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## **DE-FG02-06ER15364: Final Technical Report**

### **Nanoscale Reactivity of Clays, Clay Analogues (Micas), and Clay Minerals**

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#### **Goals and Objectives**

The overall objective of the research was to acquire mechanistic understanding of processes at the mineral-water interface that explain macroscopic observations and measurements and that provide fundamental knowledge which can be applied to critical problems such as the distribution and reactivity of environmental contaminants as well as the chemically-reactive behavior of ground water flow in porous media. There were originally two main lines of inquiry:

1. What is the nanoscale/molecular scale structure of the interface between micas or clays (phyllosilicate minerals) with aqueous solutions and how does that structure relate to the processes of sorption and secondary mineral nucleation and growth?
2. What systematic patterns control the aging kinetics of nanoparticles of iron-oxides (clay minerals) and aluminosilicate clays and the simultaneous incorporation of chemical components such as contaminant ions and organic molecules?

The basal surface of phyllosilicate minerals (micas and clays) is a primary surface on which sorption of environmental contaminants, natural organic matter, and life-sustaining nutrients occurs in natural systems. Micas are also used extensively as superb atomically-flat substrates in materials science and surface physics applications. The research accomplished under this grant has contributed to attaining a full molecular-scale description of the solid-solution interface structure of muscovite mica in contact with solutions containing monovalent and divalent cationic salts and dissolved organic matter, i.e. fulvic acid, with and without dissolved salts. The structures were obtained using synchrotron X-ray reflectivity techniques.

Fine-grained particles (i.e., nanoparticles) of metal-hydroxides, oxyhydroxides, and oxides are ubiquitous in the environment and well-known for their capacity to sorb environmental contaminants primarily through the combined effects of their high surface areas and pH-dependent surface charge. Although much is known about the synthesis of such compounds, particularly in the Fe system, and the macroscopic kinetics of the aging of metastable phases to stable phases, exact mechanisms are not well-understood. We investigated the aging of Fe-oxides from metastable to stable phases in the presence of a selected set of anions to determine mechanistic links between sorption and solid phase transformation. We also initiated a similar investigation of the formation of nanoparticles of aluminosilicate clay minerals in the presence of dissolved organic matter, i.e. humic acid.

## Results: The Structure of the Muscovite-Solution Interface

The bulk of the research carried out during the grant period comprised the dissertation of a Ph.D. student, Sang Soo Lee, at the University of Illinois at Chicago and was also carried out in collaboration with Paul Fenter and Changyong Park of Argonne National Laboratory. Four manuscripts have been published, two are in the process of being submitted, and three others are anticipated to be submitted by the end of calendar year 2008. Below we list the publications and then summarize briefly all results.

- Lee S. S., Fenter P., Park C.Y. and Nagy K.L., 2008, Fulvic acid sorption on mica as a function of pH and time using in-situ X-ray reflectivity, *Langmuir*, in press.
- Lee S. S., Nagy K. L., and Fenter P., 2007, Distribution of barium and fulvic acid at the muscovite solution interface using in-situ X-ray reflectivity. *Geochimica et Cosmochimica Acta* 71, 5763-5781.
- Lee S. S., 2007, The effect of dissolved organic matter on distribution of heavy metals at the mica-water interface, Ph.D. Dissertation, University of Illinois at Chicago, 254 pp.
- Park C., Fenter P., Nagy K. L., and Sturchio, N. C., 2006, Hydration and distribution of ions at the mica-water interface. *Physical Review Letters* 97, 016101.
- Schlegel M. L., Nagy K. L., Fenter P., Cheng L., Sturchio N. C., and Jacobsen S. D., 2006, Cation sorption on the muscovite (001) surface in chloride solutions using high-resolution X-ray reflectivity, *Geochimica et Cosmochimica Acta* 70, 3549-3565.
- Lee S. S., Nagy K. L., Park C., and Fenter P., Mercury-fulvic acid sorption on muscovite (001) surface observed with X-ray reflectivity, in preparation for submission to *Environmental Science & Technology*.
- Park C., Fenter P., Sturchio N. C., and Nagy K. L., Rb<sup>+</sup> and Sr<sup>2+</sup> adsorption at the mica (001)-electrolyte interface: Thermodynamics, interfacial structure and pH hysteresis, in preparation for submission to *Langmuir*.

X-ray reflectivity and, where possible, resonant anomalous X-ray reflectivity (RAXR) were used to determine the muscovite mica-solution interface structure in fulvic acid solutions as a function of pH and time, and in solutions containing Ba, Sr, Pb, Cu, Zn, and Hg with and without fulvic acid at selected pHs. Previously, data had been collected using X-ray reflectivity alone to determine the structure of the muscovite-solution interface in K, Cs, Ca, and Ba chloride solutions. Interpretation of these data was finalized during the period of this grant (Schlegel et al., 2006). In cases where RAXR was not or could not be applied because of experimental limitations, the positions and estimated coverages of cations could be derived based on charge-balance and space-filling constraints. With RAXR data, positions of cations in the absence and presence of fulvic acid films were determined with sub-Ångström-scale resolution. These results show that the positions and extent of uptake are correlated with pH, ion charge, ion size, ion hydration enthalpy, and binding strength to functional groups on the fulvic acid. The results also indicate that fulvic acid can compete with free cations for mica sorption sites, and the order of addition of cations to the fulvic acid (before or after addition of the mica) can change uptake amounts and positions.

Most experiments were conducted using Elliott Soil Fulvic Acid (FA) I or II (International Humic Substances Society - IHSS), and a few with Pahokee Peat Fulvic Acid and Suwannee River Fulvic Acid, also from the IHSS. With the exception of the Suwannee River FA, the fulvic acids represent the water soluble portions of the humic substances associated typically with mineral surfaces. Cation concentrations were typically 0.005 or 0.01 molal; however, additional measurements were made at concentrations both higher and lower

depending on specific characteristics of the cation and/or its interactions with FA. The experiments were conducted as described in Schlegel et al. (2006) except that when fulvic acid was present the solutions and experiments were maintained under dark conditions. All measurements were carried out at the Advanced Photon Source on both bending magnet (Sector 12) and wiggler (Sector 11) beamlines (BESSRC-CAT). Earlier data (Schlegel et al. (2006) and some of the data reported in Lee et al. (2007)) were collected by measuring rocking curves. Later reflected X-rays were imaged with a CCD area detector, which greatly shortened the time required to obtain a single data set from approximately 18-24 hours to 2-3 hours.

The main results of Schlegel et al. (2006) showed that at pH of about 5.7 the monovalent cations  $K^+$  and  $Cs^+$  adsorbed dominantly as inner-sphere complexes (i.e., close enough to the surface oxygens on the cleaved muscovite basal plane that no water could be positioned vertically below the cation above the surface) with some indirect evidence for a substantial proportion of  $K^+$  in a diffuse layer. The divalent cations  $Ca^{2+}$  and  $Ba^{2+}$  also adsorbed to a large extent as partially-dehydrated (i.e., inner-sphere-like) cations, probably fully compensating the negative charge of the muscovite surface. However, there was the possibility from the data interpretation that some of the divalent cation, particularly in the case of  $Ca^{2+}$ , could exist farther from the surface as a nominally outer-sphere entity. The general results for the monovalent cations were expected based on macroscopic experimental data in the literature, but the implication that the much more strongly hydrated divalent cations could adsorb as inner-sphere complexes was unexpected.

These results led to the collaborative development by Argonne researchers Park and Fenter of the RAXR method, which is in simple terms a combination of the X-ray reflectivity measurement (reflected X-rays measured as a function of momentum transfer  $Q$  at constant beam energy) and X-ray Absorption Near-Edge Spectroscopy (XANES), where  $Q$  is held constant and the absorption of X-rays is measured as a function of energy of the incident beam. Results of the combined approach allow determination of the total electron density profile at the interface (as reported by Schlegel et al. (2006)) and the element-specific electron density profile (as reported by Park et al. (2006)). Subtraction of the element-specific profile from the total electron density profile yields the water profile.

The main results of Park et al. (2006) showed that  $Rb^+$  adsorbed as an inner-sphere complex with some  $Rb^+$  in a diffuse layer farther from the surface, but  $Sr^{2+}$  adsorbed in nearly equal amounts as both inner- and outer-sphere complexes that fully compensated the surface charge. The data could also be interpreted to indicate that both positions of adsorbed  $Sr^{2+}$  were bound to the surface with equal strengths. It is noted that experimental considerations for the RAXR measurement required selecting a different monovalent and divalent cation from those investigated by Schlegel et al. (2006). These results have been extended to include isotherm measurements as a function of pH and cation concentration (Park et al., in prep.)

The research conducted by S. S. Lee broadened the solution composition conditions to include heavy metal cations, of importance in terms of toxicity effects in the environment, and fulvic acid. Because fulvic acid is an operationally-defined extraction of organic macromolecules with average compositional and size characteristics, its uptake on muscovite required development of a new approach for modeling the electron density distribution at the interface, which is described in detail in Lee et al. (2008).

The structure of fulvic acid adsorbed on muscovite was obtained with X-ray reflectivity and varied with solution pH in terms of interpreted continuity over the surface (i.e., whether or not it adsorbed as a film), thickness and total electron density of the film when present, and

distribution of electron density within the film perpendicular to the surface (Lee et al., 2008). In general, FA films were on the order of 10 Ångstroms thick, and the results showed evidence for changes in film structure (density and thickness) with reaction times of up to 500 hours. Films decreased in thickness with increasing pH and a continuous layer could not be observed at pH 8 and 12.

We observed using X-ray reflectivity, only, that Ba<sup>2+</sup> is adsorbed dominantly as an inner-sphere cation in the absence of fulvic acid and acts as a bridging cation in the presence of fulvic acid at pH 3.7 and 5.5, in both cases in amounts that fully satisfy the charge on the surface (Lee et al., 2007).

In contrast, Sr<sup>2+</sup> which Park et al. (2006) had shown as adsorbing in both inner- and outer-sphere positions maintains these two positions in the presence of fulvic acid, although proportionately more Sr<sup>2+</sup> resides in the outer position with additional cation in the FA film even farther from the surface (Figure 1). The amount farther out in the film increases at pH 3.5.

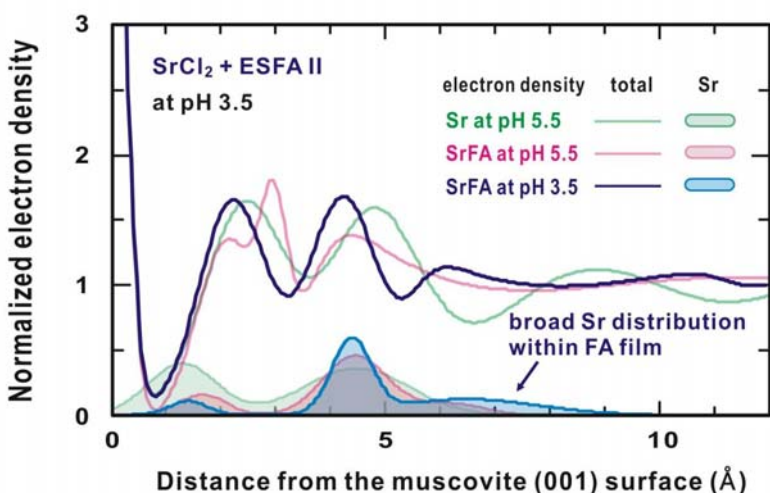


Figure 1. Upper curves are total electron density profiles for Sr<sup>2+</sup> (0.005 m Sr(NO<sub>3</sub>)<sub>2</sub>) in the presence of Elliot Soil Fulvic Acid II (100 ppm). Lower curves are the Sr<sup>2+</sup> electron density profiles from the RAXR data.

Divalent mercury, Hg<sup>2+</sup>, also adsorbs as both an inner-sphere and outer-sphere cation in the absence of fulvic acid but is broadly distributed and in comparatively higher concentration within an adsorbed fulvic acid layer at pH 2 (Figure 2). In 1 × 10<sup>-3</sup> m Hg(NO<sub>3</sub>)<sub>2</sub> solution without FA at pH 2, Hg adsorbed as both types of complexes in an amount that compensated only 37%

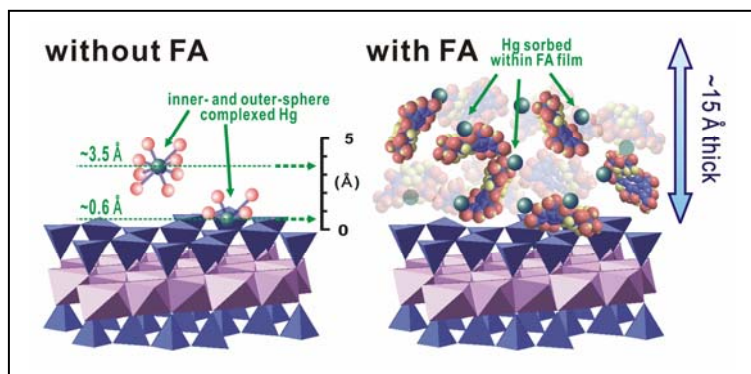


Figure 2. Schematic diagram showing Hg<sup>2+</sup> uptake at the muscovite (001) surface from an aqueous solution of 0.001 m Hg(NO<sub>3</sub>)<sub>2</sub> at pH 2 (left) and a solution of 0.001 m Hg(NO<sub>3</sub>)<sub>2</sub> and 100 ppm Elliott Soil FA II (right). Hg<sup>2+</sup> is distributed at two well-defined distances from the surface in the absence of fulvic acid, and in greater amounts throughout the organic layer in the presence of sorbed fulvic acid.

of the muscovite's surface charge; the remaining amount was compensated presumably by H<sub>3</sub>O<sup>+</sup> at this low pH. In the presence of FA, Hg was incorporated with FA, resulting in enhanced Hg (by 240%) and FA (by 43%) uptake to muscovite. As pH increases, the sorption of Hg-FA

complexes decreased significantly as a result of the increasing negative charge on the FA in addition to the reduced complexation of  $\text{Hg}^{2+}$  with FA at higher pH. When Hg reacted with pre-FA-coated muscovite at pH 3, the organic coating provided sorption sites for Hg. However, this Hg apparently was weakly bound and easily desorbed in the presence of the incident X-rays.

The extent of cation uptake within sorbed fulvic acid films on muscovite depends on pH, binding strength to functional groups in the fulvic acid, and cation hydration enthalpy, size, and charge. Below are example results for  $\text{Pb}^{2+}$  at pH 3.7.  $\text{Pb}^{2+}$  at pH 3.7 behaves similarly to  $\text{Sr}^{2+}$  at pH 3.7 both with and without FA except that the presence of the  $\text{Pb}^{2+}$  enhances to an even greater extent the amount of FA that adsorbs to the surface (Figure 3).

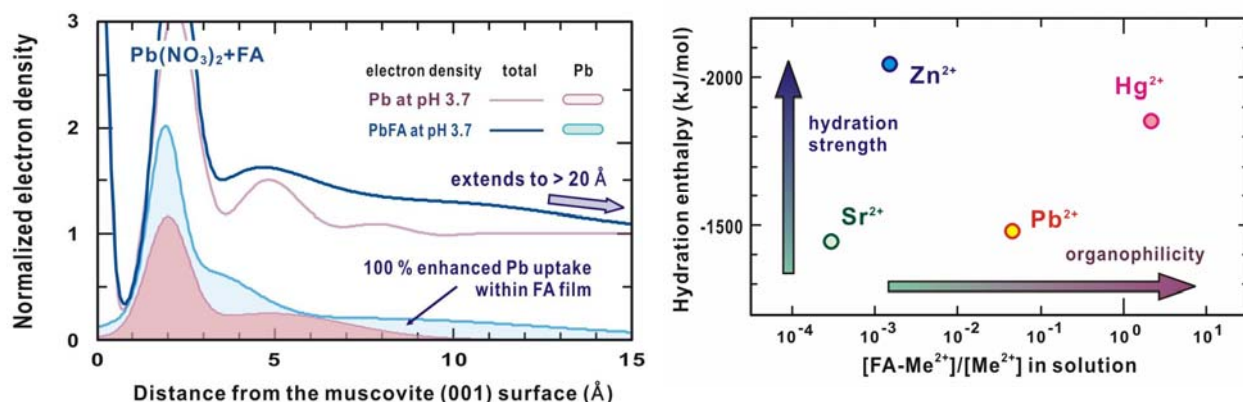


Figure 3. (left)  $\text{Pb}^{2+}$  uptake at the muscovite-solution interface from 0.01 m  $\text{Pb}(\text{NO}_3)_2$ . (right)  $\text{Pb}^{2+}$  has about the same hydration enthalpy as  $\text{Sr}^{2+}$ , but a higher binding strength to fulvic acid (higher organophilicity).

Similar data have been collected for  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . All data are in the process of being correlated to ion properties. For example, in FA-free systems, and for data measured using RAXR, the proportion of inner-sphere to total adsorbed cations at the muscovite-solution interface shows a linear relationship with cation hydration enthalpy (Figure 4).

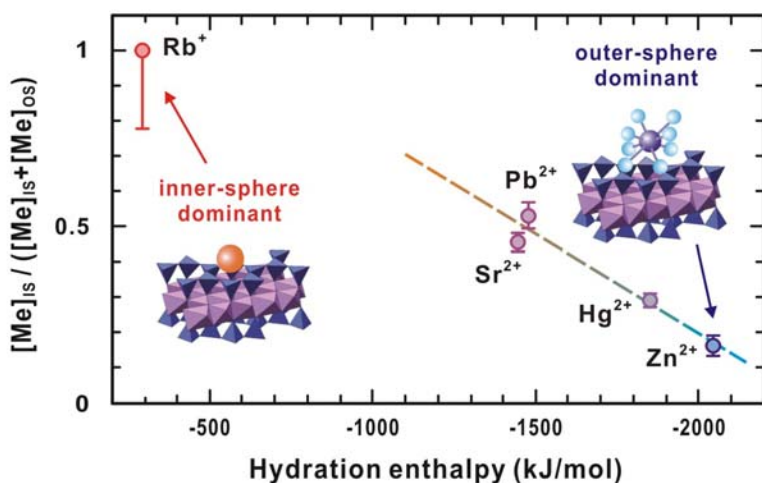


Figure 4. As ion hydration enthalpy increases the proportion of a cation that adsorbs as an inner-sphere complex decreases linearly. These kinds of data can be used to begin to extract more detailed information about the role of the muscovite surface in controlling the energetics of cation adsorption in the near-surface layer of solution.

In conclusion, the development of the RAXR technique by collaborators Park and Fenter has led rapidly to new insight with respect to the uptake of cations of the muscovite basal surface that are proving quite useful in obtaining information on the energetics of adsorption at the

molecular level. Also, we can now investigate natural organic matter films on this surface in terms of understanding how they affect the uptake of toxic metal cations.

## Results: Formation and Aging of Fe-Oxide and Clay Nanoparticles

This research was conducted by Master of Science student Rebekah Fitchett, undergraduate independent study student, Danka Andjelic, and post-doctoral researcher Ashaki Rouff, all at the University of Illinois at Chicago. The work has resulted in a thesis and two manuscripts in preparation which are listed below, followed by brief descriptions of the main results.

Rebekah Fitchett, 2006, Rhenium incorporation in aged iron-oxides as a function of pH and chromate concentration, Master of Science Thesis, University of Illinois at Chicago, 78 pp.

Rouff A. A., Cochiara S. G., Phillips B. L., and Nagy K. L., The influence of humic acid on the formation of amorphous aluminosilicates in pH 6 solutions at 25 °C, in preparation for submission to *Geochimica et Cosmochimica Acta*.

Nagy K. L., Fitchett R., and Andjelic D., The uptake of perrhenate in Fe-oxides as a function of pH, concentration, and the presence of other anions at 87 °C, in preparation.

### Formation and Aging of Fe-Oxide Nanoparticles

The effects of pH (3, 4, 5, 8, 9, 10), concentration ( $2.7 \times 10^{-4}$  to  $1 \times 10^{-2}$  mol Re/L at pH 3, 8, and 10), and other anions (nitrate at 1.5 mol/L, and chromate, bicarbonate, phosphate and sulfate each at  $2.7 \times 10^{-4}$  mol/L at pH 8) on the uptake of perrhenate, a chemical analogue for pertechnetate, in iron oxides were investigated experimentally. Solids were synthesized according to standard techniques at room temperature and immediately aged at 87 °C for approximately 70 hours. The majority of the solid phases under all conditions was hematite, but goethite was present in samples at pH values of 4, 5, and 10 in amounts of 2 to 28%, and at pH 8 with added nitrate and sulfate in amounts of 5 to 9 %.

The amount of Re incorporated in the solids decreased with increasing initial pH of the solutions, and was approximately 200 times higher in solids synthesized at pH 3 than at pH 10 at both 50 and 5000 ppm initial Re solution concentrations (Figure 5). The amount of Re in the

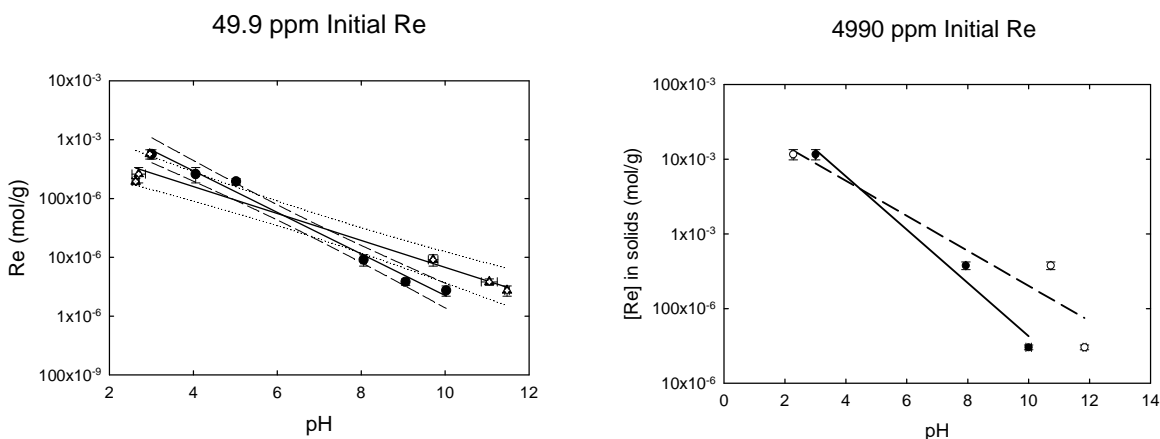


Figure 5. The amount of Re incorporated in Fe-oxides (dominated by hematite) formed from initial solutions containing 50 and 5000 ppm Re decreased by approximately a factor of 200 with increasing pH (solid symbols – initial pH; open symbols - final pH) reflecting in part a decrease in positive surface charge at higher pH and also an increase in the diffracting domain size using powder XRD.

solids as a function of concentration suggested that uptake was controlled by Langmuir adsorption isotherms (Figure 6). Within error, there was no effect of competing anions on the

### [Re] Uptake at pH 3

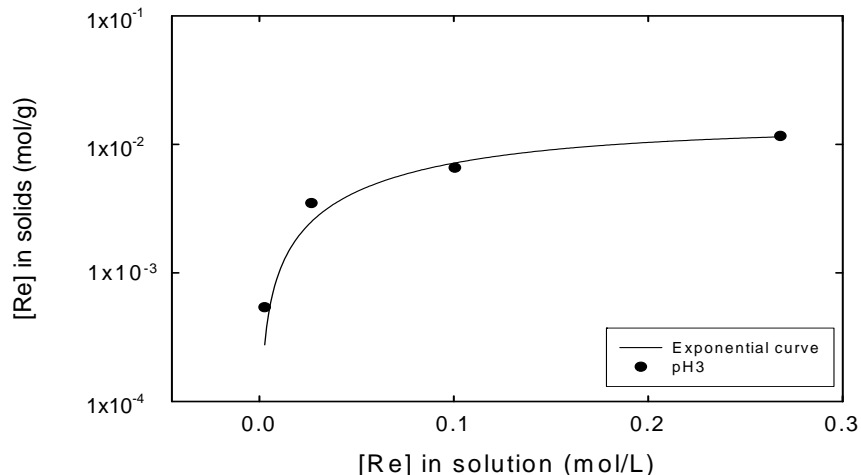


Figure 6. Re uptake in Fe-oxides as a function of initial Re concentration in solution at pH 3. The curve is an exponential fit to the data suggestive of a Langmuir isotherm.

uptake of Re at pH 8 with the exception that phosphate may have inhibited the uptake slightly (Figure 7) despite the fact that nitrate, chromate and phosphate were each taken up to a significant extent by the Fe-oxides. The amount of Re uptake at constant initial Re concentration in solution was inversely correlated to the amount of Cr uptake from variable concentration chromate solutions indicating that chromate successfully competes for surface adsorption sites with Re during the initial synthesis stage (Figure 7).

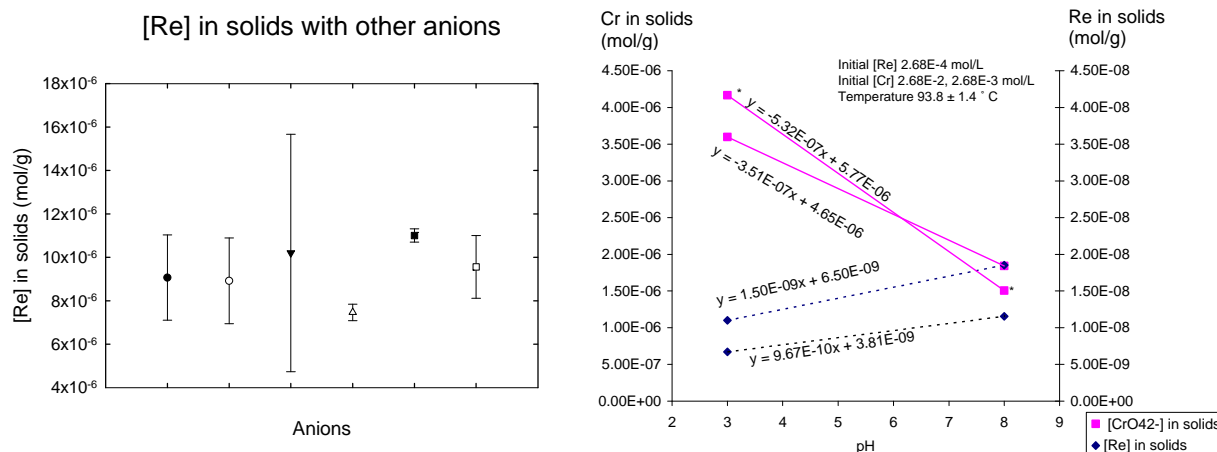


Figure 7. (Left) The amount of Re incorporated in precipitated Fe-oxides from initial pH 8 solutions containing 50 ppm Re (solid diamond) is not changed within error by the addition of 2 m nitrate (square with cross) or 2.1 x 10<sup>-4</sup> m sulfate (solid upside-down triangle), phosphate (open triangle), bicarbonate (solid square), or chromate (open square). (Right) At higher concentrations of initial chromate, and at slightly higher aging temperature (93 °C) the amount of Re incorporated in the solids is slightly lower and decreases with decreasing pH in contrast to the pattern of Cr incorporation into the solids.

EXAFS and XANES analysis was performed at PNC-CAT at the Advanced Photon Source on the solids with the highest amount of Re. The results indicate that the uptake was in

the form of perrhenate bound to surface oxygens of the initially synthesized ferrihydrite grains. Estimates of average grain size using the maximum coverage from the interpreted adsorption isotherms and assuming that adsorption of perrhenate occurs at all the available sites on the Fe-oxide surface showed an increase from low to high pH, consistent with the observed narrowing and sharpening of peaks in powder X-ray diffraction patterns of the solids with increasing pH. However, the estimates suggest grain sizes that are too large when compared with literature data indicating that either adsorption occurs only at selected sites, and/or changes the coarsening behavior of the ferrihydrite particles that are initially precipitated during the synthesis. Additional high resolution transmission electron microscopy results with EELS analysis will be conducted at UIC to attempt to answer this question prior to submission for publication.

### Formation of Clay Nanoparticles

The influence of humic acid on precipitation of aluminosilicate phases was studied in pH 6 solutions at 25 °C. Solutions were prepared with inorganic Al and Si reagents at concentrations ranging from 0.3-1.5 mM both with and without 6 ppm dissolved organic carbon (DOC) as Suwanee River Humic Acid (SRHA). For solutions with 0.5-1.0 mM Al and 0.5 mM Si, an increase in the Al/Si ratios of precipitated solids occurred at higher initial Al concentration in the presence of HA, indicative of a delayed phase transition in HA-bearing systems. Characterization of precipitates by X-ray diffraction (XRD) and Nuclear Magnetic Resonance Spectroscopy (NMR) revealed the formation of allophane and/or imogolite-like allophane (Al/Si = 2) in all samples. In both inorganic and HA-bearing samples the fraction of gel-like aluminosilicates and Al oxyhydroxide polymers increased with increasing initial Al concentration. At constant Al concentration, addition of HA resulted in an increase in the formation of allophanic material relative to rapidly polymerizing gel and oxyhydroxides. Carbon content of the solids ranged from 4 to 12 wt. % with the higher amounts corresponding to lower initial Al concentration and indicate organic material in excess of available Al binding sites suggesting precipitation of uncomplexed HA in addition to Al-HA complexes. The sorption and/or coprecipitation of organic material with precipitating Al and Si slows otherwise rapid and dominantly amorphous material polymerization and promotes the formation and stabilization of allophanic phases. These results are applicable to allophanic horizons in soils, where organics may positively influence the neogenesis of hydroxyaluminosilicates. Interaction of organics with allophane and imogolite may in turn stabilize organic material, thus sequestering what may be normally somewhat labile C in soils.

### **Summary**

With respect to the initial project goals, significant advances beyond original expectation were made in investigating the molecular-scale structure of the muscovite-solution interface, as a result of the development of the RAXR technique and a robust fitting method for modeling fulvic acid uptake. These measurements have not yet been possible on true clays, but initial attempts are underway. New data were obtained on the uptake of anions (specifically Re as a possible analogue of Tc) in precipitated Fe-oxides and dissolved natural organic matter (organic C) in precipitated clay minerals. The data provide a basis for future work to characterize precipitation and aging behavior of the solids in both systems which have relevance both to DOE environmental concerns (Tc contamination of soil and ground water) and carbon sequestration.