

## Heterogenous Selenium reduction in artificial soil aggregates

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Soils display large variation with respect to their physical, geochemical and biological characteristics on scales ranging from nanometers to kilometers. The impact of this extraordinary heterogeneity on biogeochemical processes is as of yet poorly quantified and understood. In structured soils, the aggregate scale (mm-cm) is of particular interest due to the sharp transition in pore size at the surface of aggregates. Small intra-aggregate pores limit advective transport thus facilitating the formation of chemical concentration gradients that promote strong spatial variation in biogeochemical processes. One such process is the microbial reduction of Se (VI) and Se (IV) to solid Se (0). A mechanistic understanding of Se reduction within soil aggregates may lead to improved prediction of Se transport and attenuation in soils of contaminated areas.

In order to investigate the coupling of physical and biogeochemical processes controlling Se reduction at the aggregate scale, artificial soil aggregates [1] were constructed using either uncoated sand or ferrihydrite coated sand homogenously inoculated with Se-reducing bacteria (*Thauera selenatis* or *Enterobacter cloacae* SLD1a-1). Aggregates were placed in a flow-through reactor and saturated flow of aerobic or anaerobic artificial groundwater medium was initiated. Selenate and either acetate or pyruvate, for *T. selenatis* and *E. cloacae* respectively, were provided in the inflow solution. Temporal evolution of selenite and total dissolved Se was followed in the outflow solution. Concentrations of Se associated with the solid phase were analyzed in concentric sections of each aggregate.

Compared to anaerobic experiments, the microbial reduction of selenate by *T. selenatis* was severely limited, but not inhibited under aerobic conditions. Similar results were observed for *E. cloacae*, with the inhibition in aerobic experiments being less pronounced. Given that *T. selenatis* is only capable of reducing selenate to selenite in the absence of oxygen [2] and *E. cloacae* is microaerophile [3], our experimental results suggest a localized Se reduction occurs inside the aggregates under aerobic conditions for both strains of bacteria.

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## Metal stable isotope probes of electrified interfaces

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Stable isotopes are sensitive indicators of physical and chemical processes at electrified interfaces, far from equilibrium. In a series of studies [3, 4] we have derived a relationship which combines stable isotope theory and classical statistical description of electron transfer processes that predicts an isotope fractionation at an electrified interface that is dependent on the extent of thermodynamic disequilibrium. In the laboratory, we have discovered a voltage-dependent isotope fractionation during electrodeposition from aqueous solutions of iron, zinc, lithium, molybdenum and copper metal. We have found that in all cases light isotopes are preferentially electroplated, with separations ranging from 0 to ~5 ppt—large separations for isotopes of these transition metals, especially compared with those attainable using other techniques, and observed in natural environments. In addition, we have found that the isotope separations are tunable in the laboratory—by varying the plating solution, reaction kinetics, temperature (Black *et al.* in prep), and mass transport using the rotating disc electrode [1].

Adjacent to a charge interface, the chemical species may not have the same distribution as in the bulk solution, and an entirely different speciation may develop through the reactive intermediates involved in electron transfer processes. Therefore, the isotopic composition of the double layer will not be identical to the bulk solution, even in the absence of mass transport and electron transfer effects. Therefore, one or more intermediate species may help determine the overall isotope fractionation between a bulk solution and an electroplated product.

Here we show a joint chemical/isotope model of an electrified interface, which considers mass transport, electron transfer, and chemical speciation. We combine theoretical models of the electrochemical double layer, with a mass-sensitive reservoir model of the reaction zone at an interface. The model predictions are compared directly with the experimental results.

[1] J. R. Black, E. D. Young, A. Kavner, (2010) *Geochim. Cosmochim. Acta*, **74**, 809–817. [2] Black, J. R. Umeda\*, G. Dunn, B. McDonough, W. F. & A. Kavner. (2009) *J. Amer. Chem. Soc.* **131**, 9904–9905. [3] A. Kavner, S. G. John, S. Sass, & E. A. Boyle (2008) *Geochim. Cosmochim. Acta*, **72**, 1731–1741. [4] A. Kavner, A. Shahar\*, F. Bonet, J. Simon\* & E. Young (2005) *Geochim. Cosmochim. Acta*, **69** 2971–2979.