

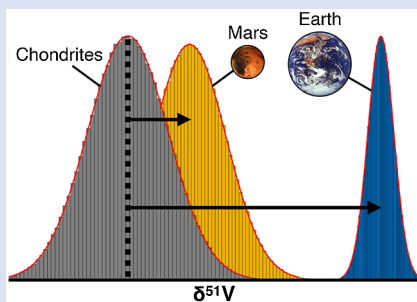
The vanadium isotope composition of Mars: implications for planetary differentiation in the early solar system

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doi: 10.7185/geochemlet.2032

Abstract



constitutes a powerful new tracer of planetary differentiation processes across the Solar System.

The V isotope composition of martian meteorites reveals that Bulk Silicate Mars (BSM) is characterised by $\delta^{51}\text{V} = -1.026 \pm 0.029 \text{ ‰}$ (2 s.e.) and is thus $\sim 0.06 \text{ ‰}$ heavier than chondrites and $\sim 0.17 \text{ ‰}$ lighter than Bulk Silicate Earth (BSE). Based on the invariant V isotope compositions of all chondrite groups, the heavier V isotope compositions of BSE and BSM relative to chondrites are unlikely to originate from mass independent isotope effects or evaporation/condensation processes in the early Solar System. These differences are best accounted for by mass dependent fractionation during core formation. Assuming that bulk Earth and Mars both have a chondritic V isotopic composition, mass balance considerations reveal V isotope fractionation factors $\Delta^{51}\text{V}_{\text{core-mantle}}$ as substantial as -0.6 ‰ for both planets. This suggests that V isotope systematics in terrestrial and extraterrestrial rocks potentially

Received 29 April 2020 | Accepted 29 June 2020 | Published 30 September 2020

Introduction

Vanadium is a refractory and moderately siderophile element with the two naturally occurring isotopes ^{51}V and ^{50}V . Variations of $^{51}\text{V}/^{50}\text{V}$ reported for terrestrial and extraterrestrial samples have been attributed to various processes, such as heterogeneous distribution of nucleosynthetically produced V (Nielsen *et al.*, 2019), kinetic and equilibrium mass dependent isotope fractionation during condensation from the protosolar nebula (Wu *et al.*, 2015; Nielsen *et al.*, 2019), early irradiation by solar irradiation (Lee *et al.*, 1998; Gounelle *et al.*, 2006; Sossi *et al.*, 2017), exposure of meteoroids to galactic cosmic rays (GCR) during their transition to Earth (Hopkins *et al.*, 2019), and/or magmatic differentiation (Prytulak *et al.*, 2017). Since V has only two isotopes, it is difficult to discriminate among the different processes that can lead to V isotope variations in geological material. Therefore, additional constraints are needed to interpret V isotope signatures in cosmochemical and geochemical contexts. To further explore the origin of $\delta^{51}\text{V}$ variations (where $\delta^{51}\text{V}_{\text{sample}} = ((^{51}\text{V}/^{50}\text{V})_{\text{sample}} / (^{51}\text{V}/^{50}\text{V})_{\text{AA}} - 1) \times 1000$, with AA being the Alfa Aesar reference solution) among terrestrial planets, a comprehensive set of V isotope data for martian meteorites was obtained. These data are compared with the value for chondrites of $\delta^{51}\text{V} = -1.089 \pm 0.029 \text{ ‰}$ (2 s.e.) (see Supplementary Information) to provide additional constraints on potential accretionary sources for Mars, and to investigate the possible mechanisms of V isotope fractionation during planetary differentiation and igneous processes.

Results and Discussion

The 24 martian meteorites investigated here represent a petrologic range of shergottites (basaltic, olivine-phyric, lherzolitic), clinopyroxene-rich cumulates (nakhilites) and orthopyroxenite (Table 1). The measured $\delta^{51}\text{V}$ for martian meteorites display a rather restricted range of values from -1.25 to -0.89 ‰ (Table 1) with a mean of $\delta^{51}\text{V} = -1.043 \pm 0.034 \text{ ‰}$ (2 s.e.). Due to their young exposure ages and relatively low Fe/V ratios most samples require very minor, if any, correction for spallation by GCR (see Supplementary Information). Corrected $\delta^{51}\text{V}$ values are all within error of each other and show no correlation with petrologic type or indicators of melting or fractional crystallisation (Fig. 1). Pooled data for the different martian meteorite groups yield indistinguishable mean $\delta^{51}\text{V}$ (Table 1; Supplementary Information), further supporting a limited effect of magmatic processes, such as partial melting and fractional crystallisation, on V isotopes. This inference is consistent with the absence of discernible, systematic $\delta^{51}\text{V}$ variations among terrestrial peridotites and basalts (see Supplementary Information), as well as lunar rock data corrected for GCR effects (Hopkins *et al.*, 2019).

Invariant V isotope compositions recorded in martian meteorites collectively indicate that BSM (and by analogy BSE) inherited its $\delta^{51}\text{V}$ signature during its accretion and/or differentiation history. Here, the GCR corrected and error weighted average V isotope composition of martian meteorites (Table 1) is used to derive the best estimate for the V isotope source signature of BSM, which yields $\delta^{51}\text{V} = -1.026 \pm 0.027 \text{ ‰}$

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Table 1 Vanadium isotope data for martian meteorites.

Sample	Fe ^s (mg/g)	V ^s (μg/g)	CRE age [†] (Ma)	δ ⁵¹ V _{meas}	2 s.d.	splits	n	δ ⁵¹ V _{corr} [§]
<i>Basaltic shergottites</i>								
Los Angeles 001	224	258	3.0	−0.95	0.12	3	8	−0.94
NWA 856	132	273	2.6	−0.94	0.13	1	10	−0.94
NWA 4864	153	325	3.0	−1.11	0.23	3	8	−1.10
Shergotty	173	310	3.0	−0.89	0.19	2	8	−0.89
Zagami	141	312	3.0	−1.15	0.23	2	14	<u>−1.14</u>
Error weighted group average								<u>−0.97</u>
<i>Olivine-phyric shergottites</i>								
EETA 79001 A	143	210	0.7	−1.02	0.19	2	6	−1.02
SaU 005	143	196	1.2	−1.12	0.24	2	14	−1.12
SaU 051	150	204	1.2	−1.03	0.21	2	11	−1.03
SaU 094	149	212	1.2	−1.11	0.20	2	4	−1.11
NWA 1068	155	207	2.8	−1.11	0.16	6	22	−1.10
LAR 06319	159	202	3.3	−1.04	0.16	2	5	−1.03
Y-980459	144	213	1.1	−1.00	0.09	1	4	−1.00
NWA 4925	149	181	0.6	−0.98	0.19	3	9	−0.98
NWA 6162	142	112	1.0	−0.90	0.15	1	4	−0.89
DaG476	122	167	1.0	−1.09	0.13	3	11	−1.09
RBT 04262	201	212	2.1	−1.04	0.06	1	3	<u>−1.04</u>
Error weighted group average								<u>−1.03</u>
<i>Lherzolitic shergottites</i>								
ALH 77005	156	162	4.3	−1.11	0.12	3	11	−1.10
NWA 1950	168	140	4.1	−1.00	0.10	2	9	−0.99
Y-000097	155	180	4.6	−1.01	0.14	1	4	<u>−1.00</u>
Error weighted group average								<u>−1.03</u>
<i>Nakhlites</i>								
Nakhla	160	192	11.6	−1.25	0.19	1	5	−1.23
MIL 03346	137	195	9.5	−1.08	0.14	2	6	−1.07
NWA 817	154	181	10.0	−0.98	0.15	1	2	−0.96
Y-000593	117	125	11.8	−1.03	0.22	1	7	<u>−1.01</u>
Error weighted group average								<u>−1.06</u>
<i>Orthopyroxenite</i>								
ALH 84001	136	201	14.7	−1.09	0.15	1	4	−1.07
Error weighted average Mars								<u>−1.026</u>
2 s.e.								<u>0.027</u>
MSWD								<u>0.991</u>

^s Iron and V concentrations are either from the literature (in italics; Lodders, 1998; Dreibus *et al.*, 2000; Sautter *et al.*, 2002; Gillet *et al.*, 2005; Basu Sarbadhikari *et al.*, 2009; Shirai and Ebihara, 2009; Kuehner *et al.*, 2011), measured by ICPMS at WHOI (bold), or estimated based on yield during column chemistry.

[†] CRE ages from Eugster *et al.* (2002), Mathew *et al.* (2003), Christen *et al.* (2005), Nagao and Park (2008), Nagao *et al.* (2008), Nishiizumi *et al.* (2011) and Wieler *et al.* (2016) except for NWA4864, which is assumed similar to the other basaltic shergottites.

[§] Vanadium isotope compositions corrected for spallogenic production of ⁵⁰V using the equation: δ⁵¹V_{corr} = δ⁵¹V_{meas} + [Fe] × CRE × 2.1 × 10^{−6}/[V] (Hopkins *et al.*, 2019).

(2 s.e., MSWD = 0.99). This value is markedly different from the mean δ⁵¹V of BSE (−0.856 ± 0.020 ‰, 2 s.e.). Understanding the cause(s) of V isotope variations among terrestrial planets could potentially provide constraints on the accretion history and building blocks of Earth and Mars, as well as isotopic effects during planetary differentiation. In the following, we explore possible explanations for the V isotope difference between Mars and chondrites, and discuss the implications for how BSM and BSE could have acquired their V isotope compositions.

Whereas stable isotope systems such as Mg, Si, Ca, and Fe in martian samples (Armytage *et al.*, 2011; Magna *et al.*, 2015; Sossi *et al.*, 2016; Hin *et al.*, 2017; Magna *et al.*, 2017) show only

limited, if any, deviations from chondritic values, large nucleosynthetic isotope anomalies have been observed for many other elements in chondrites and planetary materials including Mars (*e.g.*, ⁵⁴Cr, ⁵⁰Ti, ¹⁷O, ⁶²Ni; Warren, 2011). Given that Mars likely accreted very rapidly and early relative to Earth (Dauphas and Pourmand, 2011), the V isotope difference between Mars and Earth could denote primary spatial variability and/or temporal evolution of the nucleosynthetic V isotope composition of planetary accretion source material in the inner Solar System (*e.g.*, Warren, 2011). However, although V isotope compositions of bulk carbonaceous chondrites have been proposed to correlate broadly with nucleosynthetic anomalies of ⁵⁴Cr (Nielsen *et al.*, 2019), subsequent studies have found that the V isotope

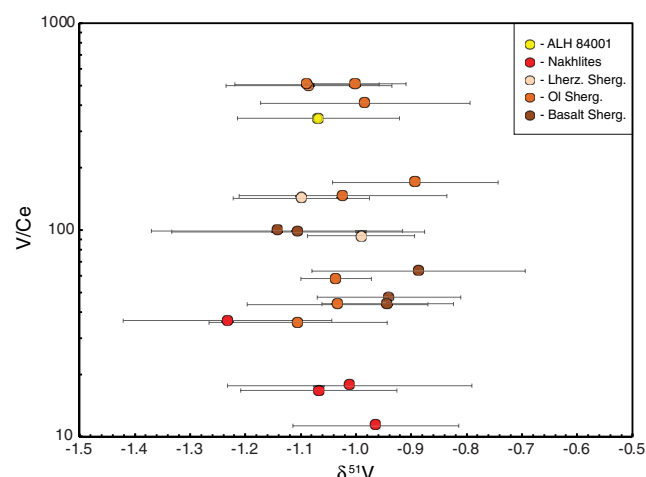


Figure 1 Martian meteorite vanadium isotopic data corrected for GCR effects plotted against V/Ce ratios. Error bars are 2 s.d. as listed in Table 1. Given that V and Ce have different partition coefficients during fractional crystallisation and melting, variations in V/Ce likely reflect a combination of these processes. The lack of systematic V isotope variation over the entire range of V/Ce implies that magmatic processes did not induce detectable V isotope variation on Mars. Ce concentrations from Yoshizaki and McDonough (2020); V concentrations from Table 1. Note log scale on y axis.

variation in bulk chondrites can be ascribed to recent production of ^{50}V from GCR spallation processes (Hopkins *et al.*, 2019). Carbonaceous, ordinary, enstatite and Rumuruti chondrite data corrected for this effect all display uniform $\delta^{51}\text{V} = -1.089 \pm 0.029$ ‰ (n = 14, 2 s.e.; see Supplementary Information). The lack of V isotope variation in chondrites compared with the large variations in *e.g.*, ^{54}Cr and ^{50}Ti implies that nucleosynthetic V isotope anomalies, if they exist, are unlikely to induce planetary scale V isotope heterogeneity. Similarly, irradiation processes are unlikely to account for planetary V isotope variations given the large abundance variations of CAIs, the most likely carriers of irradiation-induced V isotope anomalies (Sossi *et al.*, 2017), in chondrites that display uniform bulk V isotope compositions. For these reasons, V isotope variations among terrestrial planets most likely do not reflect disparities in the signatures of their accretionary materials, but are the result of planetary processes.

Although BSE has a markedly heavier composition than other solar system bodies, there are still analytically significant differences between BSM and chondrites (Fig. 2). Two sample *t* tests demonstrate that the datasets of the BSM and chondrites are characterised by statistically distinct means (see Supplementary Information). Monte Carlo simulations using the raw datasets of the BSM and chondrites that include the individual sample errors show that there exists a difference of 0.058 ± 0.051 ‰ (1 s.d.) between these two populations, with a probability of ~87 % that the V isotope composition of the BSM is heavier than that of chondrites. Using the mean $\delta^{51}\text{V}$ compositions of the BSM and chondrites, instead of the raw data, to compute these Monte Carlo simulations yields a systematic difference of 0.067 ± 0.042 ‰ (1 s.d.) between BSM and chondrites. In the likely absence of mass independent V isotope effects (nucleosynthetic or irradiation-related) on the planetary scale, we propose that the most straightforward explanation for the V isotope disparity between differentiated (Earth, Mars) and non-differentiated (chondrites) bodies corresponds to small but non-negligible isotopic fractionation during core formation.

Considering that (i) the martian core comprises ~18 % by mass of the planet (Yoshizaki and McDonough, 2020),

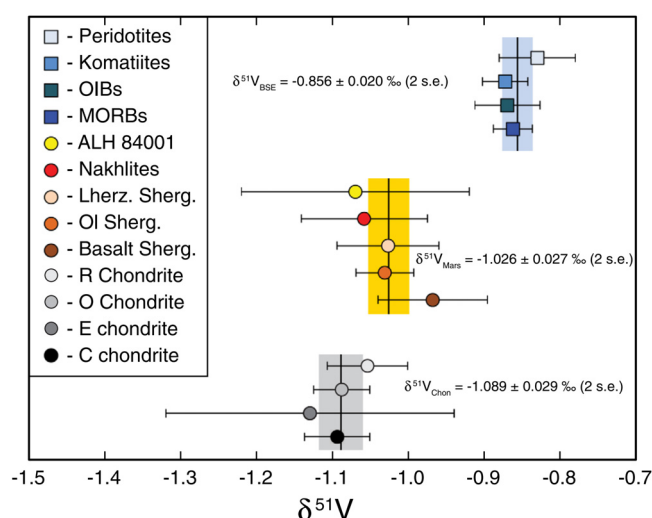


Figure 2 Vanadium isotope data for different sample types from the Solar System. Data for terrestrial samples are from Prytulak *et al.* (2013), Wu *et al.* (2018) and Qi *et al.* (2019); chondrite data are from Nielsen *et al.*, (2019) and this study (Table S-2). All data have been corrected for spallation-produced ^{50}V . Error bars for each sample group are 2 s.e. weighted by the individual sample error bars shown in Table 1. Shaded areas denote the average for those objects and error weighted 2 s.e. of the entire data population. Chondrite averages have been weighted by individual measurement errors.

(ii) ~27–60 % of martian V resides in the core (see Supplementary Information), and (iii) $\Delta^{51}\text{V}_{\text{BSM-chondrites}} = 0.067 \pm 0.042$ ‰, the martian core should be characterised by $\delta^{51}\text{V} \sim -1.11$ to -1.38 ‰. This requires a metal-silicate isotope fractionation factor of $\Delta^{51}\text{V}_{\text{core-mantle}} = -0.04$ to -0.40 ‰ (Fig. 3). Regarding BSE, it is generally assumed that the main phase of metal segregation during terrestrial core formation readily accounts for the depletion of V in the silicate Earth (O'Neill, 1991; Chabot and Agee, 2003; Wade and Wood, 2005), with 40–50 % of terrestrial V now residing in the core (*e.g.*, Wade and Wood, 2005). If bulk Earth is taken to be chondritic for V isotopes, then mass balance dictates that the core is characterised by $\delta^{51}\text{V} = -1.39 \pm 0.10$ ‰,

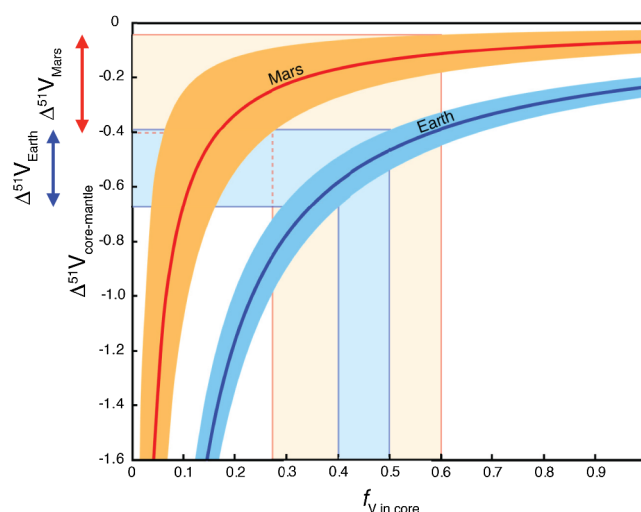


Figure 3 Modelled V isotope fractionation factors between the core and mantle of Earth (blue) and Mars (red) as a function of the fraction of total V that entered the core.

which corresponds to a metal–silicate isotope fractionation factor of $\Delta^{51}\text{V}_{\text{core-mantle}} = -0.53 \pm 0.14 \text{ ‰}$ (using $\Delta^{51}\text{V}_{\text{BSE-chondrites}} = 0.233 \pm 0.037 \text{ ‰}$, 2 s.e.). This value is somewhat larger than that required to explain the BSM–chondrite V isotope offset (Fig. 3), which could imply variations in V isotope fractionation during planetary differentiation.

The metal–silicate isotope fractionation factor required to satisfy V geochemical constraints ($\Delta^{51}\text{V}_{\text{metal-silicate}}$ up to -0.6 ‰) is substantially larger than values found for other redox sensitive stable isotope systems like Mo, Fe and Cr (all $<0.1 \text{ ‰}$; Hin *et al.* (2013), Bonnand *et al.* (2016), and Elardo *et al.* (2019)). A small core–mantle isotope fractionation factor for V is also suggested by the only available investigation of V isotope fractionation during metal–silicate partitioning, where experiments at 1.5 GPa and $\sim 1900 \text{ K}$ revealed no detectable V isotope fractionation outside the analytical uncertainty ($\sim \pm 0.2 \text{ ‰}$; Nielsen *et al.*, 2014). However, Earth's core likely formed through a complex, multi-stage process, starting as a reduced body that gradually evolved to more oxidised as Earth grew (e.g., Wade and Wood, 2005), with a final stage of core segregation in the form of immiscible metal and sulfide melts after the Moon-forming giant impact (e.g., O'Neill, 1991). Additional experiments of V isotopic partitioning at higher pressure–temperature conditions, for variable oxygen fugacities and/or chemical compositions (e.g., presence or not of light elements and other metal alloys) are needed to test the hypothesis of V isotope fractionation during core formation. Such effects have, for example, been observed for Fe isotopes (Elardo *et al.*, 2019). Notably, the sensitivity of V valence state to the oxygen fugacity during core formation offers a promising alternative for potentially inducing significant V isotope fractionation during metal–silicate partitioning. For example, the oxygen fugacity during core formation on Mars and Earth were likely different (Wood *et al.*, 2006) and may have been a contributing factor in the apparent V isotope fractionation difference between these two planets.

One outstanding challenge is to explain the strikingly heavy V isotope composition of BSE compared to BSM. Future experimental investigations may shed light on the possibility for higher temperatures and pressures during terrestrial core formation, and/or late segregation of the Hadean matte (which seemingly did not happen on Mars) to account for this difference. Based on current constraints, it appears that the late stage sulfide segregation on Earth is unlikely to have removed substantial amounts of V to the core (e.g., Wade and Wood, 2005). We, therefore, consider that the heavy V isotope composition of BSE was most likely established during the main phase of core segregation, before Moon formation. Alternative avenues of investigation to explain the heavy V isotope composition of BSE and BSM may require unusual isotope fractionation processes to operate at the core–mantle boundary, as recently proposed for Fe in the case of thermodiffusion (Lesher *et al.*, 2020). Nonetheless, we speculate that identifying the process(es) responsible for V isotope variations in terrestrial planets will ultimately allow better understanding the conditions of planetary differentiation in the Solar System.

Acknowledgements

This work was funded by NASA Emerging Worlds grant NNX16AD36G to SGN. Samples were acquired with funds from the Helmholtz Association through the research alliance HA 203 “Planetary Evolution and Life” to KM. TM contributed through the Strategic Research Plan of the Czech Geological Survey (DKRVO/CGS 2018–2022). KM acknowledges support through NCCR PlanetS supported by the Swiss National Science

Foundation. We thank Jurek Blusztajn for support in the WHOI Plasma Facility.

Editor: Anat Shahar

Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article2032>.



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Cite this letter as: Nielsen, S.G., Bekaert, D.V., Magna, T., Mezger, K., Auro, M. (2020) The vanadium isotope composition of Mars: implications for planetary differentiation in the early solar system. *Geochem. Persp. Let.* 15, 35–39.

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