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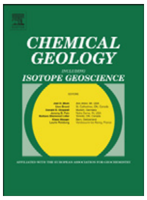

Vanadium isotope measurement by MC-ICP-MS

Fei Wu, Yuhan Qi, Huimin Yu, Shengyu Tian, Zhenhui Hou, Fang Huang *

CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, Anhui, China

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ABSTRACT

We present a method to measure vanadium (V) isotopic composition for terrestrial rocks in this study. Vanadium was efficiently separated from matrix elements by a chromatographic technique using cation- and anion-exchange resin columns, avoiding the expensive TRU Spec resin. Vanadium isotope ratios were measured using a Thermo Scientific Neptune Plus MC-ICP-MS employing a sample–standard bracketing method. The increase in instrument sensitivity significantly reduces the amount of V required for the isotope analysis. Potential effects of acid molarities and concentration mismatch on instrumental analyses were rigorously evaluated. In addition, we performed Cr- and Ti-doping experiments to ensure the precision and accuracy of V isotope measurement. The $\delta^{51}V$ values of mono-elemental V standards (BDH and USTC-V) relative to an Alfa Aesar (AA) standard solution (defined as $\delta^{51}V = [(^{51}V/^{50}V)_{sample} / (^{51}V/^{50}V)_{AA} - 1] \times 1000$) measured in our laboratory were −1.23 ± 0.08‰ (2 SD, $n = 197$) and 0.07 ± 0.07‰ (2 SD, $n = 112$), respectively. Analyses of synthetic standard solutions (element doping + matrix spiking) obtained the same $\delta^{51}V$ for the pure V solutions with a precision better than ±0.1‰ (2 SD). Vanadium isotopic compositions of 12 reference materials, including igneous rocks (with mafic to felsic compositions) and manganese nodules, were measured using this method. These reference materials including basalts: BCR-2, −0.78 ± 0.08‰ (2 SD, $n = 36$); BHVO-2, −0.83 ± 0.09‰ (2 SD, $n = 22$); BIR-1, −0.92 ± 0.09‰ (2 SD, $n = 52$); JB-2, −0.87 ± 0.06‰ (2 SD, $n = 20$); diabase: W-2, −0.94 ± 0.08‰ (2 SD, $n = 15$); andesites: AGV-1, −0.71 ± 0.10‰ (2 SD, $n = 6$); AGV-2, −0.70 ± 0.10‰ (2 SD, $n = 37$); JA-2, −0.80 ± 0.07‰ (2 SD, $n = 15$); quartz latite: QLO-1, −0.61 ± 0.03‰ (2 SD, $n = 3$); granodiorite: GSP-2, −0.62 ± 0.07‰ (2 SD, $n = 26$); and manganese nodules: NOD-P, −1.65 ± 0.06‰ (2 SD, $n = 10$); NOD-A, −0.99 ± 0.10‰ (2 SD, $n = 19$). Based on repeated analyses of the rock standards, the long-term external precision of our method is better than ±0.1‰ (2 SD) for $\delta^{51}V$. Such precision allows us to identify V isotope fractionation in high-temperature terrestrial samples, suggesting that V isotope geochemistry can be more widely used to study magmatism as well as supergene processes.

1. Introduction

Vanadium (V) is a transition metal with multiple valence states (V^{5+}, V^{4+}, V^{3+}, and V^{2+}) in nature. The proportion of vanadium with different valence states in the planetary basaltic melts and mantle peridotites is related to oxygen fugacity of the systems (e.g., Papike et al., 2005). The chemical speciation and solubility of V in water are strong functions of pH and Eh conditions (e.g., Baes and Mesmer, 1976; Takeno, 2005; Zhou et al., 2011). Therefore, vanadium has been widely used to constrain variations of redox conditions during many geological processes (Huang et al., 2015 and references therein). For example, vanadium concentrations of the bulk earth versus bulk silicate earth (BSE) have been used to understand the conditions of terrestrial accretion and core formation (e.g., Siebert et al., 2013; Wood et al., 2008). Furthermore, vanadium concentrations and its ratios relative to single valent elements with similar compatibility in peridotites and mantle-derived magma have been used as a proxy for redox condition variations of the mantle (e.g., Canil, 2002; Lee et al., 2005; Mallmann and O'Neill, 2009). Vanadium is significantly enriched in carbonaceous rocks or materials (up to 10,000 ppm) (Breit and Wanty, 1991), which can be used to trace marine oxidation state (e.g. Algeo and Maynard, 2004; Morford and Emerson, 1999). In addition, vanadium can be significantly enriched into crude oil, and the value of V / (V + Ni) is commonly used to determine crude oil grade (e.g., Ventura et al., 2015, and references therein).

Vanadium has two stable isotopes (^{51}V and ^{50}V) with relative abundances of ~99.76% and ~0.24%, respectively (Shore et al., 2010). Theoretical investigation and experimental studies have shown that isotopes of multi-valence elements can be fractionated during redox reactions (e.g., Anbar et al., 2005; Ellis et al., 2002; Schauble et al., 2004). Recently, first-principle calculations predicted that large V isotope fractionation could occur during V transportation and segregation in natural solutions via redox reaction and adsorption processes (Wu et al., 2015). Thus, V isotopic compositions of terrestrial samples may also fingerprint redox-state variations in nature.

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* Corresponding author.
E-mail address: fhuang@ustc.edu.cn (F. Huang).

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Vanadium isotopes were analyzed using thermal ionization mass spectrometry (TIMS) in early studies (Balsiger et al., 1969; Balsiger et al., 1976; Pelly et al., 1970). Because of large uncertainty of V isotopes measurement (>1‰), no isotope difference between terrestrial matters and meteoritic samples could be observed at that time. However, chromatographic experiments have implied that V isotope fractionation would occur at low temperature (Zhang et al., 2003a, 2003b).

Analytical development based on application of MC-ICP-MS over the last two decades has dramatically expanded the feasibility of high-precision stable isotope analyses in the periodic table. However, application of V isotope geochemistry is still in its infancy. The main obstacles to precise and accurate V isotope measurements by MC-ICP-MS include: (1) the double-spike method cannot be applied to correct the instrument fractionation of V isotopes because V only has two stable isotopes; (2) the high $^{51}V/^{50}V$ (~400) makes it difficult simultaneously to obtain stable signals for both ^{51}V and ^{50}V in MC-ICP-MS; (3) isobaric interferences from ^{50}Ti and ^{50}Cr on the minor ^{50}V isotope mean that the chemistry has to separate those elements effectively; and (4) multi-atom molecular interferences (e.g., $^{36}Ar^{14}N^+$, $^{36}Ar^{16}O^+$, $^{38}Ar^{14}N^+$) could produce erroneous isotope data.

Recently, highly precise and accurate V isotope data have been obtained with analysis precision better than ±0.15‰ (2 SD) (Nielsen et al., 2011; Prytulak et al., 2011). Vanadium isotopic data were reported in standard δ-notation in per mil relative to the AA V standard solution (Nielsen et al., 2011): $\delta^{51}V = 1000 \times [(^{51}V/^{50}V_{sample} / {}^{51}V/^{50}V_{AA}) - 1]$. Studies on mantle xenoliths and mafic lavas gave an estimation of the V isotopic composition of the BSE, showing that V isotopes can be fractionated during high-temperature mantle-melting processes (Prytulak et al., 2013). Vanadium isotope measurements of meteorites indicate that the silicate Earth is enriched in ^{51}V by about 0.8‰ relative to chondrites, likely reflecting the different irradiation history of the Solar System (Nielsen et al., 2014). More recently, up to ~1.5‰ variation of $\delta^{51}V$ was observed in crude oils, implying the potential application of V isotope to constraining the biogeochemical cycling of V and understanding the formation and preservation of petroleum source rocks (Ventura et al., 2015).

Despite the development of V isotope measurement with MC-ICP-MS, a more efficient procedure for chemical separation of V is needed to explore V isotope variations in nature. Application of V isotope geochemistry to high-temperature processes requires to further improvement in the analytical precision. Furthermore, there is still a lack of adequate V isotope data of reference materials for inter-lab comparison.

In this study, we present a method to measure V isotopes using MC-ICP-MS by the sample-standard bracketing technique. A chemical procedure of V purification modified after Nielsen et al. (2011) improves the time efficiency and eliminates the use of expensive TRU Spec resin. The increase in instrument sensitivity greatly reduces the abundance requirement of V for isotope analysis. We measured V isotopic compositions of 12 reference materials rock standards including 10 igneous rock standards from the United States Geological Survey (USGS) and the Geological Survey of Japan (GSJ) and two manganese nodule standards from the USGS. The reference values for these geological reference materials are helpful for future inter-lab calibration and data quality control. Based on replicated analyses of solution standards and rock standards, our long-term external reproducibility for $\delta^{51}V$ is better than ±0.1‰ (2 SD).

2. Analytical methods

2.1. Sample dissolution

Chemistry purification was carried out in a class 1000 clean laboratory equipped with class 100 laminar flow exhaust hood. All concentrated high-purity acids (HCl, HNO_3 and HF) were made through double sub-boiling distillation of the trace grade acids from Thermo Fisher Scientific. Hydrogen peroxide (30% v/v, ultrapure, AUECC) and ultrapure water (18.2 MΩ·cm) were used during the experiment. Vanadium concentrations in the analyzed reference materials vary from ~50 to ~800 ppm. 20–100 mg samples were weighed to contain 5–10 μg V for isotopic analysis. The igneous rock standards were digested in a 3:1 (v/v) mixture of concentrated HF and HNO_3 in Savillex screw-top beakers by heating at 140 °C on a hotplate for about 3–4 days. After evaporation to dryness, samples were treated with aqua regia, 6 mol L^{-1} HCl, and 8 mol L^{-1} HNO_3 in sequence and dried to remove any remaining fluorides. For manganese nodules/crusts, samples were first treated with aqua regia in Savillex screw-top beakers by heating at 120 °C on a hotplate for about two days. After evaporation to dryness, samples were dissolved with a 3:1 (v/v) mixture of concentrated HF and HNO_3 to digest the remaining oxide and silicate phases. Then, aqua regia and 8 mol L^{-1} HNO_3 were used to ensure that samples were totally dissolved. The final material was dissolved in 1 mL of 1 mol L^{-1} HNO_3 for ion-exchange separation.

2.2. Ion-exchange chromatography

In this study, chemical separation of V was achieved in a multi-step ion-exchange procedure by coupling cation- and anion-exchange columns (Table 1).

2.2.1. Cation resin procedure

Vanadium purification was first performed in a pre-cleaned Bio-Rad Poly-Prep chromatography column (9 cm high and 2 mL bed volume) loaded with 2 mL of Bio-Rad AG50W-X12 (200–400 mesh) cation resin. Fig. 1 shows the elution curves for our V purification procedures. The cation-exchange resin column was used to remove Fe, Ti, and some major matrix elements (e.g., Al, Ca, Mn, and Cr). Before loading the resin into the columns, it was cleaned by rinsing and shaking with 6 mol L^{-1} HCl and H_2O alternately for more than twice, and then 1 mol L^{-1} HNO_3 and H_2O alternately at least twice. In addition, the loaded cation resin was cleaned with 20 mL 6 mol L^{-1} HCl and 10 mL H_2O in sequence, and then conditioned with 3 mL 1 mol L^{-1} HNO_3 twice prior to any use. The sample solution with 5–10 μg V in 1 mL 1 mol L^{-1} HNO_3 was then loaded on the conditioned cation-exchange column. 4 mL of 1 mol L^{-1} HNO_3 + 0.1 mol L^{-1} HF and 1 mL 1.2 N HNO_3 were used to elute Ti and Al. Vanadium was then collected with 19 mL 1.2 mol L^{-1} HNO_3. After this step, most matrix elements (e.g., Fe, Ca, most Mn, and Cr) were still retained on the column while V was quantitatively eluted. In general, such a cation-exchange procedure was run twice to ensure that Fe and Ti were totally removed.

Elution curves can shift with variations in the amount of target element loaded to the column (e.g., An et al., 2014). To achieve a 100% recovery rate of V for different type of samples, it is necessary to test if V elution curves drift with various loading sizes. As shown in Fig. 2, although elution curves of V shift with different amounts of V, 100% recovery rate of V could be achieved if no more than 10 μg V was loaded to the column. Besides, for each sample the aliquots before and after the "V-cut" were collected to monitor V leakage during the chromatography process. After such a cation-exchange procedure, the sample was evaporated to dryness and dissolved in 1 mL dilute HCl (<0.01 mol L^{-1}; pH 2–3). Because K, Na and Mg are the main matrix elements remaining after the cation-exchange procedures, it is easy to dissolve the sample completely in dilute HCl (<0.01 mol L^{-1}; pH 2–3), avoiding the somewhat time-consuming operation described by Prytulak et al. (2011). This step is important for the next anion-exchange step, which separates V from most other matrix elements.

2.2.2. Anion resin procedure

Further purification of V was achieved through anion-exchange columns. The procedure was modified after Nielsen et al. (2011) to remove residual matrix compounds (such as K, Na, Mg, and trace Cr). A pre-cleaned Bio-Rad Poly-Prep chromatography column (9 cm high and 2 mL bed volume) was filled with 1.4 mL of Bio-Rad AG1-X8