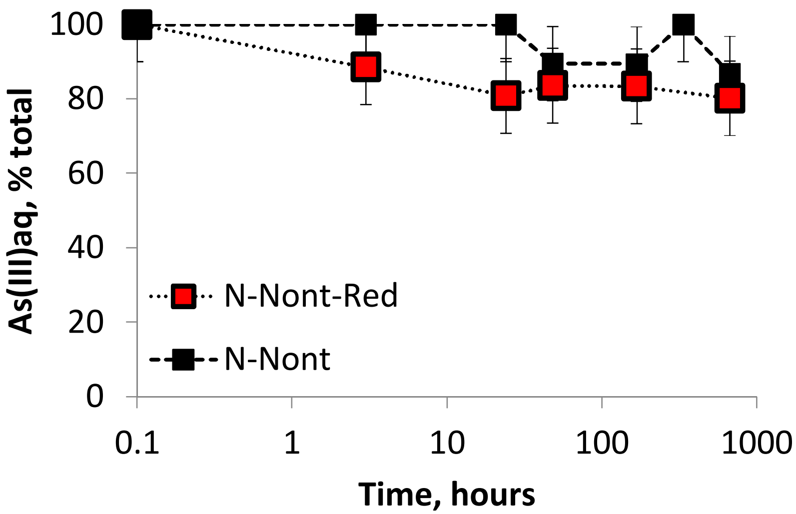
OXIC

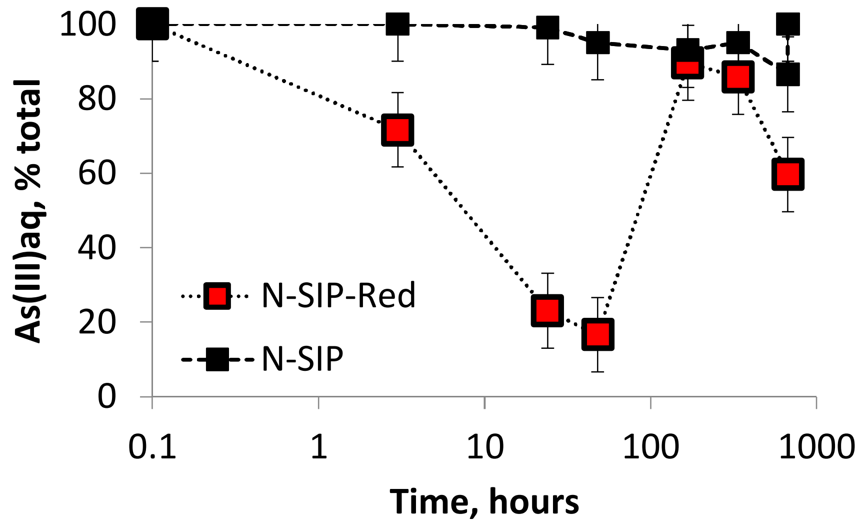


- Surfaces are inactive if no Fe(II) in the octahedral sheet;
- Surfaces are activated by partial reduction: Catalyze oxidation of As(III) by dissolved O2.

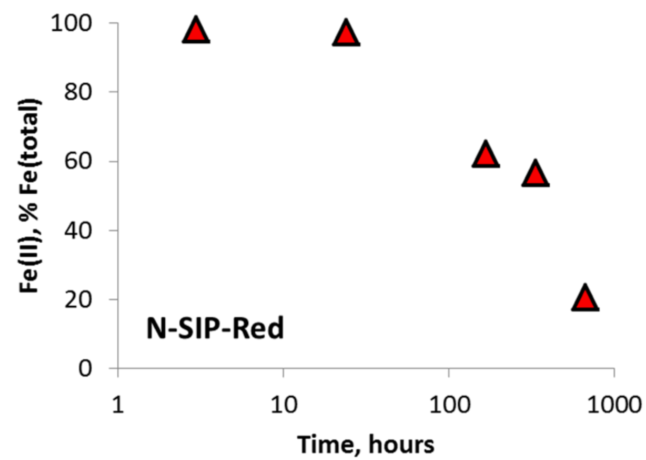
Reactivity of SIP and NAu-1

ANOXIC





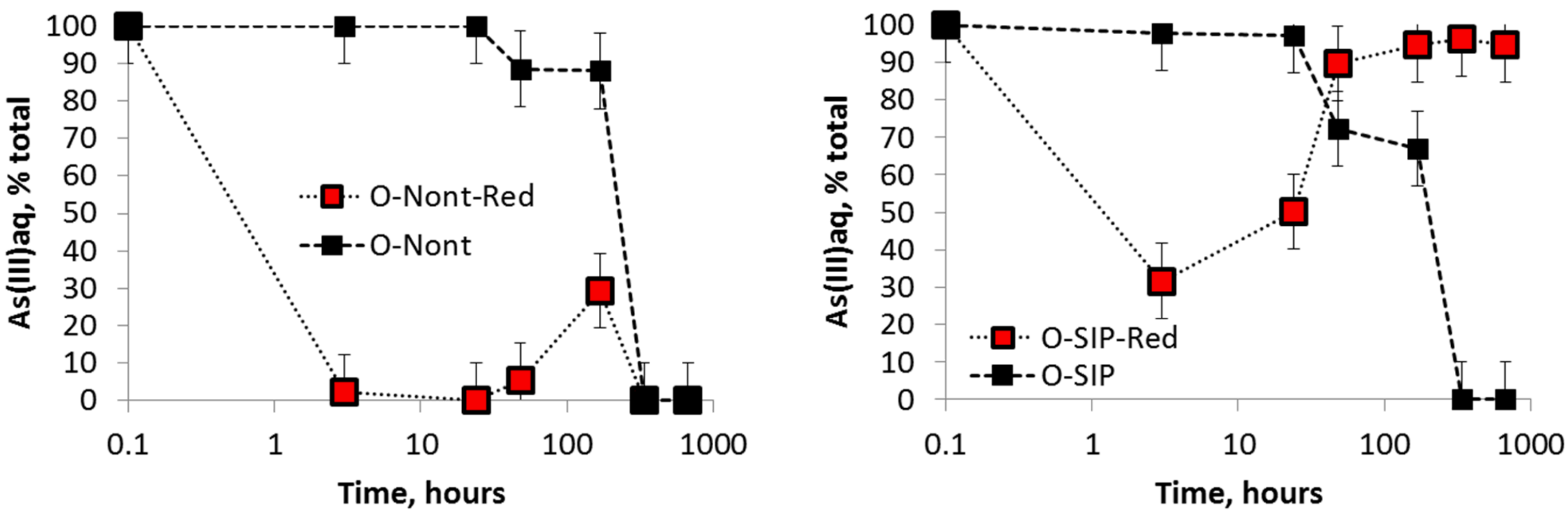
- Surfaces are activated by partial reduction:
  - Direct oxidation of As(III) by octahedral Fe(III);
  - Higher degree of oxidation for SIP vs NAu-1;

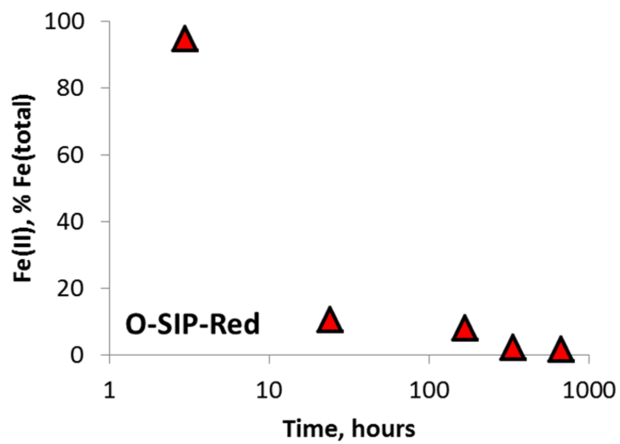


- Surfaces passivate with reaction progress.

Reactivity of SIP and NAu-1

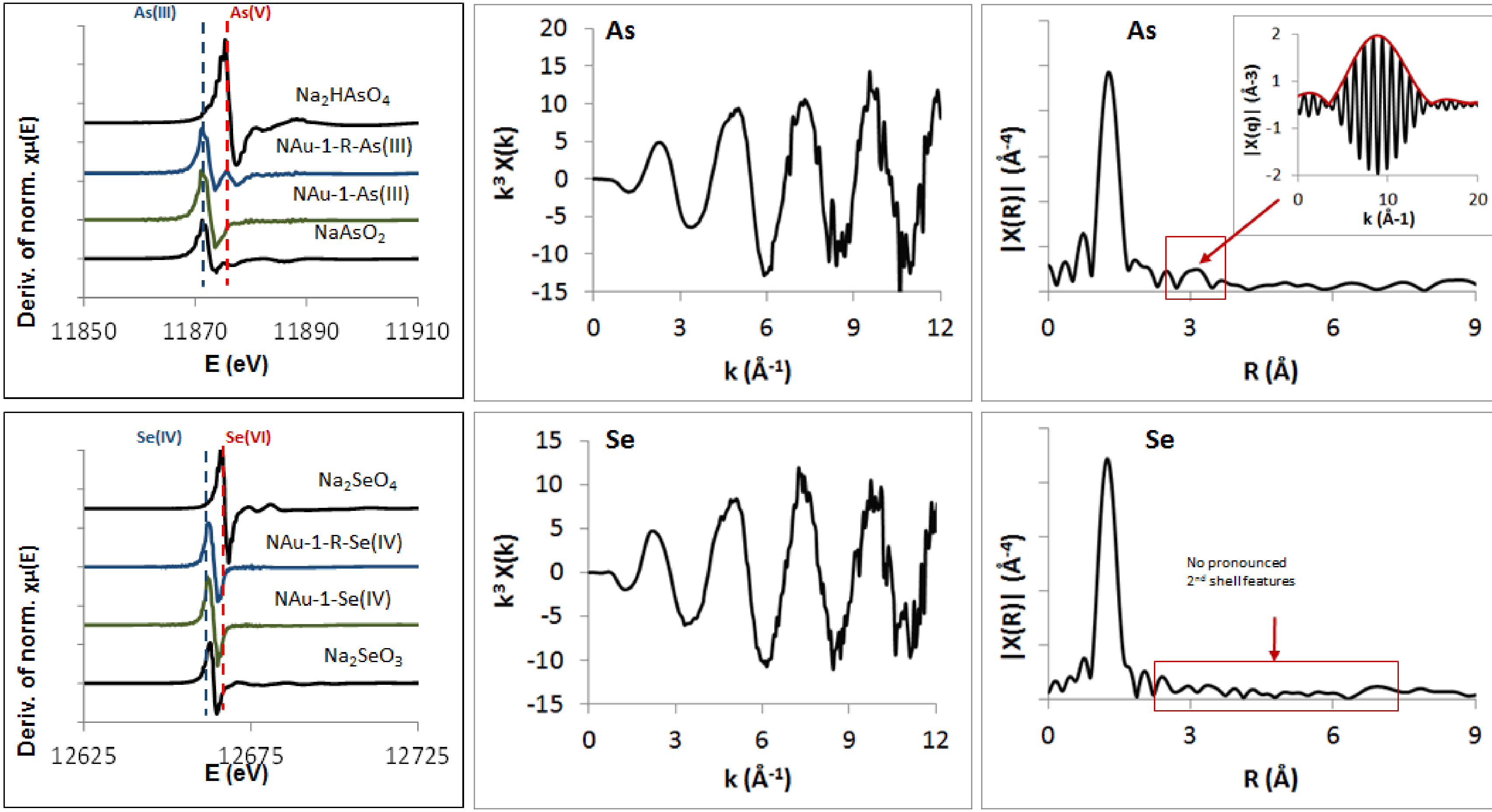
OXIC





- 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.

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



- Different reactivity towards As(III) and Se(IV) could be due to the difference in sorption complex geometry: inner-sphere bi-dentate (As), outer-sphere (Se).

Reactivity experiments

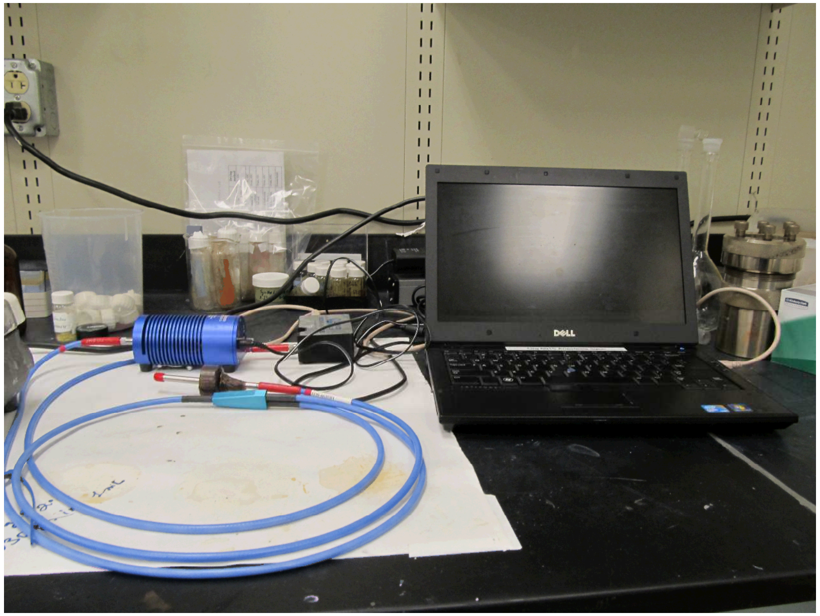
in situ measurements by Diffuse Reflectance:

Method development:

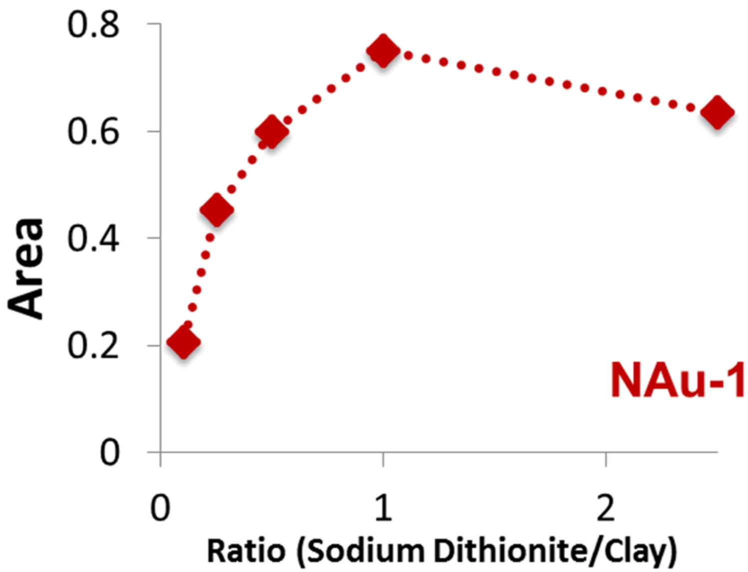
- Vary sodium dithionite to clay mineral ratio for *in situ* monitoring the Fe(II)-Fe(III) intervalence electron transfer band;
- Monitoring response vs time as clay minerals are re-oxidized.

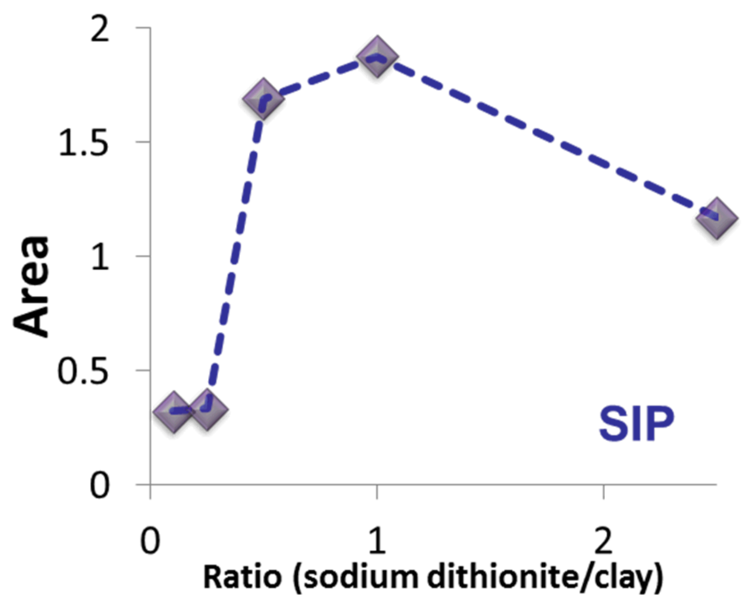
Experiments:

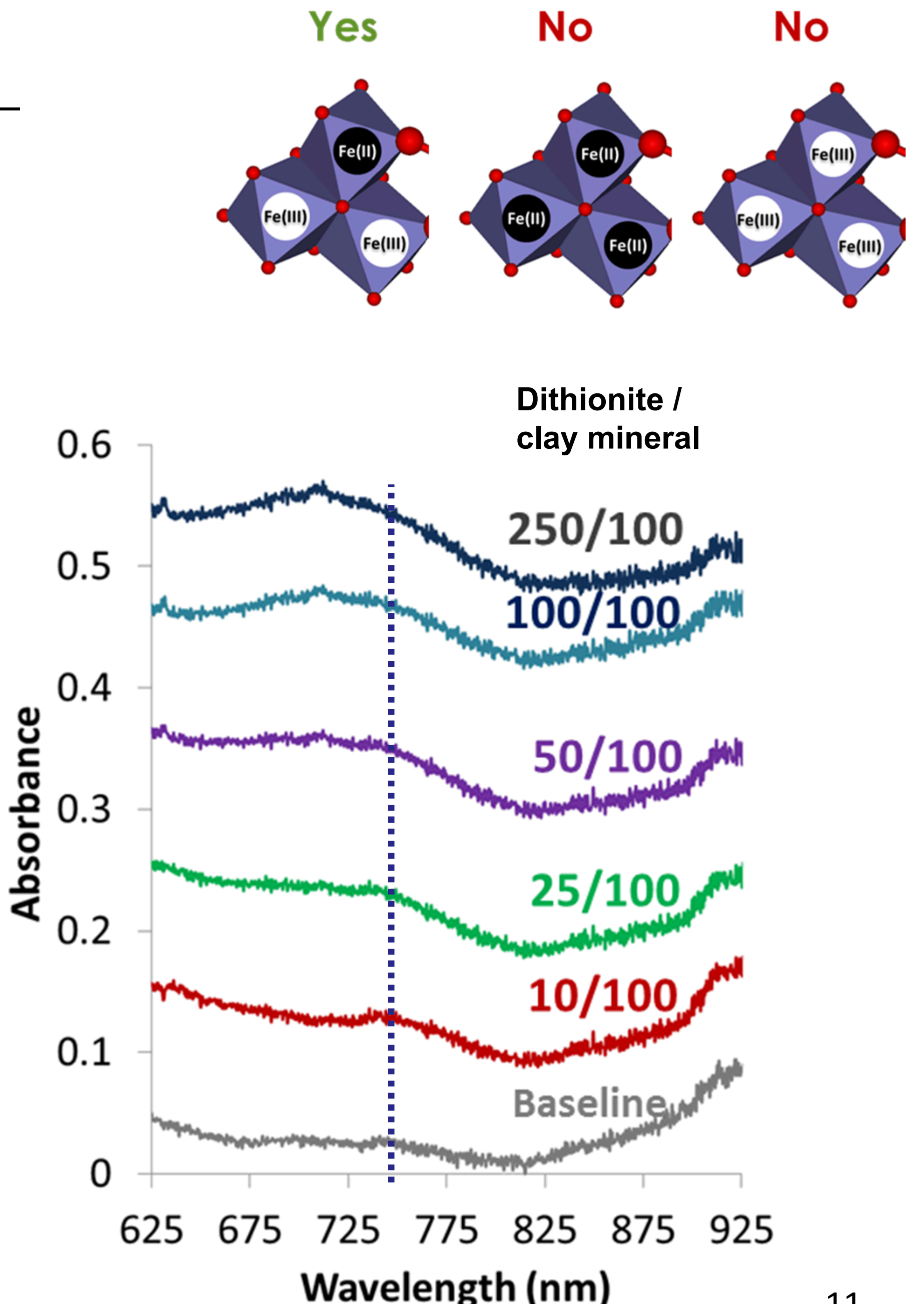
- *in situ* diffuse reflectance response when clay minerals are spiked with Fe(II), or As(III)



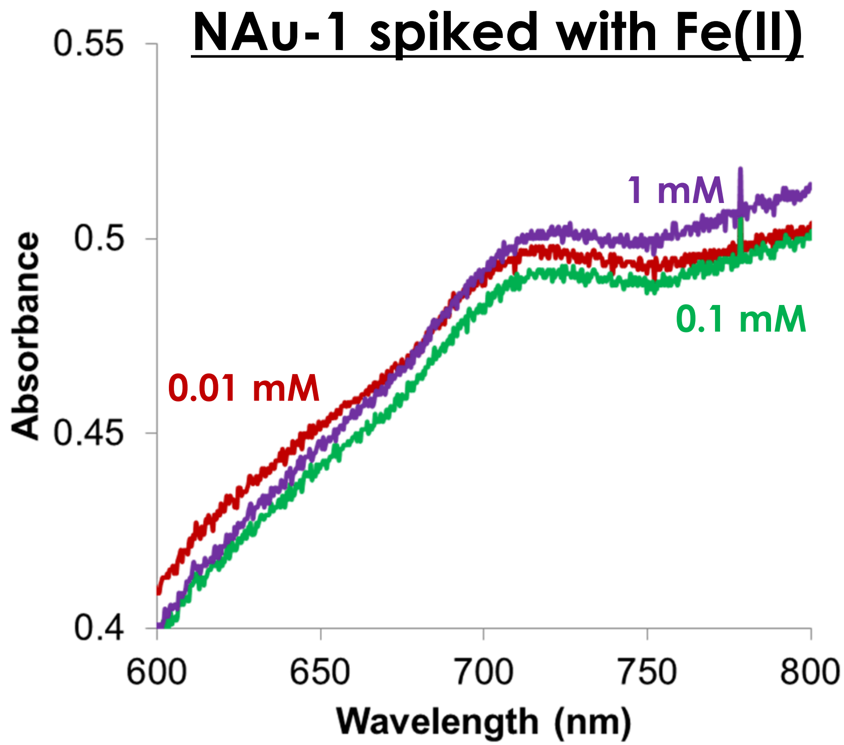
in situ diffuse reflectance

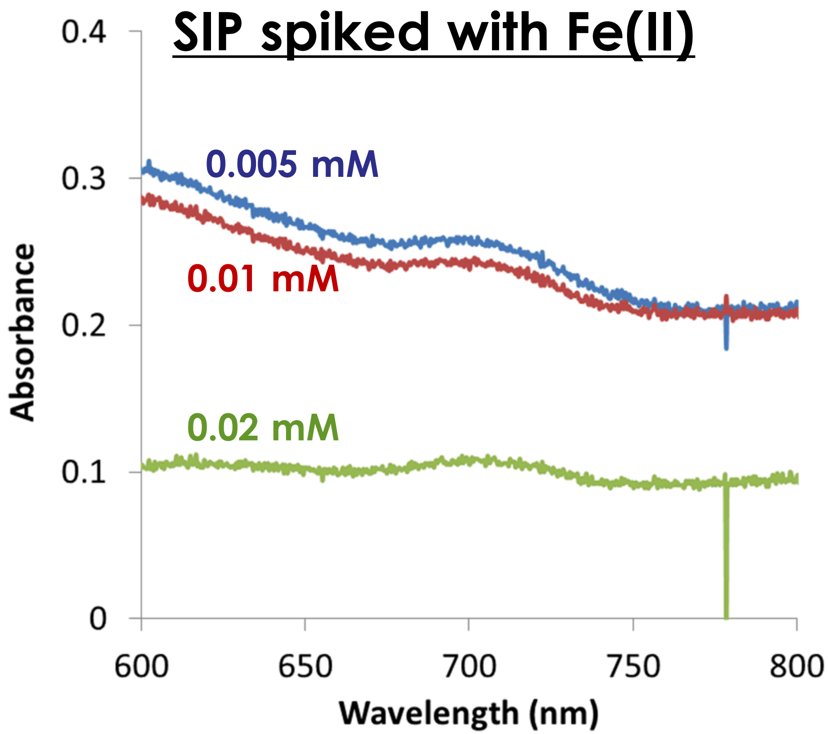


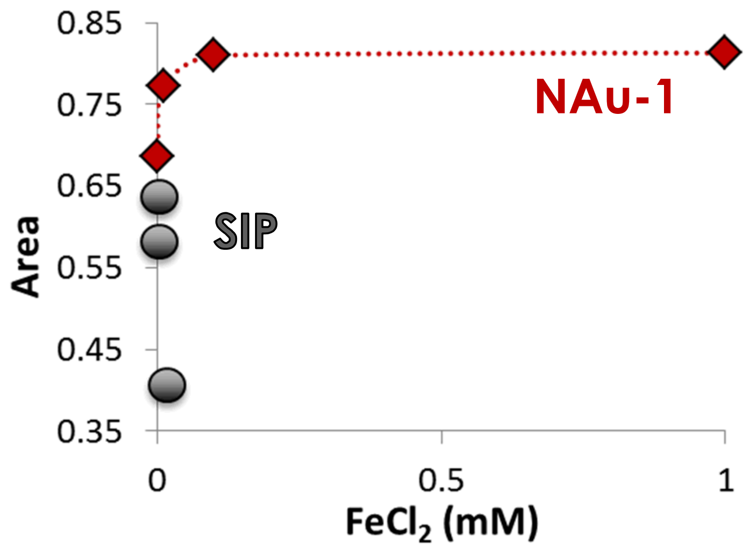




in situ diffuse reflectance

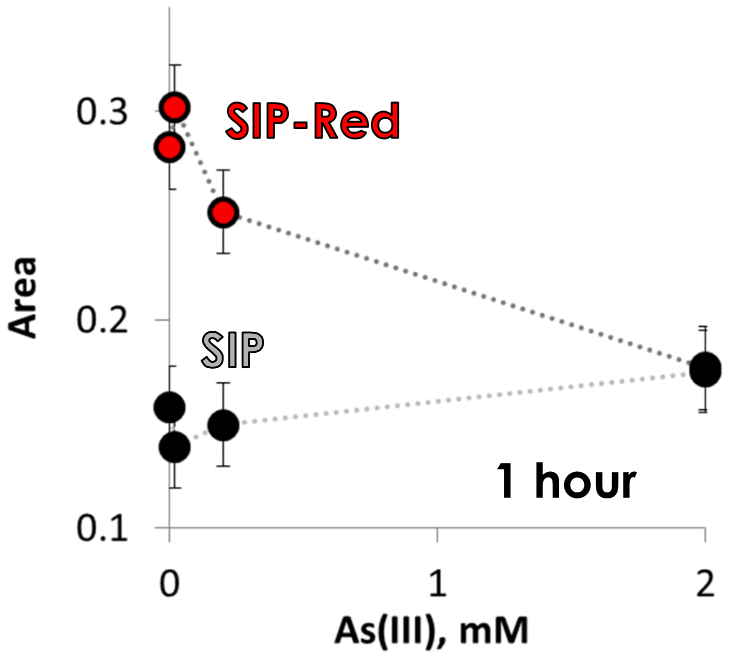


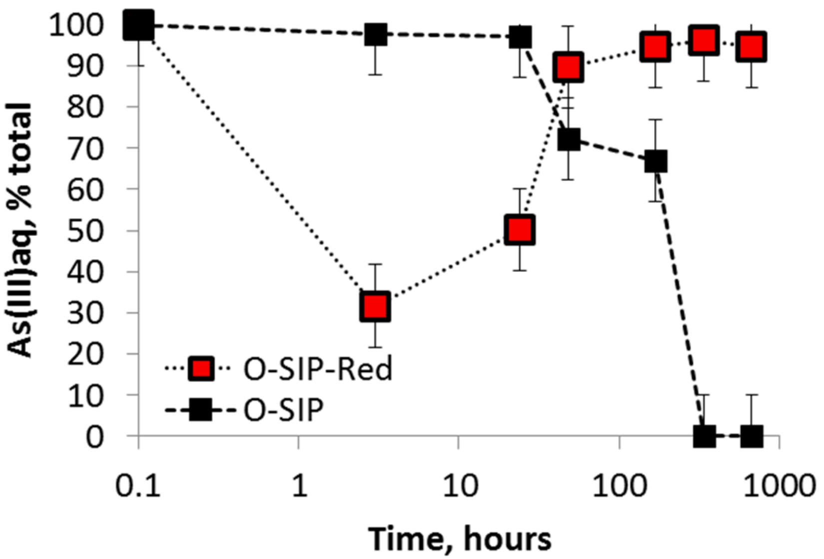


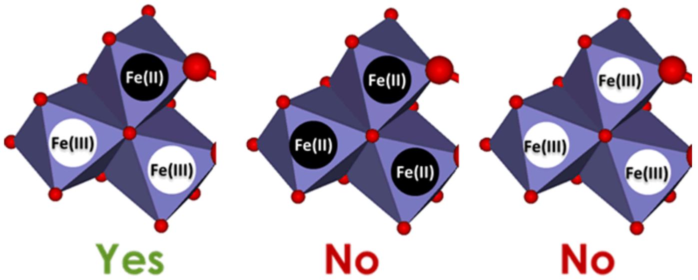


- Increase in the area with increasing concentration of added Fe(II) is indicative that Fe(II)-Fe(III) moieties are formed as Fe(II) adsorbs to the clay mineral surface.

SIP vs. activated SIP spiked with As(III)

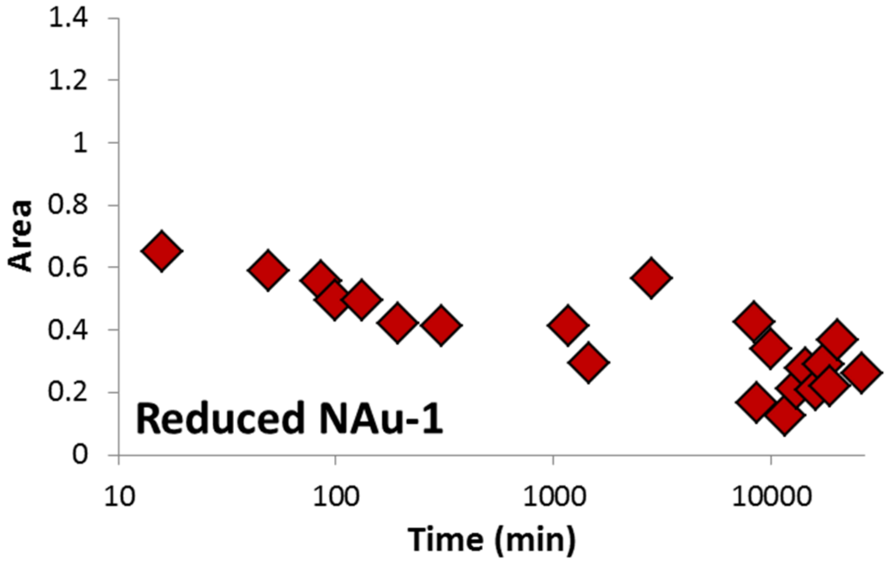


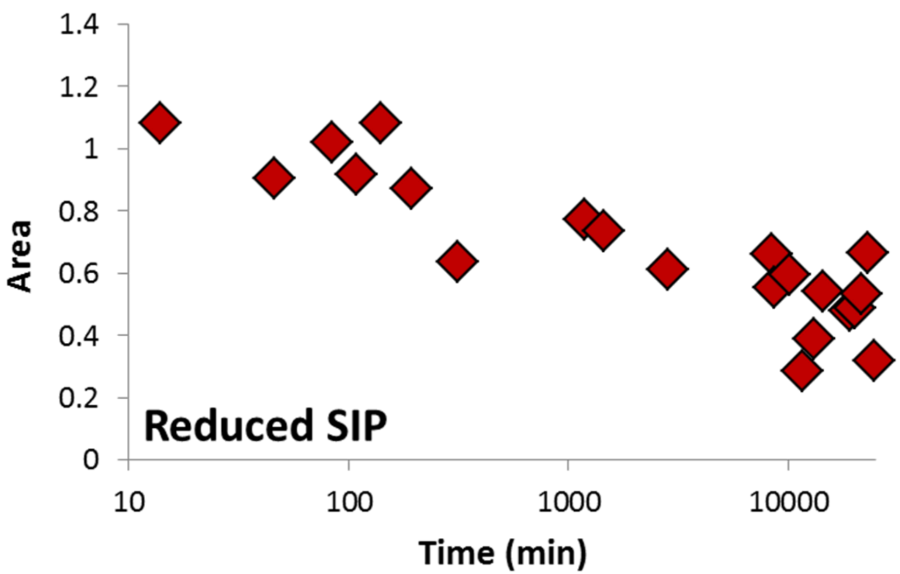




- Decrease in the area for the activated (partially reduced) SIP with increasing concentration of added As(III) is indicative that Fe(II)-Fe(III) moieties are "consumed" as it reacts with As(III).
- Area for the non-activated SIP is not affected by the concentration of As(III).

Diffuse reflectance: Summary





- Method resolution is sufficient to capture the changes in the Fe(II)-Fe(III) intervalence electron transfer band *in situ* during:
    - reduction by dithionite
    - re-oxidation by dissolved O_2
    - reactions between clay structural iron and dissolved Fe(II) and As(III).
- NAu-1 and SIP exhibit similar reactivity trends.
- Method development is needed for quantitative tests.

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. $H_2AsO_4^- + 2Fe^{2+} + 3OH^- \longrightarrow H_3AsO_3 + 2Fe_2O_3 + 2H_2O$