



# Vanadium isotope compositions of mid-ocean ridge lavas and altered oceanic crust

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## ABSTRACT

Vanadium isotope compositions of igneous rocks have the potential to constrain variations of physico-chemical conditions such as oxidation states during magmatism. Here, we present V isotope data for 27 fresh lavas (ranging from basaltic to dacitic compositions) from mid-ocean ridges, 31 altered basalts and gabbros from IODP site 1256 near the East Pacific Rise (EPR), and 2 back arc basin basalts (BABB). Our analyses of fresh mid-ocean ridge basalt (MORB) provide new constraints on the V isotope composition of MORBs, i.e.  $\delta^{51}\text{V} = -0.84 \pm 0.02\text{‰}$  (2SE,  $n = 22$ ). In addition, the mean  $\delta^{51}\text{V}$  of MORBs from individual segments is correlated with the mean ridge depth and  $\text{Na}_{8,0}$  of the segment, which might reflect the effect of melting extent on V isotope fractionation during mantle melting.

The mafic profile of intact altered oceanic crust (AOC) from the IODP site 1256 has  $\delta^{51}\text{V}$  ranging from  $-1.01$  to  $-0.77\text{‰}$ , similar to that of fresh MORBs, suggesting that V isotope fractionation is limited during alteration of oceanic crust. These results also indicate the V isotopic homogeneity of the bulk oceanic crust with average  $\delta^{51}\text{V}$  of  $-0.85 \pm 0.02\text{‰}$  (2SE,  $n = 53$ ), which is unaffected by ocean water and hydrothermal fluid alteration. Our results provide a guideline for application of V isotopes into studies of low and high temperature geochemical processes.

The evolved lavas (basaltic andesites, andesites, and dacites) from the East Pacific Rise (EPR) show apparent shifts towards heavy  $\delta^{51}\text{V}$  values with increasing degree of differentiation, which can be explained by the crystal–liquid fractionation during crystallization with an inferred isotope fractionation factor of  $\Delta^{51}\text{V}_{\text{mineral-melt}} = -0.15 \times 10^6/T^2$ . The enrichment of  $^{51}\text{V}$  with increasing differentiation degree for the 9°N Overlapping Spreading Center (OSC) lavas is consistent with direction of the isotope shift observed in lavas from Anatahan Island (Northern Mariana Arc) and Hekla Volcano (Iceland), but the magnitude (0.3‰) is much smaller than that (2‰) reported in Prytulak et al. (2017). Modeling of V isotope fractionation between mineral and melt shows that variations in redox condition are important for controlling V isotope fractionation, but insufficient to explain the dramatically different  $\Delta^{51}\text{V}_{\text{mineral-melt}}$  between 9°N OSC lavas and Anatahan/Hekla suites. More studies are necessary for better understanding of mechanisms of V isotope fractionation during magmatism.

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## 1. Introduction

Vanadium (V) is a refractory, lithophile, and slightly siderophile transition metal element with multiple valence states ( $\text{V}^{5+}$ ,  $\text{V}^{4+}$ ,

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$\text{V}^{3+}$ ,  $\text{V}^{2+}$ , and  $\text{V}^0$ ) (Huang et al., 2015). The speciation and partitioning of V in the planets, meteorites, and Moon are regulated by oxygen fugacity ( $f\text{O}_2$ ). For this reason, V has been widely used to constrain variations of redox conditions during igneous processes. For example, the speciation of V in the glasses and minerals from planetary basalts and meteorites was applied to constrain the redox variations in the inner solar system (Karner et al., 2006; Righter et al., 2016). Vanadium concentrations of the bulk Earth

versus bulk silicate Earth (BSE) were applied to understand the conditions of terrestrial accretion and core formation (e.g. Siebert et al., 2013). The ratios of V to single valent elements with similar compatibility during mantle melting (such as Sc) have been used as a proxy for redox state variations of the mantle and crust (e.g. Lee et al., 2005; Mallmann and O'Neill, 2009; Laubier et al., 2014).

Vanadium has two stable isotopes,  $^{51}\text{V}$  (99.76%) and  $^{50}\text{V}$  (0.24%), which can be fractionated between coexisting species with different bond strengths and energies during redox-related processes (e.g. Schauble et al., 2004). This principle can also be applied to the V isotope system as shown recently by the theoretical study of Wu et al. (2015), providing the potential to fingerprint redox-state variations in nature. Owing to the advance of isotope analytical methods using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), stable V isotopes can be measured with the precision necessary to identify natural V isotope variations (Nielsen et al., 2011, 2016; Prytulak et al., 2011; Wu et al., 2016). Recent studies have revealed significant V isotope fractionation during both low and high temperature processes (Gao et al., 2018; Prytulak et al., 2013, 2017; Schuth et al., 2017; Ventura et al., 2015; Wu et al., 2016), implying the promising application of V isotopes as a new tracer, especially of oxidation states in the rocky planets and Earth.

Prytulak et al. (2013) observed significant V isotope variations of peridotites with  $\delta^{51}\text{V}$  ranging from  $-0.58\text{‰}$  to  $-1.17\text{‰}$ , and suggested on this basis a bulk silicate Earth ("BSE value") of  $(-0.7 \pm 0.2\text{‰})$ . Prytulak et al. (2017) further observed significant V isotope fractionation up to  $\sim 2\text{‰}$  during magmatic differentiation in Anatahan and Hekla lavas (Prytulak et al., 2017). In contrast, measurement of igneous silicate rock standards with a large range of  $\text{SiO}_2$  (47–67 wt.%) including basalts and differentiated granitoids only showed small V isotope variations ( $\sim 0.33\text{‰}$ ) (Wu et al., 2016). Thus, it is still not clear the magnitude and mechanism of V isotopes fractionation during magmatism, hindering the application of V isotope systematics to the studies of planetary mantle–crust differentiation. More investigations for igneous rocks with high-quality V isotope data are necessary to better understand V isotope fractionation during partial melting and magma differentiation.

The mid-ocean ridge (MOR) constitutes  $\sim 75\%$  of the total global erupted magma and created most of the oceanic crust (White and Klein, 2014). Mid-ocean ridge basalt (MORB) represents the most extensive crustal reservoir of the terrestrial Earth and they also provide critical genetic and compositional links to the upper mantle (Gale et al., 2013). Although Prytulak et al. (2013) presented V isotope data for several fresh and MORB samples, more data are needed to better constrain the V isotope composition of MORBs and oceanic crust. Here, we report high-precision V isotopic compositions for 27 well-characterized fresh MOR lavas with compositions from basaltic to dacitic, 2 back arc basin basalts (BABBs), and 31 mafic rocks of the altered oceanic crust (AOC) recovered from the IODP site 1256, which represent an intact section of oceanic crust near the East Pacific Rise (EPR). The purposes of this study are to (1) evaluate V isotope fractionation during magma differentiation at MORs, (2) examine the effect of fluid–rock interaction on the  $\delta^{51}\text{V}$  of the AOC, and (3) estimate the average V isotope composition of MORB and oceanic crust. With these results, we can establish a benchmark for using V isotopes to trace differentiation process on the terrestrial Earth and rocky planets.

## 2. Sample description and geological background

### 2.1. Fresh MORB and BABB

Twenty MORB samples were measured in this study. They are predominantly N-MORBs from axial ridge sections including the EPR at  $09\text{--}10^\circ\text{N}$ , the Gakkel Ridge at  $82\text{--}87^\circ\text{N}$ , and the South East Indian Ridge at  $50^\circ\text{S}$ , with one E-MORB sample from Mid-Atlantic Ridge at  $35^\circ\text{N}$ . The full spreading rates of these ridge segments vary from less than 1.5 cm/yr for the Gakkel Ridge to about 11 cm/yr for the EPR (White and Klein, 2014). In addition, two BABB from the Lau Basin, a back-arc basin at the Australian–Pacific plate boundary, were also analyzed. All MORB and BABB samples are fresh lavas (Gale et al., 2013; Perfit et al., 2012; Wanless et al., 2010, 2012). More sample details (locations, elemental and radiogenic isotope compositions) are in the Supplementary materials. These samples span a broad range in elemental and radiogenic isotope compositions. Their MgO contents range from 5.93 to 9.08 wt.% and V from 214 to 406 ppm (Table S1). The trace element contents of these MORB range from typical N-MORB to E-MORB. The MOR basaltic andesites to dacites have MgO content from 5.98 to 0.08 wt.% and V contents from 305 to 45 ppm.

### 2.2. AOC samples from IODP 1256

IODP site 1256 ( $6^\circ 44.2'\text{N}$ ,  $91^\circ 56.1'\text{W}$ ) is located in the Guatemala Basin on the Cocos Plate, which was drilled into the oceanic crust that formed  $\sim 15$  m.y. ago on the eastern flank of the EPR during an episode of superfast spreading with rates up to 20 cm/yr (Wilson et al., 2006). Basement rocks were recovered from Hole 1256C and Hole 1256D after penetrating  $\sim 250$  m of sediments (Teagle et al., 2006). Hole 1256C is comprised of a 32 m thick lava pond between two thin sheet flows that underlie the 88.5 m thick sediment layer (Fig. 4). The main Hole 1256D started coring at 276 m below seafloor (mbsf) and penetrated 1271 m into the oceanic basement (Fig. 4).

The oceanic crust at the Hole 1256D is subdivided into four main lithological units from top to bottom based on the shipboard core observations (Teagle et al., 2006) and alteration processes (Alt et al., 2010), including a volcanic section (250–1004.2 mbsf), a transition zone (1004.2–1060.9 mbsf), a sheeted dike complex (1060.9–1406.6 mbsf), and a plutonic complex (1406.6–1521.3 mbsf) (Fig. 4). Lithostratigraphy and distribution of secondary minerals versus depth in Hole 1256D indicate an increase in the degree of hydrothermal alteration with depth, in accord with an increase in alteration temperatures (Fig. 4) (Alt et al., 2010). Low temperature alteration occurs mostly in the volcanic section with a range from  $\sim 50$  to  $135^\circ\text{C}$  (Alt et al., 2010). The transition zone is characterized by greenschist and sub-greenschist minerals in rocks with alteration temperatures of  $\sim 130\text{--}180^\circ\text{C}$  (Fig. 4) (Teagle et al., 2006; Alt et al., 2010). High temperature hydrothermal alteration occurred in the sheeted dike complex due to circulation of high-temperature ( $\sim 400\text{--}850^\circ\text{C}$ ) fluids (Alt et al., 2010). The underlying lowermost dike complexes and plutonic complex underwent high temperature contact metamorphism caused by intrusion of gabbro bodies at  $\sim 850\text{--}950^\circ\text{C}$  and is characterized by granoblastic textures (Koepke et al., 2008; Alt et al., 2010). In addition, the downhole pattern of bulk sample  $\delta^{18}\text{O}$  and  $\delta^7\text{Li}$  also reflect variations in water–rock ratio together with a downward increase of alteration temperature (Gao et al., 2012). Consequently, the Hole 1256D profile documents the transition from low temperature seawater alteration to high temperature hydrothermal alteration and contact metamorphism in the oceanic crust.

Thirty-one well-characterized samples from Site 1256 (one from hole 1256C and thirty from 1256D) were analyzed for V isotopic

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