

## Cd Partitioning in Metal-Mineral-Bacteria Systems: Testing the Surface Complexation Approach

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Minerals and bacteria represent some of the most reactive surfaces in geologic systems and adsorption onto mineral surfaces and bacterial cell walls can determine the fate, transport and bioavailability of aqueous heavy metal cations. Therefore, it is crucial to develop geochemical models that accurately account for the partitioning of metals between these surfaces and aqueous solutions. Surface complexation models are successful in two-component systems (metal-mineral or metal-bacteria); however, their ability to account for metal distribution in mixed metal-mineral-bacteria systems has not been tested. In this study, we measure partitioning of cadmium between three interacting reservoirs: an aqueous phase, and bacterial and mineral surfaces. We compare partitioning estimates from surface complexation modeling to the observed partitioning, thereby conducting a rigorous test of the applicability of the surface complexation approach to mixed metal-mineral-bacteria systems.

Two types of two-component batch adsorption experiments were performed: 1) metal-bacteria experiments in which a 10 ppm Cd solution was placed in contact with 1 g/L (wet wt.) of the gram-positive bacteria, *Bacillus subtilis*, and 2) a 10 ppm Cd solution was placed in contact with 5 g/L hydrous ferric oxide (HFO). Two types of three-component batch adsorption experiments were also conducted: 1) ones in which *B. subtilis*, HFO, and 10 ppm Cd solution were allowed to equilibrate in contact with each other, and 2) ones in which the HFO was physically, but not chemically, isolated by placing it in a sealed dialysis tube. This set-up enabled determination of the extent of Cd partitioning between the bacteria and the iron oxide surfaces.

The experiments indicate that adsorption in systems containing both bacteria and minerals can be dominated either by bacterial surfaces, by mineral surfaces, or by both types of surfaces, depending on the pH and on the bacteria:mineral ratio. The data from the two-component system adsorption experiments were used to determine stability constants for each of the important surface complexes. Using FITEQL, we use these stability constants, along with stability constants for the other surface and aqueous species in the experimental systems, to independently predict the extent of adsorption and the partitioning of Cd in the bacteria-mineral-metal systems. Results from these comparisons suggest surface complexation modeling can be used successfully to account for metal partitioning in multi-sorbent geologic systems.

## Cr Stable Isotopes: Measurement, Systematics and Applications

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We have developed a method to measure mass-dependent fractionation of Cr isotopes, determined the amount of fractionation during Cr(VI) reduction, and observed Cr isotope ratio shifts in reducing groundwaters. Toxic Cr(VI) can be highly mobile and is a common contaminant in most major industrial areas.

We use double-spiked TIMS measurements to obtain a precision of  $\pm 0.2\%$  or better on  $^{53}\text{Cr}/^{52}\text{Cr}$ , using 200ng Cr. We purify Cr for analysis via a two-step Cr(VI)/Cr(III) ion exchange method.

In anaerobic experiments with a magnetite suspension and two sediment slurries, abiotic Cr(VI) reduction to Cr(III) occurred over a period of several days and induced an instantaneous  $^{53}\text{Cr}/^{52}\text{Cr}$  shift of  $3.4 \pm 0.1\%$ . Experiments now in progress will measure microbial Cr isotope fractionation.

Samples of three basalt standards, a commercial CrO<sub>3</sub> supply, two reagent Cr compounds, and three Cr plating baths yielded  $\delta^{53}\text{Cr}$  values between  $-0.07\%$  and  $+0.37\%$  relative to NIST SRM-979. These data suggest that igneous rocks, Cr ores, commercial Cr supplies, and contaminants originating from plating baths are all isotopically close to the bulk earth. The plating bath result is intriguing. Cr(VI) reduction occurs in the electroplating process but apparently does not fractionate the isotopes greatly in this case.

We analysed eight groundwater samples from two sites where Cr(VI) contamination was likely attenuated by reduction, which produces insoluble, less toxic Cr(III).  $\delta^{53}\text{Cr}$  values ranged from  $+1.08\%$  to  $+5.79\%$ . This enrichment in the heavier isotope strongly suggests that Cr(VI) was removed from the water by reduction. We estimate 30% to 80% removal had occurred prior to sampling. Provided variability in the instantaneous isotope fractionation is not too great, and sorption does not greatly fractionate the isotopes, Cr isotopes will provide a great improvement over current methods for assessing natural attenuation of Cr(VI) in contaminated groundwater.

Cr isotopes may be useful in other geoscience studies. For example, Cr(VI) is the dominant inorganic species in the modern oceans, but Cr(III) is present and reduction may be important in the global Cr cycle. Under mildly reducing conditions, Cr speciation and cycling could change greatly.