

First-principles investigation of equilibrium V isotope fractionation in solution and during adsorption

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Vanadium is a multi-valent element and it could be used as a redox tracer for a variety of geological processes. Recently, highly precise V isotope composition can be obtained using MC-ICP-MS [1, 2], which provides a new tool to constrain the redox state of the Earth. Although there are no V isotope data to study the evolution of palaeo-environment on the Earth's surface, it is promising to understand how V isotopes are fractionated in the key processes controlling vanadium transportation and deposition in surface system, i.e., adsorption and redox reaction.

Here we present first-principles calculations to investigate V isotope fractionation among V species with different valences in solution and that during adsorption. We used a "water-droplet" method to calculate V isotope fractionation factors between main species of V³⁺, V⁴⁺, and V⁵⁺ in solution [3]. Our calculation shows that ⁵¹V is enriched in species with high valence and low coordination numbers. At 25°C, $\Delta^{51}\text{V}$ between H₂VO₄⁻ and VO²⁺ is ~4‰, much greater than the current analytical precision (~0.15‰, 2sd [1,2]). We also calculate the V isotope fractionation due to V⁵⁺ species adsorption on goethite, which is the most important mineral that adsorbs V. Our results indicate that V⁵⁺ species adsorbed to goethite is depleted in ⁵¹V compared to the V⁵⁺ species in solution by ~3‰ at 25°C.

In summary, our calculation predicts significant V isotope fractionation due to redox reaction and mineral adsorption. This implies that V isotope compositions of natural water and sediments would carry transportation information of vanadium related to redox state changing. Therefore, V isotopes can be used to as a new geochemistry tool to investigate changes of paleo fO₂ in ancient ocean and atmosphere.

[1] Nielsen S. *et al* (2011) *Geostand. Geoanal. Res.* **35**, 293-306. [2] Prytulak J. *et al* (2011) *Geostand. Geoanal. Res.* **35**, 307-318. [3] Li X.-F. *et al* (2009) *EPSL* **287**, 1-11