CONSTRAINTS ON VANADIUM ISOTOPE COMPOSITION OF MARS. David M. Davis[1,2], Sune G. Nielsen[2], Tomas Magna[3], Klaus Mezger[4]

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Introduction: The two stable isotopes of vanadium, ^{50}V and ^{51}V, have natural abundances of 0.24% and 99.76%, respectively. High precision V isotope data for chondrites and the terrestrial mantle [1-5] indicate significant V isotope variability of the Solar System materials expressed as $\delta^{51}V = 1000 \times ((^{51}V/^{50}V_{sample}/ \, ^{51}V/^{50}V_{AlfaAesar}) -1)$ with $\delta^{51}V$ values broadly ranging from −1.3 to −0.7‰. To date it is unclear what the cause(s) of this variance is. It is possible that the isotope composition of V in the Solar System could have been altered by both primordial and more recent irradiation processes that produced ^{50}V from isotopes of Ti, Cr and Fe via spallation[1]. It has also been proposed that high-energy irradiation of proto-planetary material in the solar nebula might have played a role in generating V isotope heterogeneity in the Solar System [6-8]. One notable limitation is that there are only two stable isotopes of vanadium, meaning that it is not possible to directly distinguish between processes that cause mass dependent and mass independent isotopic variations such as stable isotope fractionation, spallation, and stellar nucleosynthesis. Consequently, the observed V isotope variations could theoretically be explained by one or several of the following processes: 1) stable isotope fractionation during planetary core formation, 2) incomplete condensation or evaporation of V during planetesimal formation 3) stable isotope fractionation during igneous processing, possibly followed by impact erosion, 4) stable isotope fractionation during V redistribution caused by parent body metamorphism/metasomatism, 5) heterogeneous distribution of irradiated material in the solar system, and 6) heterogeneous distribution of nucleosynthetically anomalous material.

Here, we present V isotope data for a suite of 25 Martian meteorites in order to constrain the V isotope composition of Bulk Silicate Mars and, if possible, put the data in the context of the different hypotheses for the origin of V isotopes variability in Solar System materials.

Methods: Prior to mass spectrometry, samples were dissolved using double distilled concentrated mineral acids HF, HNO_3, HCl. Vanadium was separated from sample matrix by a four-step cation/anion exchange chromatography procedure [9, 10]. V isotope ratios were measured using a Neptune MC-ICPMS; housed at the Plasma Mass Spectrometry Facility of the Woods Hole Oceanographic Institution (WHOI). Isotope compositions were calculated using standard-sample bracketing against the Alfa Aesar reference standard that has $\delta^{51}V = 0$‰. Each unknown sample was interspersed with the reference standard from BDH Chemicals that has now been measured in four different labs with the identical result of $\delta^{51}V = -1.2$‰ [5, 6, 8, 9]. The mass spectrometer was operated in a medium resolution mode, which ensured that all significant polyatomic isobaric interferences in the mass spectrum (^{48}Ti, ^{49}Ti, ^{50}V, ^{51}V, ^{52}Cr and ^{53}Cr) were resolved from the isotopes of interest [11]. ^{51}V was collected using a Faraday cup equipped with a 10^{10} Ω resistor, whereas Faraday cups with conventional 10^{11} Ω resistors were used for all other masses. Samples and standards measured had a V concentration of 600-800 ng/ml, which produced an ion beam of ~2 nA on ^{51}V and ~0.005 nA on ^{50}V. The method consumed about 300 ng per analysis and yielded an external precision of ~0.15‰ (2sd), which was assessed on the basis of repeat measurements of USGS reference materials AGV-2 and BCR-2 that have also been analyzed in previous studies [7-10]. All samples were measured multiple times (between 34 and 24 individual measurements) and most samples were processed as two separate splits that were taken independently through the chemical separation procedure.

Results and Discussion: The analyzed Martian meteorite samples cover all major lithological types (shergottites, nakhlites, chassignites, cumulate orthopyroxenite ALH 84001). Martian meteorites show a range $\delta^{51}V$ from $\delta^{51}V = -1.3$ to −0.9‰ with average $\delta^{51}V = -1.07\pm0.04$‰ (2se). There are no clear systematic V isotope differences between different types of SNC meteorites (shergottites, nakhlites and chassignites). However, there is a correlation between $\delta^{51}V$ values and aluminum (Al_2O_3) contents of ultramafic samples (lherzolites, pyroxenites and dunites) whereby the lightest V isotope compositions are observed at the lowest (Al_2O_3) concentrations(Fig. 1). A similar correlation with roughly the same slope has also been observed for terrestrial peridotites [5]. The process responsible for generating the V isotope variation in ultramafic samples is currently unclear, but could be

related to isotope fractionation during melting and/or fractional crystallization [5]. Irrespective of the ultimate reason, it appears that this process operates on both Earth and Mars causing V isotope fractionation of a similar magnitude.
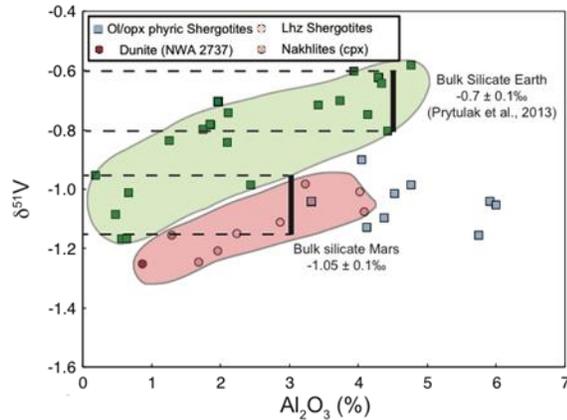

Fig. 1: $\delta^{51}V$ versus bulk-rock Al_2O_3 contents in Martian meteorites (lherzolites, pyroxenites, dunites) and terrestrial samples.

The two trends are offset from each other by about 0.3‰. More melt-like shergottites also display V isotope compositions ($\delta^{51}V \sim -1.1$‰) that are significantly lighter than terrestrial mantle derived basalts ($\delta^{51}V \sim -0.9$‰) at similar Al_2O_3 contents [12]. Given that the vast majority of V in both Mars and Earth resides in their mantles and that most evidence suggests these to have relatively high (Al_2O_3) concentrations [5], we use literature estimates for the (Al_2O_3) concentrations in the mantles of Earth and Mars (4.45% and 2.9%, respectively) [13, 14] to estimate the V isotope compositions of bulk silicate Mars and Earth (BSM and BSE) based on the correlations in Fig.1. These estimates yield $\delta^{51}V_{BSE} = -0.70\pm0.10$‰ and $\delta^{51}V_{BSM} = -1.05\pm0.10$‰, which implies that the silicate portions of the two planets have distinct V isotope compositions at bulk planetary scales and that the light V isotope composition of BSM is an intrinsic feature of Mars (and not merely an observation related to the sample suite investigated).

It is notable that the V isotope composition of BSM is within error of that found for chondritic meteorites, which are characterized by $\delta^{51}V = -1.20$‰ ± 0.22‰ (2sd) [5]. This similarity suggests that silicate Mars is broadly chondritic in terms of V isotope composition, in agreement with previous models of its bulk composition and accretion time scales [13, 15]. As such, it appears most likely that core formation on Mars was not associated with detectable V isotope fractionation, which is consistent with previously pub-

lished metal-silicate partitioning experiments that revealed no discernible V isotope fractionation [1].

Earth, however, does not appear to have any meteoritic equivalent in terms of V isotopes, which either implies that the higher pressure of terrestrial core formation compared to Mars induced significant V isotope fractionation, or that the material that accreted to form Earth contained material unusually enriched in ^{51}V.

References:

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