

The Effect of Calcium Carbonate Coatings on Cr(VI) Reduction at the (111) Surface of Magnetite

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Calcium carbonate grain coatings are found in many soil environments and are thought to play an important role in modification of the chemical reactivity of mineral grains in soils and sediments with respect to contaminant species. The importance of iron, aluminium, and manganese oxyhydroxide grain coatings in the sorption and sequestration of inorganic ions from solution is well understood (Sposito 1989; McBride 1994), however an equal understanding of the role played by calcium carbonate in environments dominated by calcareous sediments has not been achieved.

This work investigates the effect of calcium carbonate coatings on the reductive sorption and immobilization of hexavalent chromium [Cr(VI)O₄²⁻] at the magnetite-aqueous solution interface. Hexavalent chromium is a highly available aqueous species which is of potential hazard to plants and animals due to its high toxicity and poor sorption characteristics at near neutral pH. The risk posed by chromium in the environment can be greatly decreased by reduction to its trivalent oxidation state, which is less toxic and forms stable sorption products. Reduction of Cr(VI) to Cr(III) can occur on mineral surfaces which contain zero- or divalent iron, such as magnetite, Fe(II)Fe(III)₂O₄ (Peterson et al. 1996). We have used synchrotron photoemission and X-ray absorption spectroscopies to study the reduction of hexavalent chromium at the magnetite (111) surface (Kendelewicz et al. 1999) and observed that the magnetite surface becomes passivated towards chromium(VI) sorption following the build-up of an ~15Å thick layer of a CrOOH-like phase.

In this study, calcium carbonate films of varying thickness have been grown from solution on atomically clean single crystal magnetite (111) surfaces in a nitrogen-filled glove bag attached to our UHV system. We have used a combination of

UHV synchrotron photoemission (Fe 2p, Cr 2p, Ca 2p, O 1s, C 1s) spectroscopy, X-ray absorption near-edge spectroscopy (O K-edge, C K-edge, Cr L-edges, Fe L-edges, and Ca L-edges) and electron- and force- microscopies in order to monitor the formation of carbonate coatings on the magnetite (111) surface and the subsequent reaction of CrO₄²⁻ with the surface.

Comparison of calcium L-edge and oxygen K-edge NEXAFS spectra for the coatings with spectra from model carbonates show strongest agreement with those collected from aragonite. The Ca L-edge NEXAFS spectra become more calcite-like following dosing with Cr(VI) containing solution, which provides evidence for dissolution/reprecipitation of the calcium carbonate layer. For thin coatings, Cr L-edge NEXAFS confirms that all chromium on the surface is Cr(III), indicating that the carbonate layer is not thick enough to retard the electron transfer from Fe(II) to Cr(VI). Our oxygen K-edge data are less conclusive, with contributions from the bulk iron oxide, the surface carbonate layer, and any chromium (oxy)hydroxide phase formed. However, O K-edge spectra taken using surface-sensitive Auger electron detection following chromium dosing show good agreement with data for chromium dosing on clean magnetite surfaces, where Cr-oxyhydroxide layers were observed.

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