

Mechanisms of Electron Transfer to and Fe(II) Dissolution From Montmorillonite Clay Minerals

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Clay minerals are an environmentally important class of minerals known to play a central role in a variety of geochemical reactions. The most important particles from the standpoint of soil chemistry are approximately 1 μm in size. Substitutional iron atoms can alter the activity of these small clay particles. Although clays contain substitutional iron in the interior octahedral layers of the particle, they are known to be redox labile and can be readily and reversibly converted from Fe(III) to Fe(II) (eg. Stucki, et al., 1995). Once it has been reduced to Fe(II), structural iron in the octahedral layer of montmorillonite is easily removed from the mineral. Fe(II) is preferentially removed with respect to Fe(III) from montmorillonite under mildly acidic conditions (Grundl and Reese, 1997) or in the presence of organic ligands (Kostka, et al., submitted). A rise in pH causes a “green rust” like coating to precipitate. Green rust is another highly active compound that is known to play a role in the reduction of certain organic pollutants (Erbs et al., 1999, Haderlein and Pecher, 1998).

Our research conducted to date has concentrated on demonstrating the usefulness of Scanning Transmission X-Ray Microscopy (STXM) and X-ray Absorption Near Edge Spectroscopy (XANES) to better understand the process of Fe(II) dissolution out of montmorillonite and the subsequent precipitation as a mixed valent green-rust like coating. Soft x-ray absorption spectroscopy has been chosen because the rich L-edge fine structure of 3d transition metals provides information about the oxidation state, site symmetry, spin state, and crystal field splitting of the metal ions (Cressey et al., 1993). In addition, STXM opens up the possibility to study small particles in their wet fully hydrated states, which becomes especially important for layered compounds like clays or green rusts.

The samples investigated originated from a series of electro-osmotic experiments in which a low voltage electric field was applied to a montmorillonite sample. The resulting direct current flow of electricity is carried by cations in the interstitial water of the clay that, in turn, forces water to flow from anode to cathode. The voltages used are sufficient to electrolyze water, generating H^+ at the anode (the upstream electrode) and OH^- at the cathode (the downstream electrode). A low pH front caused by anodically generated H^+ ions migrates through the clay. Bulk chemical analyses indicate that Fe(II) originally in the clay is selectively leached by the low pH front, travels downstream and is precipitated near the cathode where the pH abruptly rises. In the precipitation zone, the clay turns a deep green color, suggestive of mixed valent iron precipitate. All samples were prepared and kept under strict anoxic conditions in a glovebox and transferred to the beamline without any contact to air oxygen.

Chemical analyses indicate that the original clay (41-B) contains approximately 32,000 ppm Fe (tot), of which 3900 ppm is Fe(II). The clay in the anodic zone (41-A) is slightly depleted in both Fe(tot) (approximately 26,000 ppm) and Fe(II) (1000 to 3100 ppm). The green precipitation zone (41-G), which is quite small with respect to the anodic zone, is enriched in Fe(tot) (40,500 ppm) and highly enriched in Fe(II) (14,200 ppm). This thin green, Fe(II)-rich zone that occurs exactly at an abrupt rise in the pH is presumed to be a zone where chemical conditions would strongly favor the formation of green rust-like coatings around clay particles. XANES, STXM

and X-ray Photoelectron Spectroscopy (XPS) experiments were performed on all three of these samples in order to corroborate the presence of a mixed valence iron coating and to study the distribution of oxidation states of iron within the precipitates and the clays. XANES spectra were obtained using total electron yield sample to ground measurements (TEY-XANES).

TEY-XANES of the original clay (41-B) and clay from the anodic zone (41-A) are essentially the same (Fig. 1) except 41-B shows a much higher signal to noise ratio compared to 41-A, probably because of less charging. The slight depletion in Fe(tot) of 41-A relative to 41-B may account for that. The equivalence of spectral features of both samples gives preliminary evidence that there is no pronounced preferential mobilization of a single charge state of iron from the probed overall sample depth of approximately 100 Å of the clay surrounding the anode. Thus, the mobilized Fe(II) which accumulates on 41-G may originate either from a very thin surface layer (<10 Å) or inner bulk structures of the clay particles, the latter of which would not have been probed by TEY-XANES and the former might have been diluted by the overall probing depth (~100 Å). Because of the poor signal to noise ratio we also cannot rule out that some of the mobilized iron(II) may come from the top 100 Å layer involving a bigger mobilization area within the electro-osmotic cell than was sampled. Figure 2 shows a second set of TEY-XANES spectra and the associated difference spectra of 41-B and clay from the precipitation zone (41-G). It is clear that 41-G has a stronger iron signal (white line intensity) and a strong contribution from a Fe(II)/Fe(III) component. The signal is indicative of surface accumulation of a mixed valent iron species, the signature of which could not unequivocally be assigned to a green rust compound. Both of these results are in agreement with the chemical data and could be reproduced by independent measurements on different days.

STXM differs from XANES in that it is a transmission technique and bulk composition of single grains or even profiles across single grains can be investigated within the spatial resolution limit of the instrument (~100 nm). Sample preparation follows the description given in Rothe et al. (1999). The reference clay sample obviously contains particles which almost exclusively contain iron in the 2+ charge

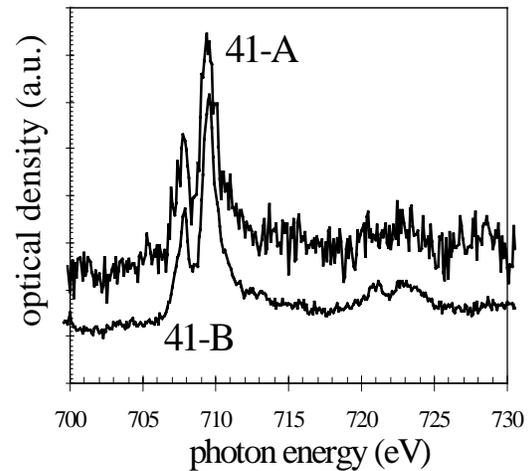


Figure 1. TEY-XANES of the original clay 41-B (reference sample) and clay 41-A (anodic zone).

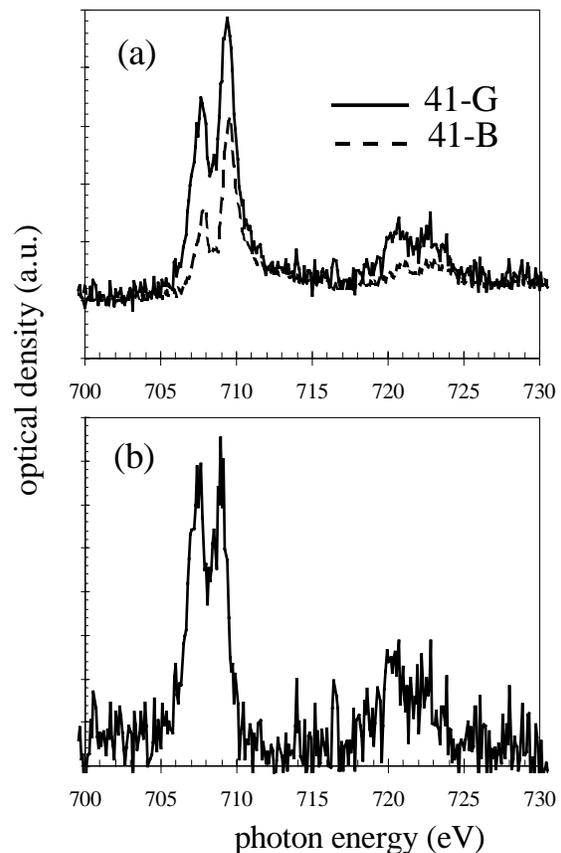


Figure 2. TEY-XANES of the original clay 41-B (reference sample) and clay 41-G (cathodic zone) (a) and difference spectrum of both samples (b).

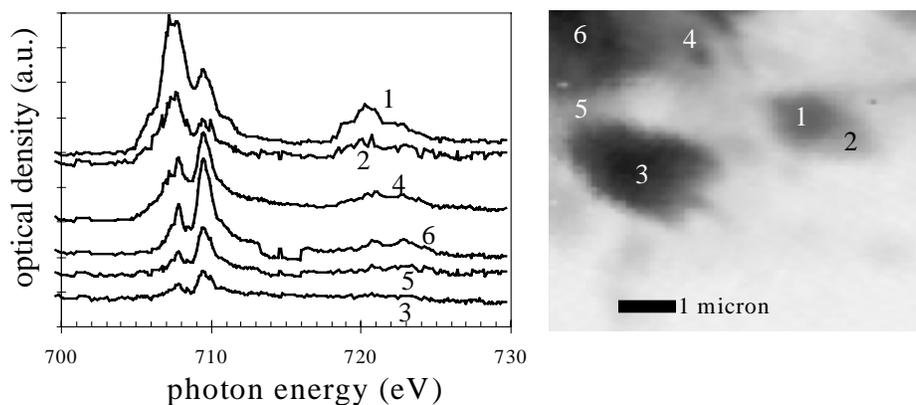


Figure 3. STXM image at the Fe L_{III} -edge of sample 41-B and XANES taken at different positions (1-6)

state (labeled 1 and 2 in Fig. 3) and others that are completely oxidized (labeled 3, 5, and 6 in Fig. 3). Both charge states of iron seem to be inhomogeneously distributed among all clay particles. The capability of detecting grain-to-grain variability is not possible using more standard techniques such as X-ray diffraction or bulk chemical testing and also gives complementary information to spatially averaged TEY-XANES. In general, 41-G (Fig. 5) shows more Fe(II) character than 41-A (Fig. 4), as expected from bulk chemical results. The bulk structure of 41-A seems to be depleted of Fe(II) which gives strong evidence that some of the iron accumulating on

41-G is from the bulk structure ($> 100 \text{ \AA}$ depth) of the original clay surrounding the anode. The spectral signature of Fe(II) containing grains of 41-G is completely different than the spectral features of Fe(II) containing particles of sample 41-B and is pointing more to a superposition of both valence states of iron. Again, STXM does show a certain amount of grain-to-grain variability in these samples. We also found clay particles in 41-G with Fe(III) as the dominant iron species (labeled 15, 16 in Fig. 5). In order to verify homogeneity of single particles with respect to iron charge state distribution, spectra were taken at the resolution limit along transects across single clay particles (indicated with a white line in Fig. 5). This technique did not work in these samples because the iron content within a given area at the resolution limit is too low and the spectra became noise limited. Future STXM experiments are planned on bacterially reduced clays that contain approximately 17% (170,000 ppm) iron and we hope to overcome this problem.

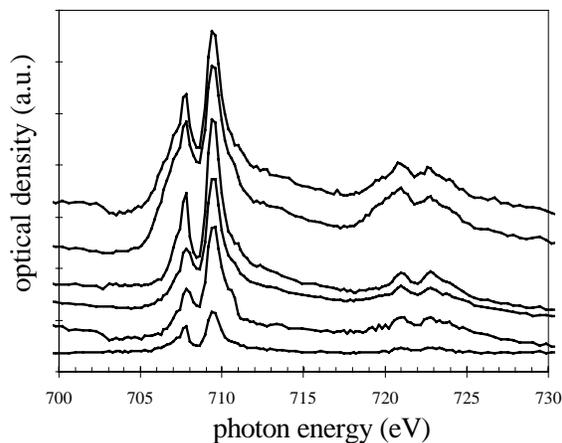


Figure 4. XANES taken from different clay particles of a STXM stack of sample 41-A.

The most surface sensitive technique, XPS, has been applied as well. Experimental problems having to do with particle charging effects have been solved by changing sample preparation techniques. We are expecting useful information about surface iron composition soon.

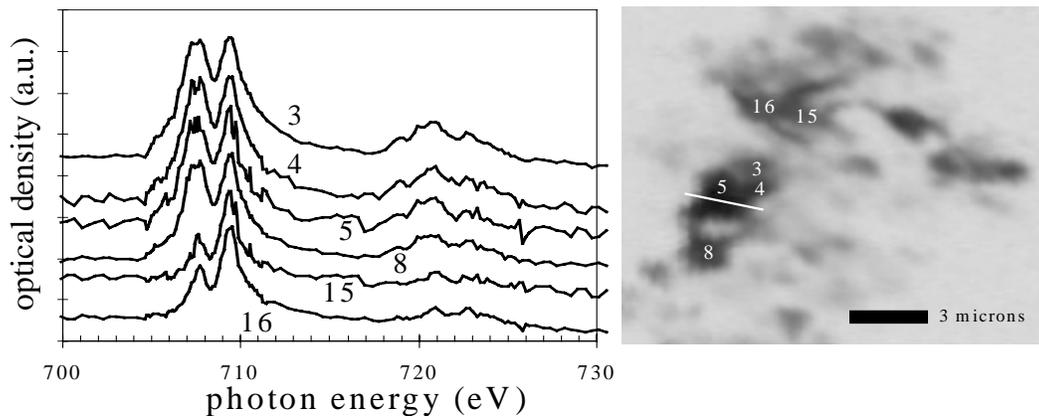


Figure 5. STXM image of sample 41-G and XANES taken at different positions (labeled with numbers)

From the research outlined above, we can draw the following conclusions and define directions for further research.

- Grain to grain differences are something that can be uniquely detected by this method. Grain to grain differences have also been found for Mn-nodules, green rusts, and magnetite.
- TEY-XANES spectra agree with chemistry and support the hypothesis that a green rust precipitate is coating the clay. An unequivocal identification of this coating using XANES is unlikely. Most Fe-oxide minerals (eg. goethite, hematite, lepidocrocite) yield largely the same spectra. If new XPS experimental techniques are successful, further information may be obtained about the surface coating.
- Upcoming work with reduced clays will allow the comparison of surface iron vs structural iron in these clays. These reduced clays contain much more Fe(II) than the current samples and will not be a subject to noise limitations. In addition, the Fe(II) is contained within the structural lattice of the clay and as such should yield distinctly different information from the current samples with surface iron.
- Comparison of these results to earlier test runs of the same samples has proven that our protocols for the strict anaerobic handling of these samples is essential to the study of iron valence states in clays.

REFERENCES

- (1) Cressey, G.; Henderson, C.M.B.; van der Laan, G. *Phys. Chem. Minerals* 1993, 20,111-119.
- (2) Erbs, M.; Hansen, H.C.B.; Olsen, C.E. *Environ. Sci. Technol.* 1999, 33,307-311.
- (3) Grundl, T.; Reese, C. *J. Hazardous Materials* 1997, 551,187-201.
- (4) Haderlein, S.B.; Pecher, K. Pollutant reduction in heterogenous Fe(II)/Fe(III) systems. In: D.L. Sparks, T. Grundl, Eds.; American Chemical Society: Washington, 1997; in press.
- (5) Kostka, J.E., Wu, J., Nealson, K.H., and Stucki, J.W. 1999. sub. to *Geoch. et Cosmochim. Acta*.
- (6) Rothe, J.; Kneeder, E.M.; Pecher, K.; Tonner, BP.; Nealson, K.H.; Grundl, T.; Meyer-Ilse, W.; Warwick, T. J. *Synchrotron Rad.* 1999, in press.
- (7) Stucki, J.; Bailey, G.; Gan, H. Redox reactions in phyllosilicates and their effects on metal transport. In: H. Allen, Ed.; Lewis Publishers, 1995.

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