



Planar oxides as a novel approach to metal ion sorption studies: From the lab to the field

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While much research has been conducted to understand how the mineralogy, chemical composition and surface properties of the solid phase affect metal sorption under controlled laboratory conditions, there has been limited success in translating these results to large, field scale processes. The purpose of this work is to investigate the use of planar oxides as tools for metal ion sorption studies that can be used in both laboratory and field settings. To do this, a three-step approach was used.

In the first step, Pb(II) sorption to planar γ -Al₂O₃ surfaces relative to pure phase γ -Al₂O₃ was investigated using a suite of spectroscopic techniques (ToF-SIMS, XAS and XPS). The relative quantitative sorption of Pb(II) to the planar γ -Al₂O₃ was found to be comparable to that on the bulk. XAS analysis showed that the coordination geometry and local binding environment of the Pb(II) complexes were similar on the two surfaces over a range of Pb(II) loadings, a mixture of corner-sharing monodentate and edge-sharing bidentate complexes with Pb(II) coordination geometries ranging from distorted trigonal pyramidal to distorted pentagonal.

Second, the complexity of the planar surface was increased by creating mixed Fe-Al oxides of varying elemental composition, morphology and crystallinity. This was accomplished by coating the planar γ -Al₂O₃ using different initial Fe(III) concentration, reaction times and number of coating sequences. The chemical and physical forms of the resultant coatings were characterized using ToF-SIMS, SPX, SRD, SEM and N₂ BET surface area measurements. Significant changes in the elemental composition and distribution of Fe(III) were seen with changes in the reaction parameters. The crystalline form of the Fe phase present in the coating could not be identified. This, coupled with unexpectedly low SSAs suggests the presence of a mixed Fe-Al oxide rather than a layer of Fe(III) on top of the planar surface. The relative differences in composition and form of these coatings should lead to variations in both the chemical and biological reactivities of these surfaces.

The third step involved placing the planar γ -Al₂O₃ with varying Pb(II) loadings directly into natural sediments. Changes in Pb(II) concentrations as a result of initial Pb(II) loading, emplacement time and redox conditions were examined using ToF-SIMS, and changes in the surface morphology were examined by SEM. Pb/Al ratios, as well as interaction between the planar oxides and the surrounding sediments, varied as a function of time and initial Pb(II) loading as evidenced by the changes in the surface morphologies, Pb(II) surface concentrations and changes in correlations with Fe and S present in the surrounding sediments. Results from these experiments provide new information about the sorption behavior of Pb(II) under various experimental conditions and indicate that planar oxides can be used in a variety of ways to better understand factors controlling metal sorption processes in natural environments.