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**Planar Oxides as a Novel Approach to Understanding Metal Ion Sorption to Natural Oxide Surfaces: An EXAFS Investigation of Pb(II) Sorption to Gamma Alumina Surfaces**

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Beamline(s): X11A

**Introduction**: This work introduces planar oxides as a novel approach to understanding metal-ion interactions with clay mineral and oxide surfaces in the natural aquatic environment. Planar oxides are thin, flat coatings of uniform thickness prepared on a metal substrate. As such, they offer unique advantages over the previously used pure phase oxides in investigating metal-ion sorption behavior both in the laboratory and in the field. Also, because of their surface morphology, planar oxides lend themselves to a variety of spectroscopic techniques, including EXAFS. The purpose of our study is two-fold. First, it is necessary to show that usable EXAFS data can be collected from metal-ions sorbed on these planar materials. Second, EXAFS analysis is needed to compliment results from previous work comparing the sorption behavior of Pb(II) on pure phase and planar $\gamma$-$Al_2O_3$ [1].

**Methods and Materials**: Pb(II) sorption complexes formed on pure phase and planar $\gamma$-$Al_2O_3$ oxides were investigated using EXAFS analysis. Pb(II) coverages ranged from 0.1 $\mu$mol/m$^2$ to 10.0 $\mu$mol/m$^2$. Measurements were made in fluorescence mode using a Lytle detector. EXAFS data for select solid and aqueous Pb model compounds were also collected.

**Results**: Data analysis is currently underway, and preliminary workup of the data allow for an assessment of our accomplishments relative to our two objectives. Our first goal was to obtain data from the pure phase materials over our range of coverages to connect our present work to previous studies [2,3]. Good data were collected on these materials (figs. 1, 2). These data are currently being processed to obtain structural parameters (distance, number, and identities of nearest neighbors). Fig. 1 shows comparisons of the EXAFS data for Pb sorbed to planar and powder alumina. The data for the planar oxides are considerably noisier than that of the bulk oxides. Nonetheless, it is clear that we can obtain usable EXAFS data for Pb sorbed to planar oxides under varying conditions, with a detection limit under the given conditions being between $\Gamma_{TOT}$ = 1 to 4 $\mu$mol/m$^2$ Pb. Our second objective was to use the EXAFS results to assist in interpreting results from previous work [1]. Further analysis of the data is necessary to make any conclusions about Pb(II) sorption behavior on the planar $\gamma$-$Al_2O_3$ compared to the known behavior on the bulk oxide materials.

**Conclusions**: EXAFS data were successfully collected on novel materials to be used in metal-ion sorption studies. It was shown that Pb(II) sorption complexes formed on planar $\gamma$-$Al_2O_3$ could be characterized using EXAFS analysis. Factors to be improved upon to increase the signal to noise ratio and decrease the detection limit include collecting data at cryogenic temperatures and the use of a solid state detector instead of the Lytle detector used in this experiment. Future goals of this work include more specifically defining the behavior of Pb sorbed to the planar oxides relative to the bulk oxides and probing the transition from monomeric to multimeric surface Pb species.

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**References**:

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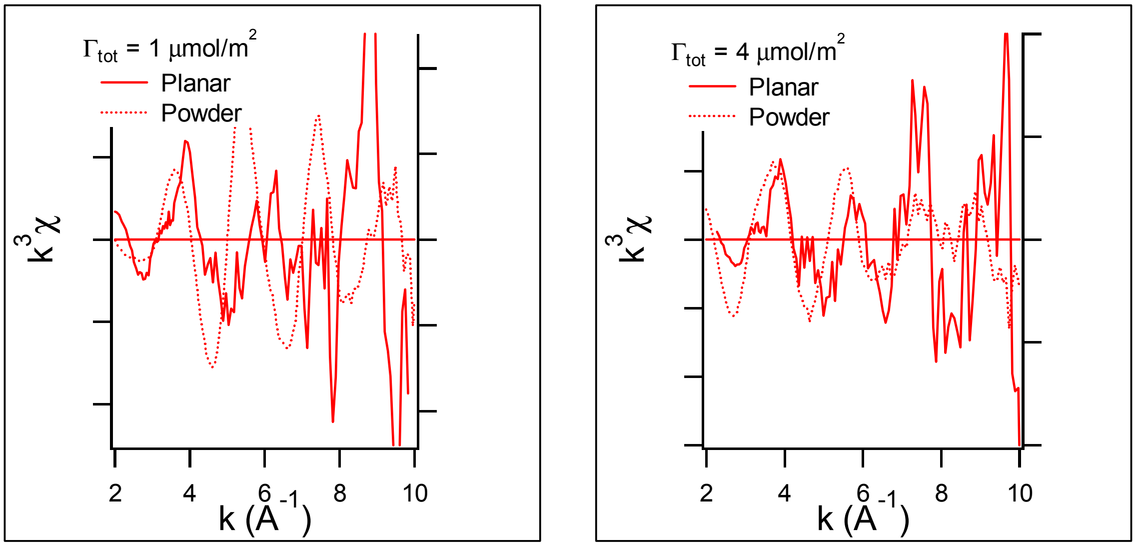


Figure 1: Comparison of EXAFS spectra for Pb sorbed to planar and powder $\gamma$-$Al_2O_3$ for $\Gamma_{tot}$ = 1 µmol/m$^2$ (left) and 4 µmol/m$^2$ (right).

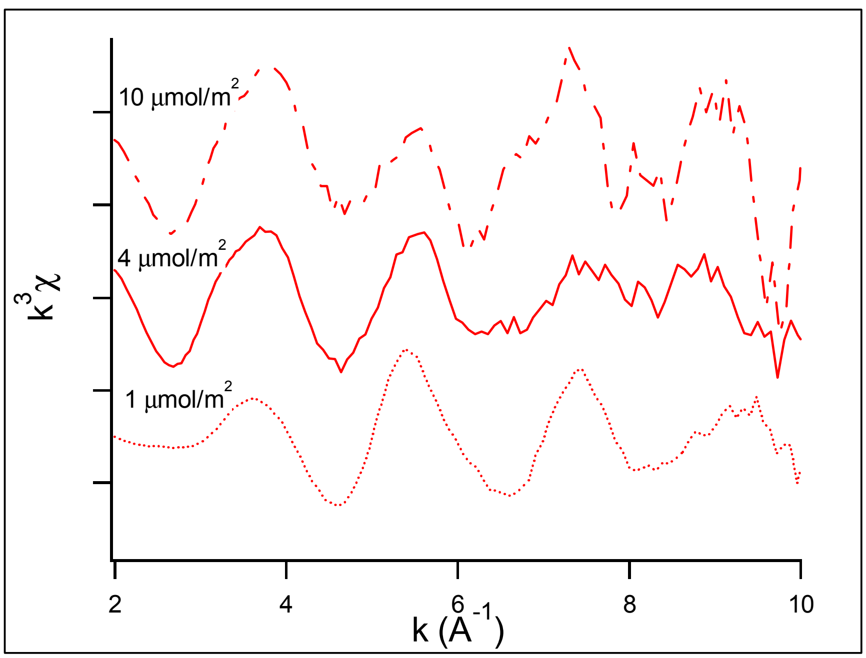


Figure 2: Comparison of EXAFS spectra for Pb sorbed to powder $\gamma$-$Al_2O_3$ at different $\Gamma_{tot}$