The vanadium redox cycle: biological and mineralogical considerations in diffusion-limited environments

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Mounting evidence of the adverse effects of V(V) in humans has spurred its addition onto the USEPA's Contaminant Candidate List at a notification level of 50 µg L^{-1}. Groundwater concentrations of V surpass this notification level in multiple regions throughout the state of California, with the highest concentrations found in the Central Valley. Fluctuations in the water tables below these regions as a result of extraction and precipitation events lead to variations in redox conditions that enhance or inhibit the release of V from sediments into the groundwater. While it is typically present in the +3, +4 or +5 oxidation state, the solubility and mobility of V is highly dependent on its speciation, increasing with charge. As a result, V(IV) and V(V) are the dominant species encountered in groundwater. In this study, we investigate coupled redox interactions that influence the partitioning of V between its +4 and +5 oxidation states. Using a multi-chamber reactor design, we mimic a diffusion-limited sediment environment from which both aqueous and solid-phase time-series samples can be aquired. To simulate competative processes that lead to redox cycling of V, dissimilatory metal reducing bacteria (*Shewanella oneidensis*) and common environmental oxidants (Mn(III/IV) oxides) were selected for placement in each of two chambers. To examine the effect of different oxidant types on the partitioning of V between the +4 and +5 oxidation states, we ran parallel experiments where V(IV) oxidation was mediated by the reduction of either hexagonal birnessite or manganite. In both cases V(V) reduction was mediated by *S. oneidensis* relying on lactate as an electron donor. Solid-phase transformations, as well as the development of secondary V and Mn phases, were tracked by X-ray absorption spectroscopy, while aqueous methods were used to quantify the rates of V transformation. The results of this study provide much needed data on the relative influence of biological and mineralogical processes on the transformation of V in the environment, with implications for groundwater quality.