RUBIDIUM ISOTOPE COMPOSITION OF MARS. X.J. Zhang[1], Z. Tian[1], J.M.D. Day[2], F. Moynier[3], and K. Wang[1], [1]Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130, USA (judyzhang@wustl.edu), [2]Scripps Institution of Oceanography, La Jolla, CA 92093, USA. [3]Université de Paris, Institut de Physique du Globe de Paris, CNRS UMR 7154, 1 rue Jussieu, Paris F-75005, France.

Introduction: Differentiated terrestrial bodies such as Earth, Mars, Moon and 4-Vesta exhibit various extents of depletion of volatile elements compared to the Sun, which represents the bulk Solar System [1, 2]. Distinguishing potential early Solar System processes that led to these apparent volatile depletions is crucial for understanding the formation and long-term habitability of terrestrial planets. Isotopic compositions of moderately volatile elements (MVE) such as K, Rb, Zn, and Cu can provide insights on potential processes that determine the volatile budgets of planetary bodies [3-8]. Previous studies have applied K isotopic variations among Earth, Mars, the Moon, and 4-Vesta to suggest that planetary volatile contents result from variable volatile loss processes during planetary accretion [3, 9-10].

Rubidium is a highly incompatible lithophile MVE that is geochemically similar to K. Combined Rb-K isotope variations can provide further constraints on the mechanism of volatile depletion affecting terrestrial planets. Rubidium and K isotopic compositions of Earth, the Moon, and 4-Vesta [4-5] are positively correlated, suggesting that the mass-dependent fractionation related to volatile processes potentially accounts for the K isotopic variations in terrestrial planetary bodies rather than nucleosynthetic anomalies [3]. However, the current Rb isotopic dataset is incomplete. The Rb composition of Mars has not yet been reported likely due to analytical challenges associated with the low Rb abundance in most martian meteorites, small degrees of Rb isotopic fractionation expected between Earth and Mars that requires high analytical precision to distinguish, and difficulties in elemental separation. Here, we present the first dataset of high-precision Rb isotopic composition of a suite of martian meteorites covering major compositional groups along with terrestrial geostandards. These new Rb isotope results, together with isotopes of other MVE in the literature would shed light on the process(es) of volatile depletion for terrestrial planetary bodies.

Samples and Methods: Nine martian meteorites, including 1 basaltic shergottite, 1 olivine-phyric shergottite, 1 picritic shergottite, 5 nakhlites, and 1 basaltic breccia were analyzed for their Rb isotopic composition. One lunar mare ilmenite basalt (12005) was also analyzed for comparison with literature [4-5]. Sample digestion and elemental separation of Rb were completed in the Isotope Cosmochemistry Lab at Washington University. About 50 to 250 milligrams of samples were dissolved using a combination of concentrated HNO_3, HF, and HCl on a hotplate. The chromatography method, which largely follows previous literature [4-5, 11], consists of three steps with AG 50W-X8 (200 to 400 mesh) cation resin columns plus a last step with a Sr-Spec resin column to completely remove K from Rb. The Rb yield after chemical separation was above 94%. The calibration curve of the last step (Sr-Spec resin) is shown in Fig. 1. Matrix elements V (up to 1000% of Rb) and Ti (up to 100% of Rb) can be found in the final cuts. We performed Rb isotopic measurements with V and Ti doping from 10% to 1000% to test potential matrix effects, which are demonstrated to be negligible in the V and Ti range observed in our samples. High-precision Rb isotope analyses were performed using a Thermo Scientific Neptune Plus MC-ICP-MS coupled with an Elemental Scientific APEX omega sample introduction system. Standard sample bracketing was used to correct for the instrumental fractionation. The typical analytical uncertainty (95% c.i.) of this study is about 0.03 ‰. Rb isotopic compositions ($\delta^{87/85}$Rb) are reported relative to the Rb isotopic standard NIST SRM 984.

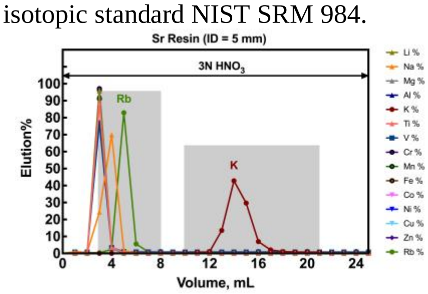

***Figure 1.** The elution curves of Rb and matrix elements. Our method fully separates Rb from K.*

Results: The δ^{87}Rb of terrestrial geostandards AGV-2, BCR-2, BIR-2, and G-2 are measured to be -0.203 ± 0.020‰, -0.143 ± 0.010‰, -0.146 ± 0.018‰, and -0.245 ± 0.013‰ respectively. The δ^{87}Rb of geostandards analyzed in this study agree with literature values (Fig. 2; [4-5]).

Rubidium isotopic variations exist among different compositional groups of martian meteorites (Fig. 2). The δ^{87}Rb of the shergottites measured range from -0.029 to -0.101‰, while the nakhlites have significantly heavier δ^{87}Rb ranging from 0.210 to 0.535‰. The hot desert found basaltic breccia NWA 7034 shows the lightest Rb isotopic composition of -0.212‰.

Discussion: The average δ^{87}Rb of shergottites is estimated to be -0.064 ± 0.092 ‰. There is no difference between different subtypes of shergottites. Since some aqueous alteration evidence (*e.g.*, iddingsite) has been observed for nakhlites [*e.g.*, 12], we use shergottite samples to define the the bulk silicate Mars Rb composition. The δ^{87}Rb Mars is higher than the δ^{87}Rb of -0.12 ± 0.06‰ estimated for the bulk Earth [4], while being lighter than the δ^{87}Rb of the Moon (+0.05 ± 0.12 ‰; [4-5]) as well as the δ^{87}Rb of eucrites (+0.55 ± 0.12‰; [4]). There are positive correlations between δ^{87}Rb and δ^{41}K of Earth, Mars, the Moon, and 4-Vesta (Fig. 3). Both the Rb and K isotopic compositions show strong correlation with the surface gravity of planetary bodies [3]. As the planetary mass and the surface gravity decrease in the order Earth > Mars > Moon > 4-Vesta, the δ^{87}Rb and δ^{41}K values increase. These correlations can be explained by various degrees of volatile loss/retention determined by the final accreted masses. During volatile loss, the heavier isotopes of K and Rb are preferentially retained compared to the lighter isotopes. Therefore, if the mass (*i.e.*, escape velocity) of the planet is smaller, the planet would have experienced more volatile loss that produces heavier δ^{87}Rb and δ^{41}K values. This observation supports the previous studies on K and Zn isotopes [2, 3], which suggests that the depletion of MVE observed in terrestrial planets result from planetary-scale processes, instead of nebular-scale processes (*i.e.*, nucleosynthetic anomalies of planetary building blocks [13] or incomplete condensation), which would not produce strong correlations between K and Rb isotopic composition with planetary surface gravity. We also note there is no correlation between Rb isotopes and the heliocentric distances of the four planetary bodies, which suggests that the Rb isotope variation among these terrestrial planets is not likely to be caused by the mixing of volatile-poor and -rich reservoirs (*i.e.*, inner vs. outer solar system sourced materials).

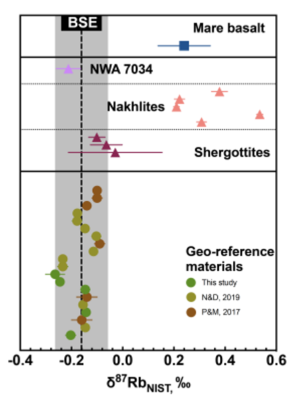

Figure 2. *δ^{87}Rb of martian meteorites, lunar mare basalt and terrestrial geostandards in this study compared to the BSE and literature values [4, 5].*

This is also the first time that distinct Rb isotopic compositions have been observed among different major geochemical subdivisions of martian meteorites (shergottites, nakhlites and basaltic breccia NWA 7034). Several scenarios could account for Rb isotopic variations. One possibility is martian chemical weathering. Previous studies have shown that chemical weathering in terrestrial settings leads to heavier δ^{87}Rb in more chemically altered terrestrial rocks [14]. The same processes on the martian surface could produce stronger effects on nakhlites which underwent low-temperature aqueous alteration (*e.g.*, [12]). However, chemical alteration on Mars at the meantime should also fractionate K isotopes, which has not been observed [3]. Alternatively, nakhlikes and shergottites may sample Martian reservoirs with heterogenous volatile loss histories [15], where Rb, as a trace element, is affected differently relative to K. Future studies are needed to verify this Rb isotopic difference among major geochemical subdivisions of martian meteorites. More data will be presented during the LPSC conference.

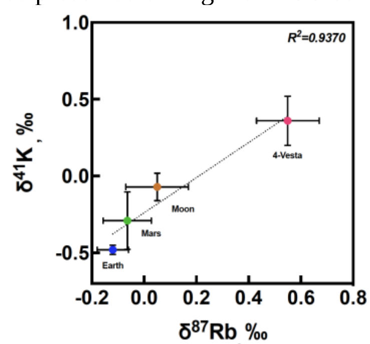

Figure 3. *Average δ^{41}K versus δ^{87}Rb of the four terrestrial bodies (Earth, Mars (shergottites), Moon, and 4-Vesta) [3-5, 8-9].*

Acknowledgments: K. Wang acknowledges support from NASA (Emerging Worlds Program grant #80NSSC21K0379). We also thank Antarctic Search for Meteorites (ANSMET), NASA's Johnson Space Center, the Smithsonian National Museum of Natural History, and the Field Museum of Natural History for kindly providing the samples used in this research.

References: [1] Davis A. (2006) *Meteorites and the early solar system II*, 295-307. [2] Day J.M.D. and Moynier F. (2014) *Phil. Trans. R Soc. A*, 372, 20130259. [3] Tian Z. et al. (2021) *PNAS*, 118, e2101155118. [4] Pringle E. A. and Moynier F. (2017) *EPSL*, 473, 62-70. [5] Nie N. X. and Dauphas N. (2019) *Astrophys. J. Lett.*, 884, L48. [6] Paniello R. C. et al. (2012) *Nature*, 490, 376-379. [7] Moynier F. et al. (2006) *GCA*, 70, 6103-6117. [8] Luck J.M. et al. (2005), *GCA*, 69, 5351-5363. [9] Tian Z. et al. (2019), *GCA*, 266, 611-632. [10] Tian Z. et al. (2020), *GCA*, 280, 263-280. [11] Zhang Z. et al. (2018) *J. Anal. At. Spectrom.*, 33, 322-328. [12] Lee M. R. et al. (2018), *Meteoritics & Planet. Sci.*, 53, 2395-2412. [13] Ku Y. and Jacobsen S. B. (2020) *Sci. Adv.*, 6, eabd0511. [14] Zhang Z. et al. (2021) *GCA*, 313, 99-115. [15] Udry A. et al. (2020) *JGR Planets*, 125, e2020JE006523.