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Vanadium isotope fractionation during adsorption of V(V) onto manganese oxides

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The vanadium isotope system ($\delta^{51}V$) of marine sediments has emerged as a promising proxy to track ocean redox evolution throughout the Earth history. This application relies on distinct geochemical behaviors and associated isotopic fractionations of V under different redox conditions. Among them, V(V) adsorption onto Fe-Mn (oxyhydr)oxides under oxic conditions is thought to be accompanied by the largest magnitude of isotope fractionation, but this process has not been experimentally investigated.

Here we determine V isotope fractionation factors ($\alpha_{sorbed\text{-}aqueous}$) through batch experiments of V(V) adsorption onto synthetic birnessite with different initial V concentrations (50-400 μM) and pH conditions (6-8). The results show preferential enrichment of light V isotope in the remaining pool, consistent with the natural investigation (Wu et al., 2019). These fractionations follow a Rayleigh fractionation model, yielding $\alpha_{sorbed\text{-}aqueous}$ from 0.9991±0.00009 to 0.99945±0.00012. Specifically, the $\alpha_{sorbed\text{-}aqueous}$ is independent with pH condition ($R^2 < 0.1$), but decrease with initial V concentration ($R^2 = 0.98$). This effect of initial concentration could be attributed to the formation of mononuclear inner-sphere complexes dominated by a bidentate mononuclear edge-sharing configuration under a low-concentration condition and of outer-sphere complexes or weakly adsorbed species under a higher-concentration condition. This study provides an essential constraint on V isotope fractionation when applying the V isotope system to reconstruct marine redox evolution in the past.

Reference

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