

# Investigation into the Mechanisms Controlling Vanadium Transformation and Competitive Retention between Manganese and Iron oxides

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Vanadium is an understudied transition metal present in many terrestrial systems that undergo redox cycling. Vanadium was recently added to the Contaminant Candidate List (CCL3) by the USEPA, and several forms of oxyanionic V<sup>V</sup> are known to induce strain on mammalian biological systems via the inhibition of enzymes integral to intracellular signaling [1,2]. Recent studies have reported concentrations of V in groundwater wells of California's Central Valley at several orders of magnitude greater than the EPA suggested notification level of 50 µg L<sup>-1</sup> [3,4]. However, biogeochemical controls on V mobility in the environment are poorly understood, making it difficult to predict its fate and transport in contaminated aquifers. In this study, we present several experiments detailing the behavior of V<sup>IV</sup> in a modeled soil system using a ubiquitous manganese and iron oxide (birnessite and goethite, respectively). To interrogate these interactions, we have developed adsorption isotherms for V<sup>V</sup> and V<sup>IV</sup> to assess the capacities of these minerals for V adsorption. To assess the competitive adsorption and oxidation interactions between these oxides and the oxycationic VO<sup>2+</sup>, we used a multi-chambered reactor, similar to that used in Ying et al. 2012 [5]. This setup allowed for time-sensitive measurements of non-equilibrium states to elucidate mechanisms of transformation and adsorption at environmentally relevant concentrations of V, which were selected based on previous studies [3,4,6]. Integral to the characterization of this system was the use of synchrotron radiation provided by the Stanford Synchrotron Radiation Lightsource. This allowed us to utilize X-Ray Absorption Near Edge Spectroscopy and Extended X-Ray Absorption Fine Structure Spectroscopy at the V and Mn K-edges respectively. Orca chemistry software is being used model the adsorption structures and species present, as described by the XAS data.

[1] Stern et al. (1993) *Biochem. Cell Biol.* **71**, 103-112. [2] Irving and Stoker (2017) *Molecules* **22**, 2269. [3] Wright and Belitz (2010) *Ground Water* **48**, 515-525. [4] Wright et al. (2014) *Applied Geochemistry* **48**, 41-52. [5] Ying et al. (2012) *Geochimica et Cosmochimica Acta* **96**, 294-303. [6] Burke et al. (2012) *ES&T* **46**, 3085-3092.