



# First-principles investigation of vanadium isotope fractionation in solution and during adsorption



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## ARTICLE INFO

### Article history:

Received 1 February 2015

Received in revised form 4 June 2015

Accepted 24 June 2015

Available online 10 July 2015

Editor: D. Vance

### Keywords:

vanadium isotope  
equilibrium isotope fractionation  
density functional theory  
redox  
adsorption

## ABSTRACT

Equilibrium fractionation factors of vanadium (V) isotopes among tri- (V(III)), tetra- (V(IV)) and penta-valent (V(V)) inorganic V species in aqueous system and during adsorption of V(V) to goethite are estimated using first-principles calculation. Our results highlight the dependence of V isotope fractionation on valence states and the chemical binding environment. The heavy V isotope (<sup>51</sup>V) is enriched in the main V species following a sequence of V(III) < V(IV) < V(V). According to our calculations, at 25 °C, the equilibrium isotope fractionation factor between [V<sup>5+</sup>O<sub>2</sub>(OH)<sub>2</sub>]<sup>-</sup> and [V<sup>4+</sup>O(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> ( $\ln \alpha_{V(V)-V(IV)}$ ) is 3.9‰, and the equilibrium isotope fractionation factor between [V<sup>5+</sup>O<sub>2</sub>(OH)<sub>2</sub>]<sup>-</sup> and [V<sup>3+</sup>(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>] ( $\ln \alpha_{V(V)-V(III)}$ ) is 6.4‰. In addition, isotope fractionation between +5 valence species [V<sup>5+</sup>O<sub>2</sub>(OH)<sub>2</sub>]<sup>-</sup> and [V<sup>5+</sup>O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> is 1.5‰ at 25 °C, which is caused by their different bond lengths and coordination numbers (CN). Theoretical calculations also show that light V isotope (<sup>50</sup>V) is preferentially adsorbed on the surface of goethite. Our work reveals that V isotopes can be significantly fractionated in the Earth's surface environments due to redox reaction and mineral adsorption, indicating that V isotope data can be used to monitor toxic V(V) attenuation processes through reduction or adsorption in natural water systems. In addition, a simple mass balance model suggests that V isotope composition of seawater might vary with change of ambient oxygen levels. Thus our theoretical investigations imply a promising future for V isotopes as a potential new paleo-redox tracer.

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## 1. Introduction

Vanadium (V) is a redox sensitive element that has been widely used to constrain variation of redox conditions during many geological processes, including core-mantle segregation (e.g., Siebert et al., 2013), mantle evolution and melting (e.g., Lee et al., 2005), and low temperature processes on the Earth's surface (e.g., Breit and Wanty, 1991). Especially as V has multiple valences in seawater, it can be used as a redox tracer to study paleo-environment

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and paleo-oceanography (e.g., Algeo and Maynard, 2004). As a conservative or near conservative element with a residence time of ~100,000 years in seawater (about 20 times longer than the seawater cycle) (Morford and Emerson, 1999), V is nearly uniformly distributed in the ocean. Therefore, understanding transportation and removal of V in the seawater and precipitation of V into marine sediments has global implications. Furthermore, industrial exploitation of V could result in environmental problems as V is toxic to plants, animals, and human bodies (e.g., McCrindle et al., 2001). For regulation and evaluation of potential V pollution, it is important to identify the source and monitor V transportation and attenuation in solution.

An understanding the chemical behavior of V in water is important to understand the cycling of V in surface environments. V undergoes very complex hydrolysis in solution, where

the species of V in solution are controlled by pH, Eh, concentration and aquatic chemistry. Fig. 1 shows the Eh–pH diagram for V aqueous in dilute V solutions ( $[V]_{\text{total}} < 10^{-4}$  mol/L), which applies to most natural water including seawater and freshwater. In oxidizing conditions, V is mainly presented as V(V) in the form of vanadate oxyanion ( $\text{HVO}_4^{2-}$  and  $\text{H}_2\text{VO}_4^-$ ) in natural water. At environmentally-impacted sites, which are typically associated with mining activities, V(V) could also form polynuclear species such as decavanadate ( $\text{H}_x\text{V}_{10}\text{O}_{28}^{x-6}$ ) or metavanadate ( $(\text{VO}_3)_x^{x-}$ ) at high concentrations. V(V) is highly soluble and mobile, and is the most toxic form of V in solution. Meanwhile, adsorption of V(V) onto iron and manganese oxides or clay minerals is one of the main controls of V concentration in modern seawater (Trefry and Metz, 1989; Elderfield and Schultz, 1996), river water (Auger et al., 1999), and groundwater (e.g., Breit, 1995). Under mildly or strongly reducing conditions, dissolved V(V) tends to be reduced to V(IV) or further to V(III) by organic compounds or  $\text{H}_2\text{S}$  (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). V(IV) species are less soluble than V(V) and thus are apt to coprecipitate with minerals and organic substances (Breit and Wanty, 1991; Morford and Emerson, 1999), while V(III) species are insoluble and tend to precipitate from natural water as solid oxide or hydroxide (Wehrli and Stumm, 1989). Therefore, transportation and segregation of V in solution is mainly controlled by redox state variation and mineral adsorption–desorption.

V has two stable isotopes,  $^{50}\text{V}$  (0.24%) and  $^{51}\text{V}$  (99.76%). Highly precise and accurate V isotope data have recently been obtained due to the advancement of instruments (MC-ICP-MS) and chemical purification techniques (0.12–0.15‰, 2SD, Prytulak et al., 2011; Nielsen et al., 2011). V isotope data are expressed as:  $\delta^{51}\text{V} = [(^{51}\text{V}/^{50}\text{V})_{\text{sample}} / (^{51}\text{V}/^{50}\text{V})_{\text{reference}} - 1] \times 1000$ . Studies on mantle xenoliths and mafic lavas gave an estimation of the V isotopic composition of bulk silicate earth, and showed that V isotope can be fractionated during high-temperature magmatic processes such as mantle melting and mineral fractional crystallization (Prytulak et al., 2013). V isotope measurement of meteorites indicates that the silicate Earth is enriched in  $^{51}\text{V}$  by about 0.8‰ relative to chondrites, likely reflecting the different irradiation history of the solar system (Nielsen et al., 2014).

Theoretical investigation and experimental work has shown that isotopes of multi-valence elements (e.g., Cr and Fe) can be fractionated during redox reactions (e.g., Anbar et al., 2005; Ellis et al., 2002; Schauble et al., 2004). Because V also has various valences in natural systems, remarkable fractionation of V isotopes is expected. Thus V isotope compositions of terrestrial samples may fingerprint redox-state variation.

It is important to understand how V isotopes are fractionated during processes controlling V transportation and deposition in the Earth's surface system, i.e., adsorption and redox reactions. To present, there has been no experimental work to investigate V isotope fractionation among V species with different valences and during mineral adsorption. With advancements in computational chemistry, equilibrium isotope fractionation factors can be obtained by first-principles calculations. Quantum chemistry calculations combined with the Urey model or Bigeleisen–Mayer equation (Bigeleisen and Mayer, 1947; Urey, 1947) can provide a reliable way to obtain isotope fractionation factors. This method has been successfully applied to calculate equilibrium isotope fractionation factors of many systems such as Fe, Cu, Zn, Cr, and Ge (e.g., Anbar et al., 2005; Fujii et al., 2014; Li et al., 2009; Schauble et al., 2004; Sherman, 2013).

In this study, V isotopic equilibrium fractionation factors of selected V species with valences +3, +4, or +5, including  $[\text{V}^{5+}\text{O}_3(\text{OH})]^{2-}$ ,  $[\text{V}^{5+}\text{O}_2(\text{H}_2\text{O})_4]^+$ ,  $[\text{V}^{5+}\text{O}_2(\text{OH})_2]^-$ ,  $[\text{V}^{4+}\text{O}(\text{H}_2\text{O})_5]^{2+}$ ,  $[\text{V}^{4+}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3]$ , and  $[\text{V}^{3+}(\text{OH})_3(\text{H}_2\text{O})_3]$  were calculated using density functional theory. Among these,  $[\text{V}^{5+}\text{O}_3(\text{OH})]^{2-}$  and

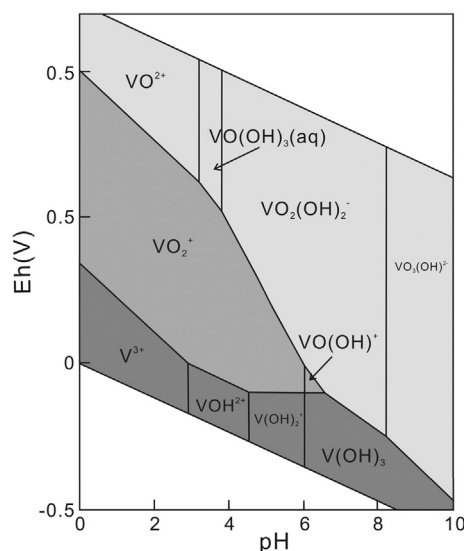


Fig. 1. Eh–pH diagram for vanadium aqueous species in the system V–O–H at 25 °C and 1 atm.  $[V]_{\text{total}} < 2 \times 10^{-5}$  m (modified from Baes and Mesmer, 1976).

$[\text{V}^{5+}\text{O}_2(\text{OH})_2]^-$  are dominant V(V) species in natural water under oxidic conditions (Fig. 1).  $[\text{V}^{5+}\text{O}_2(\text{H}_2\text{O})_4]^+$  is the main form of V(V) in acid solution ( $\text{pH} < \sim 2$ , Fig. 1).  $[\text{V}^{4+}\text{O}(\text{H}_2\text{O})_5]^{2+}$ ,  $[\text{V}^{4+}\text{O}(\text{OH})_2(\text{H}_2\text{O})_3]$ , and  $[\text{V}^{3+}(\text{OH})_3(\text{H}_2\text{O})_3]$  were investigated since they are among the common inorganic V(IV) and V(III) forms in solution under anoxic and euxinic conditions (Fig. 1). We also calculated the V isotope fractionation due to adsorption of V(V) species on the surface of goethite, since goethite, as a representative mineral adsorbent, is one of the most stable iron oxides and oxyhydroxide phases, and exists widely in chemical sediments and weathered soil (Langmuir et al., 1997). To reinforce the reliability of our results, we further calculated the V isotope fractionation factors of  $\text{V}^{4+}\text{O}$ -Lactate complex systems ( $\text{VO}(\text{D}(-)\text{-lact})$ ,  $\text{VO}(\text{L}(+)\text{-lact})$  and  $[\text{VO}(\text{lact})_2]^{2-}$ ), which could be compared with the chromatographic experimental results from Zhang et al. (2003). The purpose is to constrain V isotope fractionations caused by redox reaction in solution and adsorption on the mineral surface. This work provides a theoretical approach to employ V isotopes to investigate variations of redox conditions in paleo-ocean and paleo-atmosphere and to trace the source and transportation of anthropogenic V.

## 2. Methods

### 2.1. First-principles calculations

Mass dependent equilibrium isotope fractionation factors were calculated using the Urey model (Urey, 1947) or the Bigeleisen–Mayer equation (Bigeleisen and Mayer, 1947). The isotope fractionation factors are reported in the form of  $10^3 \ln \alpha_{A-B}$  ( $10^3 \ln \alpha_{A-B} = 10^3 (\ln \beta_A - \ln \beta_B)$ , where  $\beta_A$  and  $\beta_B$  represent the reduced partition function ratio of phase A and B, respectively). The reduced partition function ratio ( $\beta_A$ ) of element X of phase A is calculated in a harmonic approximation, using the Teller–Redlich rule to simplify the calculation procedure (Redlich, 1935). The reduced partition function ratio depends on temperature and vibrational frequencies. The equation used to calculate the reduced partition function ratios is below:

$$\beta_A = \frac{Q^*}{Q} = \prod_i^{3N-6} \frac{\mu_i^*}{\mu_i} \frac{e^{-1/2\mu_i^*}}{(1 - e^{-\mu_i^*})} \frac{(1 - e^{-\mu_i})}{e^{-1/2\mu_i}} \quad (1)$$

where  $Q$  is the vibrational partition function, and \* refers to the heavy isotope system. All the calculations were run over  $3N - 6$

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