



The stable vanadium isotope composition of the mantle and mafic lavas



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ABSTRACT

Vanadium exists in multiple valence states under terrestrial conditions (2^+ , 3^+ , 4^+ , 5^+) and its isotopic composition in magmas potentially reflects the oxidation state of their mantle source. We present the first stable vanadium isotope measurements of 64 samples of well-characterized mantle-derived mafic and ultramafic rocks from diverse localities. The $\delta^{51}\text{V}$ ranges from -0.27‰ to -1.29‰ , reported relative to an Alfa Aesar (AA) vanadium solution standard defined as 0‰ . This dataset is used to assess the effects of alteration, examine co-variation with other geochemical characteristics and define a value for the bulk silicate Earth (BSE). Variably serpentinised peridotites show no resolvable alteration-induced $\delta^{51}\text{V}$ fractionation. Likewise, altered mafic oceanic crustal rocks have identical $\delta^{51}\text{V}$ to fresh hand-picked MORB glass. Intense seafloor weathering can result in slightly ($\sim 0.2\text{--}0.3\text{‰}$) heavier isotope compositions, possibly related to late-stage addition of vanadium. The robustness of $\delta^{51}\text{V}$ to common alteration processes bodes well for its potential application to ancient mafic material. The average $\delta^{51}\text{V}$ of mafic lavas, including MORB, Icelandic tholeiites and lavas from the Shatsky Rise large igneous province is $-0.88 \pm 0.27\text{‰}$ 2sd. Peridotites show a large range in primary $\delta^{51}\text{V}$ (-0.62‰ to -1.17‰), which covaries positively with vanadium concentrations and indices of fertility such as Al_2O_3 . Although these data suggest preferential extraction of heavier isotopes during partial melting, the isotope composition of basalts ($\delta^{51}\text{V} = -0.88 \pm 0.27\text{‰}$ 2sd) and MORB glass in particular ($\delta^{51}\text{V} = -0.95 \pm 0.13\text{‰}$ 2sd) is lighter than fertile peridotites and thus difficult to reconcile with a melt extraction scenario. Determination of fractionation factors between melt and mineral phases such as pyroxenes and garnet are necessary to fully understand the correlation. We arrive at an estimate of $\delta^{51}\text{V}_{\text{BSE}} = -0.7 \pm 0.2\text{‰}$ (2sd) for the bulk silicate Earth by averaging fertile, unmetasomatised peridotites. This provides a benchmark for both high and low temperature applications addressing planet formation, cosmochemical comparisons of the Earth and extraterrestrial material, and an inorganic baseline for future biogeochemical investigations. Whilst $\delta^{51}\text{V}$ could relate to oxidation state and thus oxygen fugacity, further work is required to resolve the isotopic effects of oxidation state, partial melting, and mineral fractionation factors.

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1. Introduction

Radiogenic isotopic compositions measured in mantle rocks and mantle-derived magmas provide compelling evidence for the

existence of mantle heterogeneity as well as constraints on its creation and preservation (e.g., Hofmann, 2003; Zindler and Hart, 1986). However, long-lived radiogenic isotope signatures are not without ambiguity. The variability in isotopic compositions of Sr, Nd, Pb, and Hf, for example, reflects the time-integrated fractionation of parent from daughter element. The magnitude of this elemental fractionation, the initial source composition and the age of the fractionated material all contribute to uncertainty in interpreting the final isotope composition. Thus, deducing the

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often multi-stage journey of the mantle and its melts is inherently non-unique using radiogenic isotopes.

Stable isotopes offer valuable complementary information to the evidence provided by long-lived radiogenic isotopes; particularly since neither time nor parent–daughter fractionations need be considered. Instead stable isotope fractionation is driven by temperature related equilibrium fractionations, relative mass differences, bond strengths, and kinetic processes (see review by Schauble, 2004). Of particular interest is the inverse relationship between temperature and magnitude of isotope fractionation (Urey, 1947). Since isotope fractionation at high temperatures was, until recently, considered negligible, stable isotope variability in the mantle or its melts has been attributed to the recycling and incorporation of surface material. Oxygen and sulphur isotopes have long been used in this manner to deduce the presence of sedimentary or hydrothermally altered material in the source of mantle melts (e.g., Chaussidon et al., 1987; Eiler et al., 1996). However, oxygen is a major constituent of the mantle, so large amounts of material are needed to impact oxygen isotope signatures. Sulphur isotopes are generally measured on sulphides and can show large isotope fractionations (e.g., Chaussidon et al., 1987; Bekker et al., 2009). However, sulphides are not always present in samples of interest, and the susceptibility of sulphur to volatile, degassing-driven isotope fractionation is a concern in erupted lavas. So-called ‘non-traditional’ stable isotopes have become increasingly prevalent in mantle studies.

For example, stable isotope systems of elements such as lithium (e.g., Elliott et al., 2006) and thallium (e.g., Nielsen et al., 2006) have been employed to trace small contributions of surface materials into the source of mantle-derived melts.

Advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) technology have greatly improved analytical precision, facilitating the exploration of small variations in stable isotopes at high temperatures of elements traversing the entire periodic table (e.g., Halliday et al., 2010). Research has focused on teasing out the causes of ubiquitous non-traditional stable isotope fractionation and applying this new information to geologic questions. This task is aided by resurgence in theoretical consideration of high temperature stable isotope fractionation after a long period with little work (e.g., Bigeleisen and Mayer, 1947; Schauble, 2004; Schauble et al., 2001, 2009; Urey, 1947). In particular, isotope systems of the period four transition metal elements are being increasingly studied. Multiple oxidation states of some transition metals and the prediction that changes between oxidation states can be linked to isotope fractionation (e.g., Schauble, 2004) means that transition metal stable isotopes potentially provide key information about, for example, the physical conditions of a mantle source (e.g., oxygen fugacity) rather than simply a test for crustal recycling.

Iron isotopes were amongst the first transition metal to have been investigated for high temperature fractionation (e.g., Zhu et al., 2000) and thus are perhaps currently the best understood. High temperature iron isotopic fractionation has been linked to changing oxygen fugacity (e.g., Dauphas et al., 2009; Williams et al., 2004, 2005), magmatic differentiation (Hibbert et al., 2012; Schuessler et al., 2009; Teng et al., 2008; Weyer and Ionov, 2007; Williams et al., 2004, 2005) and diffusion (Teng et al., 2011; Weyer and Seitz, 2012). Far fewer data are available for chromium stable isotopes at high temperatures, with initial results indicating negligible fractionation in major terrestrial reservoirs (Schoenberg et al., 2008). Hence, it is still unclear if the redox behaviour of transition metal isotopes provides new, robust proxies for mantle oxygen fugacity.

We have developed the first method able to measure stable vanadium isotopes to a precision useful for geologic problems

(Nielsen et al., 2011a; Prytulak et al., 2011). Here we present the first investigation of vanadium isotopes in mafic and ultramafic igneous rocks in order to determine the applicability of vanadium isotopes to mantle processes.

1.1. Vanadium and vanadium isotopes: applications and aims

Vanadium is a moderately incompatible, refractory transition metal existing in multiple valence states (V^{2+} , V^{3+} , V^{4+} , V^{5+}) at terrestrial conditions. Many studies have taken advantage of redox properties of vanadium and the strong relationship between vanadium partitioning and oxygen fugacity (e.g., Canil, 1997). These include investigation of the oxidation state of the mantle through time (e.g., Lee et al., 2003; Li and Lee, 2004), the oxidation state of subduction zones (e.g., Lee et al., 2005), core formation (e.g., Wood et al., 2008), oceanic anoxia (e.g., Emerson and Huested, 1991; Tribouillard et al., 2006), hydrocarbon and crude oil genesis (e.g., Lopez et al., 1995), and nitrogen fixation (e.g., Bellenger et al., 2008). Whilst useful, elemental studies are prone to uncertainties such as initial source concentration, degree of melting and partitioning relationships. Stable isotopes may provide more straightforward information.

Changes in oxidation state are theoretically predicted, and experimentally demonstrated to result in fractionation of stable isotopes (e.g., Schauble et al., 2009; Urey, 1947; Zhu et al., 2000). Vanadium may be particularly advantageous in this respect given the number of oxidation states available. Considering the large array of potential applications to problems in Earth science, it might be surprising that to date no high precision vanadium isotope data exist. This lack of vanadium isotope data is due to two major analytical obstacles. The first is that the $^{51}V/^{50}V$ of the only two stable isotopes, ^{51}V (99.76%) and ^{50}V (0.24%), is ~ 420 . The analytical challenge is compounded by the existence of direct isobaric interferences from ^{50}Cr and ^{50}Ti on the minor ^{50}V isotope. The first separation and measurement protocol that overcomes these difficulties for silicate matrices has been developed (Nielsen et al., 2011a; Prytulak et al., 2011). This study presents the first investigation of high temperature fractionation of stable vanadium isotopes in mantle and mantle-derived mafic melts with three general aims

- 1) Evaluate the range of natural isotope fractionation in the mantle and mafic mantle-derived melts
- 2) Assess the fidelity of the isotope signature to common alteration processes
- 3) Estimate the stable vanadium isotope signature of the bulk silicate Earth.

2. Materials

Exploration of new isotope systems is hindered without basic geochemical context. Therefore bulk rock major elements are the minimum characterization requirement for the samples in this study. Trace element and isotopic data are also available in most cases. Every effort has been made to investigate samples previously studied for other ‘non-traditional’ stable isotope systems (e.g., Li, Mg, Fe, and Cr). Full major and trace element characterization and GPS locations (where available) for the 64 samples in this study can be found in the literature, and is also compiled in the [Electronic Appendix](#). A supplemental figure is included with the global locations of all samples in this study.

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