Using surface complexation modeling to quantify bioavailability of metals to bacteria

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Determining the controls on metal bioavailability is crucial in order to understand the geomicrobiology of geologic systems with high metal concentrations, such as acid mine systems or contaminated soils, and in order to optimize bioremediation strategies aimed at remediating those types of systems. In addition, the controls on the rates of several environmentally significant metabolic processes, such as mercury methylation or bacterial reduction/oxidation of metals, are poorly understood. The key to improved models of all of these geomicrobiological processes is the ability to quantitatively model bacterial metal bioavailability. Metal adsorption onto bacterial cell walls represents the first interaction of a metal with the cell, and for this reason we hypothesize that accessibility of the metal to the cell is directly related to, and can be predicted by, cell wall metal speciation.

In the research that will be discussed, we test the hypothesis that bacterial surface speciation and concentration of heavy metals controls the bioavailability of those metals. Previous models of metal bioavailability (e.g., the Biotic Ligand Model) characterize metal binding onto a wide range of organisms using a generic, unspecified metal-binding biotic ligand that does not account for the many complexities of metal adsorption reactions onto biological surfaces. These models often fail because of these overlooked complexities in adsorption reactions. Over the past 15 years, we have learned much about the mechanisms involved in metal binding onto bacterial cell walls, and have developed quantitative surface complexation models based primarily on x-ray absorption spectroscopy and bulk adsorption measurements.

In this presentation, I will review my group's work to improve surface complexation models of bacterial metal binding, and to use those models to quantify the controls on the bioavailability of aqueous metals to bacteria. We have shown that bacterial chemotactic response and the enzymatic reduction of U(VI) are two examples of adsorption-controlled processes. The extent and rate of both of these processes can be directly related to the concentration of metal adsorbed onto the bacterial cell wall. Therefore, improving the sophistication and accuracy of surface complexation models of metal adsorption onto bacteria will lead to improved quantitative models of bacterial processes in realistic complex systems.

"Normal" Southern Volcanic Zone basalts behind the arc at 34˚15′-34˚45′ S

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The section of the Southern Volcanic Zone (SVZ) between ~33˚S and 34.5˚S is distinguished from the more southerly SVZ by its distinct geochemical signature – namely, ^{87}Sr/^{86}Sr > ~0.7045, Sr/Y > 35, La/Yb > 12, and major element characteristics typical of the High-K andesite series. Also charactieristic of the northernmost segment of the SVZ is a lack of basaltic lavas on the volcanic front (basaltic andesites are common). The distintive geochemical characteristics of the Northern SVZ magmas suggest a unique source, either in a lower crustal hot zone [1] / MASH zone [2], where mantle melts are hybridized by extensive partial melts of deep lower crust, or by incorporation of eroded crustal materials into the mantle source itself [3,4]. The lack of primitive basaltic materials in the NSVZ makes it difficult to directly assess the nature of the subarc mantle in this region. We have sampled seven olivine basalt lava flows, tephra rings, maars, and cinder cones from just behind the volcanic front (~50 km from the arc axis) between 34˚15′ and 34˚45′ S. Although these basalts do not necessarily represent the mantle source beneath the arc front, they do provide some constraints on the mantle composition at this latitude. The Sr isotopic composition of these primitive basalts is ^{87}Sr/$^{\cancel{86}}$Sr = 0.7040 ± 0.0004 (2σ), which is statistically different from the basaltic andesites and andesites located on the arc front at the same latitude, which have ^{87}Sr/$^{\cancel{86}}$Sr = 0.7050 ± 0.0004 (2σ). Neodymium isotopes show the same trend, with less overall varibility.

The basalts from behind the arc at 34˚15′ to 34˚45′ S have isotopic compositions essentially identical to those found in arc front lavas from the SVZ south of 35˚. It is certainly possible to imagine scenarios in which the mantle directly behind the arc could be compositionally decoupled from the mantle directly beneath the arc. Nonetheless, the existence of typical SVZ mantle in the atypical NSVZ region suggests that mantle source contamination by eroded crustal materials is not a pervasive feature at these latitudes. The strong contrast in source composition over 50 km E-W can be compared to the relative homogeneity of the NSVZ (radiogenic Sr) signature over ~150 km N-S at the arc front. Alternatively, the arc front lavas in the SVZ may be sourced in a hybridized lower crustal hot zone, while the behind-arc samples are sourced from the mantle itself with little crustal interaction. The lack of crustal interaction is consistent with thinner crust behind the arc, as well as the occurrence of these monogenetic basaltic features along lineations, suggesting that the low-volume melts have exploited planes of weakness in the overlying crust.

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[2] Hildreth and Moorbath (1988) *CMP* **98**, 455-489.
[3] Stern (1991) *Geology* **19**, 78-81.
[4] Kay et al. (2005) *GSA Bull.* **117**, 67-88.