Surface Complexation Modeling of Cd Adsorption onto High-Affinity Binding Sites on *Shewanella oneidensis* Bacterial Cells

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Previous studies of metal adsorption onto bacteria have used a surface complexation modeling approach to account for the pH dependence of the adsorption behavior, but many of these studies were conducted only under relatively high metal-loading conditions. Recently, low, but significant, concentrations of high-affinity sulfhydryl binding sites have been discovered on bacterial cell envelopes (1, 2). Here, we test whether Cd binding occurs onto these high-affinity binding sites by conducting Cd binding experiments at a range of metal loading conditions, and we use a surface complexation modeling approach to calculate the stability constant for the important Cd bacterial surface complex involving the high affinity site.

We measured Cd adsorption onto *Shewallana oneidensis* as a function of pH under metal loadings of 2.5 – 25.0 μmol/$g_{wet\ biomass}$. Under all metal loading conditions, a 2-site model involving Cd adsorption onto Site 1 (pK_a=3.9) and Site 3 (pK_a=7.0) provides the best fit to the data. The calculated stability constants for the Cd-Site 1 complex are similar under the different metal loadings. However, the calculated value of the stability constant for the Cd-Site 3 complex increases significantly as metal loading decreases from 25 to 2.5 μmol/$g_{wet\ biomass}$, indicating that the adsorption mechanism for Site 3 changes as metal loading changes and that a single adsorption reaction can not account for the data as a function of metal loading. We use the data, in conjunction with EXAFS constraints on the binding mechanisms (1), to constrain stability constants for Cd surface complexes involving both the high- and low-affinity sites on the bacteria. The resulting set of stability constants can account for the Cd adsorption behavior as a function of both pH and metal loading. This approach is crucial in order to use surface complexation modeling to account for metal adsorption onto bacteria under low metal-loading conditions where these high affinity binding sites can dominate adsorbed metal budgets.

[1] Mishra *et al GCA* 2010, **74**, 4219-4233 [2] Yu *et al Chemical Geology* 2014 (submitted)