

Vanadium sorption to reduced iron minerals in seawater: a Synchrotron-based XAS study

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Vanadium (V) is an ubiquitous trace metal in the environment and possesses a unique redox-sensitive geochemistry [1]. The utility of the distinctive geochemistry of V is broad and ranges from industrial (e.g., V redox flow batteries) to paleoenvironmental research applications (e.g., as a proxy for ancient ocean chemistry) [2]. The fate of vanadium in the environment is highly dependent on its speciation, which can vary from +3 to +5 – pentavalent V being the most mobile form. From an environmental perspective, V contamination is a considerable concern with its rising anthropogenic use and associated waste production [3].

Scavenging by particulates is one of the major controls on V in the aquatic environment [4]. Interactions of V with reduced iron minerals have recently been reported in a freshwater context [5,6], however, the sorption of V by iron minerals in reducing marine environments remains poorly studied. Here we use Synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy to probe solid-phase V speciation following sorption to green rust (GR) and iron monosulfide (FeS) in seawater. The results provide evidence that V is reduced to a mix of V(V) and V(IV) during sorption to GR, whereas sorption to FeS results in rapid and complete reduction to V(III) (Figure 1 and 2). Subsequent oxidation of V-bearing GR and FeS results in the incorporation of reduced V(IV) into the newly formed lepidocrocite, thus potentially limiting the further mobility of V in the environment. Our findings have implications for the fate of V(V) in the presence of iron minerals in ferruginous marine systems.

References

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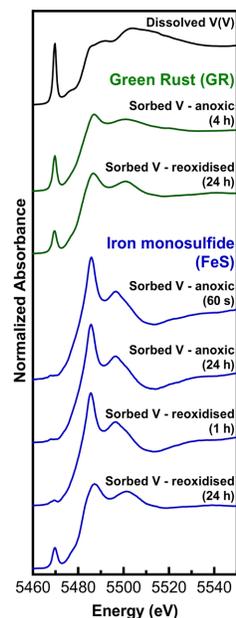


Figure 1. XANES spectra showing the reductive sorption of V(V) by green rust (GR) and by FeS in seawater (pH 8.1, salinity = 35), and subsequent reoxidation of V-bearing reduced iron minerals.

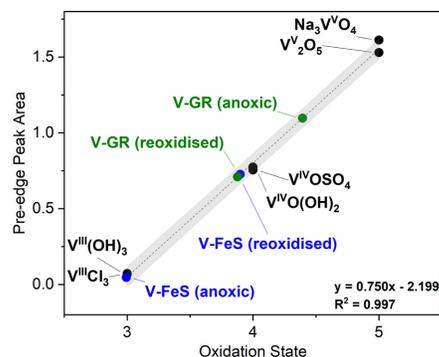


Figure 2. Results from XANES pre-edge peak analysis showing the reductive sorption of V(V) by green rust (GR) and by FeS in seawater (t = 24 h, pH 8.1, salinity = 35), and subsequent reoxidation of V-bearing reduced iron minerals.