ROBL-CRG	**Experiment title:** **Characterization of Mn Speciation on Clay Minerals**	**Experiment number**: Run-Nr. 670
Beamline: BM 20	**Date of experiment**: from: Nov. 3 2007 to: Nov. 5 2007	**Date of report**: Nov. 6, 2008
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Report:

In these experiments we adsorbed Mn(II) to montmorillonite under different ionic strength and pH conditions (Figure 1). Results from these experiments suggest that Mn(II) adsorbed in the interlayer, presumably as a fully hydrated hexaqua complex, has much slower oxidation rates than Mn(II) adsorbed on the edge sites via surface complexation.

This experiment was a first attempt at collecting XAFS data on a new expeirmental system. Results from the experiment were used to prepare a proposal to submit to a joint USA-NSF and Germany-DFG International Collaboration funding program.

XAFS data were collected on six samples and two standards. The XAFS for the low Mn concetrated samples had a significant amount of noise and showed evidence of a multi-electron excitation, there-by making advanced data analysis challenging. One sample was air dried, which allowed for denser packing of the clay, and subsequently better S/N. Preliminary evalaution suggest that air drying did not have any affect on the Mn oxidation state, thus this may be a suitable method for preparing low loading samples for XAFS analysis. We are seeking funding to continue these expeiments, and the data collected in this run was critical to providing initial data to support our hypothesis: Oxidation kinetics, speciation, and reactivity of Mn on mineral surfaces are a function of the type of interaction between the Mn cation and the surface (i.e., electrostatic or covalent bonds). XAFS is the ideal tool to investigate the chemistry occurring in these systems.

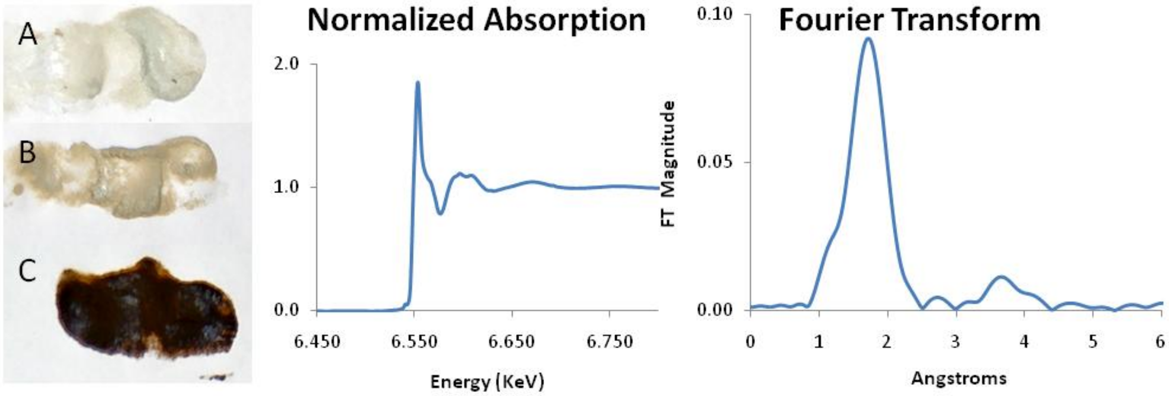

Figure 1. Mn-clay mineral equilibration experiments. Photographs A, B, C show color differences in montmorillonite-Mn pastes smeared on paper. Photo A is a paste of clay incubated with Mn(II) for 15 days, ionic strength 0.0005 pH=4.1, and adsorbed Mn=329 mmol kg^{-1}. Photo B is a paste of clay incubated with Mn(II) for 1 day, ionic strength 0.1 pH=6.0, and adsorbed Mn=42.6 mmol kg^{-1}. Photo C is a paste of clay incubated with Mn(II) for 15 days, ionic strength 0.1 pH=6.4, and adsorbed Mn=52.2 mmol kg^{-1}. The photos show that the color of the clay mineral is a function of the loading levels, equilibration conditions, and time. The color is visual evidence of speciation differences. Spectra show Mn K-edge normalized XANES and Fourier transform of EXAFS for clay mineral in sample A equilibrated for 6 days. From the normalized absorption spectrum (i.e., XANES) the oxidation state can be determined. The Fourier transform of the EXAFS spectrum shows relative positions of the backscattering peaks in the molecular environment of the adsorbed Mn. These preliminary experiments suggest that there are unique molecular speciation and oxidation states of Mn on clay minerals, and XAFS spectroscopy data can be collected to allow for discovery of these species.