Stable Vanadium Isotopes as a Redox Proxy in Magmatic Systems?

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Abstract
Recycling pathways of multivalent elements, that impact our understanding of
diverse geological processes from ore formation to the rise of atmospheric
oxygen, depend critically on the spatial and temporal variation of oxygen
fugacity ($fO_2$) in the Earth’s interior. Despite this importance, there is currently
no consensus on the relative $fO_2$ of the mantle source of mid-ocean ridge basalts
compared to the sub-arc mantle, the region that is central to the mediation of
crust-mantle mass balances. Here we present the first stable vanadium isotope
measurements of arc lavas, complemented by non-arc lavas and two co-genetic
suites of fractionating magmas to explore the potential of V isotopes as a redox
proxy. Vanadium isotopic compositions of arc and non-arc magmas with similar
MgO overlap with one another. However, V isotopes display strikingly large,
systematic variations of $\sim 2\%_{\text{o}}$ during magmatic differentiation in both arc and
non-arc settings. Calculated bulk V Rayleigh fractionation factors ($1000\ln\alpha_{\text{min-melt}}$
of -0.4 to -0.5%) are similar regardless of the oxidation state of the evolving
magmatic system, which implies that V isotope fractionation is most influenced
by differences in bonding environment between minerals and melt rather than
changes in redox conditions. Thus, although subtle $fO_2$ effects may be present, V
isotopes are not a direct proxy for oxygen fugacity in magmatic systems.
Keywords: vanadium, stable isotopes, magmatic fractionation, oxygen fugacity,
magnetite
**Introduction**

Oxygen fugacity ($fO_2$), the chemical potential of oxygen, varies over ten orders of magnitude in igneous systems (Carmichael, 1991). Knowledge of mantle $fO_2$ is of critical importance for understanding the speciation of fluids in subduction zones and thus the efficiency of elemental transfer from slab to surface. Oxygen fugacity is often reported in log units relative to a buffer reaction, commonly fayalite-magnetite-quartz (FMQ). Early study of mantle $fO_2$ employed oxygen thermobarometry, proposing that subduction zones generally are more oxidized (>FMQ +1) than the mantle source of mid-ocean ridge basalts (~ FMQ) (e.g., see review of Frost & McCammon, 2008).

However, the association of mantle $fO_2$ with tectonic setting has become contested following the introduction of novel approaches to its determination. The development of new proxies based on ratios of redox to non-redox sensitive elements, such as V/Sc and Zn/Fe, coupled with synthesis of global chemical databases such as GEOROC (http://georoc.mpch-mainz.gwdg.de/georoc/) and PETDB (http://www.earthchem.org/petdb), has led to the counterintuitive proposal that there is no difference in $fO_2$ between the mantle sources of arc and MORB lavas (Lee et al., 2005; 2010). The Fe$^{3+}$/ΣFe ratios in melt inclusions, however, are most consistent with a more oxidized mantle wedge compared to the source of MORB (e.g., Kelley & Cottrell, 2009). To explain the apparent discrepancies between independent estimates of $fO_2$, processes subsequent to magma generation such as degassing and crystal fractionation have been invoked, as these might lead to elevated Fe$^{3+}$/ΣFe of arc lavas (e.g., Mallmann & O’Neill, 2009; Lee et al., 2010). Evidence gleaned from both experimental and
natural suites is conflicting, with cases of Fe\textsuperscript{3+}/ΣFe increasing, decreasing and
remaining invariant during magmatic degassing and crystallisation (e.g., Brounce
et al., 2014; Waters & Lange, 2016). Thus lingering uncertainty as to the cause of
elevated Fe\textsuperscript{3+}/ΣFe in arc lavas fuels continued debate.

The stable isotope composition of multivalent elements is theoretically linked to
\textit{fO}_2. High temperature fractionation of stable isotopes is dictated by the
vibrational frequencies of chemical bonds, with higher frequencies having larger
bond force constants (\textit{K}) and preferring heavier isotopes. An instructive estimate
of the force constant is given by the mean bond strength: the quotient of average
valence and co-ordination number (Pauling, 1929). Thus, atoms associated with
higher oxidation state and/or lower co-ordination should, on average,
incorporate a greater proportion of heavier isotopes. Therefore the possibility of
resolving transition metal stable isotope variations in high temperature settings
has the potential to define mantle \textit{fO}_2 more clearly. Although it is tempting to
employ simple comparative geochemistry (i.e. heavier isotope compositions
equate to more oxidizing conditions), the interplay between co-ordination
environment and valence state is vital to interpreting the effect of changing \textit{fO}_2
on isotope fractionation.

\textbf{Vanadium as a redox proxy}

Vanadium is a moderately incompatible, refractory multivalent (2+, 3+, 4+, 5+)
element and its strong partitioning relationship with \textit{fO}_2 is well-established (e.g.,
Canil, 1997; Toplis & Corgne, 2002; Mallmann and O’Neill, 2009). In all major
mantle phases, vanadium becomes more incompatible with increasing \textit{fO}_2,
leading to the application of V as a redox proxy (e.g., Shervais, 1982; Canil, 1997; Lee et al., 2005; Mallmann & O’Neill, 2009). However, using concentrations alone results in $f_{\text{O}_2}$ uncertainties on the order of 1-2 log units due to variations in degree of melting, original source concentration, and fractionating mineral assemblages (Lee et al., 2003).

Vanadium has two stable isotopes, $^{51}$V and $^{50}$V. Their ratio is reported as per mil deviations, $\delta^{51}$V, relative to the AA (Alfa Aesar) V solution standard, defined as 0‰ (see Nielsen et al., 2011). The extreme natural $^{51}$V/$^{50}$V ratio of ~420 coupled with isobaric interferences from $^{50}$Cr and $^{50}$Ti on the minor $^{50}$V isotope have historically prevented analyses to a precision useful for high temperature applications. These obstacles were recently overcome, and the first analytical protocol to determine $\delta^{51}$V to a precision better than ±0.15‰ 2sd (Nielsen et al., 2011; Prytulak et al., 2011) demonstrated resolvable variations in igneous rocks of different silica content ($\delta^{51}$V$_{\text{basalts}} < \delta^{51}$V$_{\text{andesites}}$). We present the first $\delta^{51}$V measurements directly exploring the potential of $\delta^{51}$V as a redox proxy. Specifically, we investigate the effect of magmatic evolution and determine if a resolvable $\delta^{51}$V difference exists between arc and non-arc lavas.

**Methods**

Previous work using $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios suggests that Mariana arc basalts are generally ~ 1-2 log units more oxidized compared to Icelandic basalts (e.g., Brounce et al., 2014; de Moor et al., 2005; Moune et al., 2007; Shorttle et al., 2015). We choose forty whole rock samples from three lava suites for study: 1) primitive arc lavas of the Mariana Central Island Province (CIP; Elliott et al.
1997), 2) co-genetic lavas from Anatahan volcano in the Mariana arc (Wade et al., 2005) and 3) co-genetic lavas from Hekla volcano, Iceland (Savage et al., 2011). Published major, trace and isotopic data are found in Table S-1.

Chemical separation and measurements were made at Oxford University and Imperial College London, following Nielsen et al. (2011). Description of methods and isotopic data are found in the supplemental information and Table S-2.

Results & Discussion

Two key observations arise from Figure 1: First, there is a striking range of ~2‰ towards heavy δ54V with progressive differentiation in both suites of lavas, which is an order of magnitude larger than Fe isotope variations in fractionating magmas (e.g., Schuessler et al., 2009; Sossi et al., 2012). Second, basaltic lavas from the Marianas, Iceland and MORB have overlapping δ54V.

The remarkable magnitude of high temperature δ54V fractionation towards heavy values with magmatic evolution is unlikely to be due to changing fO2 because the δ54V variation is similar for both suites. Instead, the primary control on isotope fractionation appears to be differences in mineral-melt bonding environment. Oxide minerals such as (titanomagnetite host the majority of V in magmatic systems. Trivalent vanadium is preferentially incorporated in the VI-fold sites of (titanomagnetite, the thermodynamically stable configuration (O’Neill and Navrotsky, 1984) resulting from its high octahedral site preference energy. Vanadium’s oxidation and co-ordination in silicate melts is not constrained by stoichiometry, but is always higher and lower, respectively, than
in co-existing (titano)magnetite (Righter et al., 2006). Thus (titano)magnetite
(and other ferromagnesian minerals) should be isotopically light, and
crystallization will lead to a progressively heavier residual melt. A significant
departure to heavy $\delta^{51}$V is observed at $\sim$60 wt% SiO$_2$ at Anatahan, and $\sim$55 wt%
at Hekla, although petrographic and chemical evidence demonstrates oxide
fractionation occurring earlier in both suites. Indeed, significant
(titano)magnetite crystallisation and removal is necessary to impact the $\delta^{51}$V
signatures whilst melt V concentration is relatively high. We speculate that the
more complex magma chamber processes at Anatahan, where lavas are generally
more evolved, are responsible for the lighter and more variable $\delta^{51}$V in MgO
lavas between 2 and 4 wt% MgO compared to Hekla (Fig. 1b).

Self-consistent models of fractional crystallization of coctic phases have been
constructed to account for systematic variations in major and trace element
concentrations, as well as isotopic compositions in Hekla and Anatahan lavas
(Fig. 2). Input parameters and results are provided in the supplemental
information (Table S-3). Given the strong dependency of V partitioning on $fO_2$, it
is of particular interest to assess how the partition coefficient of V in
(titano)magnetite differs between the two suites. A $D_{\text{mag}}^{\text{V}}$ of 32±4 is calculated
from analyses of Anatahan lavas (de Moor et al., 2005), a value that reproduces
major, trace and isotopic trends very well. The required $D_{\text{mag}}^{\text{V}}$ for Hekla lavas,
however, must be significantly higher ($\sim$42) to reproduce the data. The relative
difference in $D_{\text{mag}}^{\text{V}}$ between the two suites is consistent with lower $fO_2$ at Hekla
than Anatahan (e.g., Toplis & Corgne, 2002). The same input parameters are used
to perform Rayleigh calculations to estimate the bulk V isotope fractionation
factor (Fig. 3). Both suites require large $\Delta^{51}V_{\text{min-melt}}$ fractionation factors on the order of $1000\ln\alpha_{\text{min-melt}}$ of -0.4 to -0.5‰. Arguably, a larger fractionation factor is required for Anatahan versus Hekla, however, the effect is subtle and difficult to confidently resolve within the current analytical precision.

Clearly, differences in mineral-melt bonding environment are key to producing large $\Delta^{51}V$ fractionations. However, prior to significant (titano)magnetite crystallization, $\Delta^{51}V$ is identical within uncertainties in arc lavas, Icelandic lavas and MORB at similar MgO contents (Fig. 1). If interpreted as a direct $f_{O_2}$ proxy, this conflicts with oxybarometry in peridotites, but is notionally consistent with their similar V/Sc ratios. This conclusion hinges, however, upon the assumption of a homogeneous source, both with respect to V/Sc and $\Delta^{51}V$, an assumption that may be violated. For instance, $\Delta^{51}V$ becomes isotopically lighter in progressively depleted (clinopyroxene-poor) peridotites (Prytulak et al., 2013) and the arc mantle wedge has been inferred to be markedly depleted (e.g., Woodhead, 1993, Nebel et al., 2015) with respect to the source of MORB. In the absence of a common source, observations of similar V/Sc and $\Delta^{51}V$ must be explained.

Primary arc magmas are notoriously rare, thus most information is garnered from basaltic andesites with Mg# too low (~0.5 assuming 20% $Fe^{3+}$) to be in equilibrium with normal mantle (~0.9). Isotope fractionation during partial melting is possible, although high temperatures should minimize the effect. It is, however, perplexing that the well-constrained $\Delta^{51}V_{\text{MORB}}$ is isotopically lighter than most peridotites and the bulk silicate Earth ($\Delta^{51}V_{\text{MORB}} = -0.95 \pm 0.13‰$; $\Delta^{51}V_{\text{BSE}} = -0.7 \pm 0.2‰$; Prytulak et al., 2013). The peridotite trend towards lighter
\[ \delta^{51}V \] with progressive depletion thus negates a simple explanation of isotope fractionation during melt extraction (Prytulak et al. 2013). Given the strong evidence for mineral-melt fractionation, early phases should be considered. For example, water-rich magmas crystallize Cr-rich spinel before olivine (Fieg et al. 2010), potentially scavenging V. Oxide fractionation will drive remaining liquid to heavier \( \delta^{51}V \), thus early spinel crystalisation is a viable mechanism to increase \( \delta^{51}V \) in arc magmas. If arc magmas are derived from a depleted source with a lighter initial V isotope composition than the MORB source, it is therefore possible that the competing effects of source depletion and Cr-spinel fractionation result in similar \( \delta^{51}V \) in mafic arc and non-arc magmas. Mineral separate data and the analysis of more primitive magmas are required to investigate this premise since it is currently not possible to evaluate the magnitude of isotopic increase due to early Cr-rich spinel, and/or partial melting, as there are no V concentration and \( \delta^{51}V \) on spinel and scant peridotite whole rock data.

If arc magmas are derived from more depleted mantle than MORB, their source should have lower \( \delta^{51}V \) and V/Sc. This effect on V/Sc will be exacerbated if depletion occurs at high \( fO_2 \). Therefore, the observation of similar \( \delta^{51}V \) and V/Sc ratios in high MgO lavas from both settings can be interpreted as evidence of arc melting under more depleted, oxidized conditions. The concept is illustrated with two hypothetical sources in Figure 4a with examples of simple forward trace element modal (Fig 4b) and non-modal (Fig 4c) melting models comparing V/Sc in lavas derived from these two sources (Fig. 4 b, c). Overall, the effect of source depletion (i.e. less V) coupled with higher \( fO_2 \) (and thus lower D\(_V\)) appears
to offset a more fertile (i.e. more V) less oxidized (higher Dv) source to yield similar V/Sc. Thus the confluence of $\delta^{51}V$ and V/Sc in arc and MORB lavas may paradoxically require differences in their source $fO_2$. Clearly, there are many possible solutions to such models, and the absolute values of V/Sc are very sensitive to input parameters (see supplemental information), however, given the assumption of a more oxidized, depleted arc source, the similarity of V/Sc in arc lavas and MORB at 10-15% melt is relatively straightforward to reproduce.

Irrespective of the trade-offs involved in interpretation of relative oxidation states of arc and non-arc lavas, Rayleigh fractionation of oxide phases is dominantly responsible for the magnitude of observed V isotope fractionation in differentiating magmatic suites. Subtle $fO_2$-related variations are perhaps overprinted onto first order bonding-environment induced fractionations, but these require a much richer understanding of $\delta^{51}V$ variations during magmatic processes to be applicable. Therefore, elemental partitioning of V yields a more direct relationship with $fO_2$ than the current understanding of V isotopes at high temperatures permits.

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**Figure Captions**

**Figure 1.** $\delta^{51}$V variations with SiO$_2$ (a) and MgO (b) in chosen sample suites. CIP = Central Island Province. MORB data from Prytulak et al. (2013). Uncertainties on isotope measurements are external 2 sd.

**Figure 2.** Cotectic fractional crystallization models. Each small symbol represents a 5% crystal fractionation increment. See supplemental information for input parameters. Symbols and uncertainties as in Figure 1.

**Figure 3.** Rayleigh fractionation calculations with same parameters as Figure 2. Symbols and uncertainties as in Figure 1.

**Figure 4.** (a) Conceptual effect of depletion and oxidation on V/Sc ratios from two hypothetical spinel peridotite sources, (b, c) Modal and non-modal melting model examples for the sources in (a) with grey fields highlighting reasonable melting degrees. Partition coefficients, modal compositions and melting reactions are detailed in the supplemental information. DM = depleted mantle, DDM = depleted MORB mantle, F = melt fraction.
Anat $D^\text{mag}_V = 32$
Hek $D^\text{mag}_V = 42$