POTASSIUM ISOTOPE COMPOSITION OF MARS REVEALS A MECHANISM OF PLANETARY VOLATILE RETENTION.

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Introduction: From the first fly-by space probes to the more recent ‘Perseverance’ and ‘Tianwen-1’ missions, “follow the water”, and more broadly “volatiles”, is one of the key themes of martian exploration. The ratio of the volatile element K over the refractory elements (Th, U) is commonly used as a proxy for the volatile depletion of terrestrial planets. Using elemental abundances derived from martian meteorites and spacecraft data, earlier studies set a paradigm of a volatile-, water-, and OH-rich Mars compared to the Earth [1, and refs. therein]. Nonetheless, inherent difficulties in determining the volatile budget of bulk silicate Mars (BSM), as well as the inconsistency between GRS data and meteorite measurements in terms of their K/Th, make it challenging to deduce the volatile inventories of bulk Mars and to directly compare the volatile depletions among differentiated bodies in the Solar System.

Here, we provide an alternative for evaluating the nature of volatiles on Mars using K isotopes. Systematic volatile depletions among terrestrial planets have long been recognized, yet the mechanisms for such depletions remain unsettled (*e.g.,* nebular-scale partial evaporation and incomplete condensation and accretion of nebular components versus planetary-scale volatile loss during accretion or a magma ocean phase [2]). New K isotope data obtained from martian meteorites have fundamental implications for mechanism(s) of volatile retention for planets.

Samples and Methods: Twenty martian meteorites (23 subsamples) were analyzed here, covering several geochemical and petrological types: 2 basaltic shergottites, 3 lherzolitic shergottites, 5 olivine-phyric shergottites, 1 picritic shergottite, 7 nakhlites, 1 chassignite, and 1 basaltic regolith breccia.

The detailed sample dissolution and chemical purification procedures via ion-exchange chromatography were described elsewhere [3]. High-precision K isotope analyses were performed using a Thermo Scientific Neptune Plus MC-ICP-MS, coupled with an Elemental Scientific APEX omega sample introduction system, which enhances signal intensities while suppressing the production of hydrides and oxides. A conventional standard-sample-standard bracketing technique was applied. NIST SRM 3141 was used as a reference K isotope material. The internal reproducibility is typically ~ ±0.05‰ (2SE). The long-term reproducibility of ~ ±0.11‰ (2SD) was evaluated from measurements of BHVO-2 over 20 months in different analytical sessions [3].

Results: No systematic differences are observed among different geochemical and petrological subtypes, indicating an isotopically homogeneous K reservoir in Mars. There is no obvious isotopic fractionation during igneous process, as δ^{41}K does not correlate with the corresponding bulk Mg#. One Nakhla subsample shows a clear offset towards lighter δ^{41}K relative to other martian meteorites. Its low K/Al and K/Nb along with elevated Ba/La are suggestive of aqueous modifications of this sample on the martian surface [4].

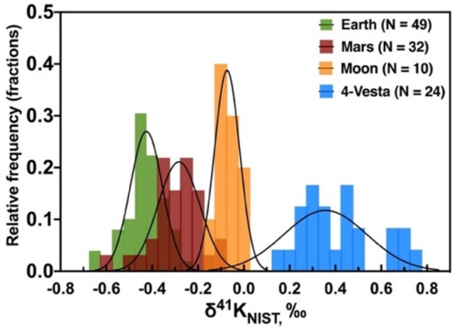

Fig. 1. Histogram and “Summed Gaussian” plot of the δ^{41}K of the four inner Solar System parent bodies studied to date. Data sources:[5-9].

The average δ^{41}K of martian meteorites, excluding the hot desert find NWA 7034 and one isotopically light Nakhla subsample, is –0.28 ± 0.18‰, 2SD (n = 30; this study and [8,9]), and is the current best estimate for the δ^{41}K of BSM. The summed Gaussian distribution *(Fig. 1)* demonstrates the δ^{41}K differences among four differentiated parent bodies: Earth, Mars, Moon, and Vesta. Such differences are statistically significant on the basis of a two-sample Student’s t-test. The δ^{41}K of the BSM is 0.15‰ heavier than that of the BSE (–0.43 ± 0.17‰ [5]), but is 0.21‰ and 0.64‰ lighter than that of the bulk silicate Moon (–0.07 ± 0.09‰ [6]) and Vesta (+0.36 ± 0.16‰ [8]), respectively.

Discussion: The average $\delta^{41}K$ for bulk silicate Earth, Mars, Moon, and Vesta correlate tightly with their surface gravity ($R^2 = 0.995$, *Fig. 2*). The Mn/Na, which serves as an index for accretionary volatilization, also correlates well with the average $\delta^{41}K$ for the four parent bodies ($R^2 = 0.870$, *Fig. 2*) as stronger loss of Na was favored from objects with lower gravity. More importantly, the correlation between parent body gravity and corresponding $\delta^{41}K$ extends to the highly volatile water *(Fig. 3)*. This implies that the water contents and $\delta^{41}K$ may be coupled. A key question is what mechanism(s) tied $\delta^{41}K$ to parent body gravity?

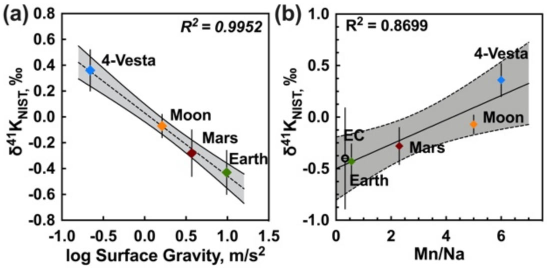

Fig. 2. (a) Average $\delta^{41}K$ of the four bodies versus their corresponding surface gravity. (b) Average $\delta^{41}K$ of enstatite chondrites and the four bodies versus their Mn/Na. Data source:[5-12].

Nebular processes. Nebular-scale partial evaporation or incomplete condensation could potentially shape the K isotope systematics of planetary precursors. Admixing of early-accreted volatile-depleted planetary feedstocks and later-added volatile-rich components would generate variations in $\delta^{41}K$. The tight correlation observed between $\delta^{41}K$ and body gravity is, however, inconsistent with this scenario, as $\delta^{41}K$ heterogeneity in precursors would be expected to produce more scattered $\delta^{41}K$ signals among planetary bodies. A nucleosynthetic anomaly in K that was not homogenized within the protoplanetary disk is another potential cause for $\delta^{41}K$ variations in parent bodies [9]. However, to date known nucleosynthetic isotope anomalies are limited to elements whose 50% T_c are above 1400K [13], and these do not correlate with parent body gravity. Taken together, it is unlikely that $\delta^{41}K$ variations in the inner Solar System stem from nebular processes, and that the correlation with object gravity is mere coincidence.

Planetary-scale processes. Volatile loss and consequent isotopic fractionation during accretion has been used to explain the alkali-budgets of small bodies [14]. A similar concept has also been adopted in simulations of collisional accretion to account for the Mg isotopic composition of the Earth [15]. This model implies that the average $\delta^{41}K$ for bulk silicate planets is attributed to time-integrated volatile depletion during the accretion phase. Nonetheless, the Moon, which uniquely formed by a single-stage collision between the proto-Earth and a Mars-sized impactor, differs in $\delta^{41}K$ from that of Earth. This indicates that regardless of the accretion and differentiation history, the ultimate $\delta^{41}K$ inventory of a bulk planet is determined by its final accreted mass. Large bodies such as Earth and Venus could retain volatiles more efficiently once their sizes exceeded the size threshold required for volatile retention. Small bodies with insufficient surface gravity, in contrast, would allow preferential loss of light K and hence leave the residue isotopically heavy.

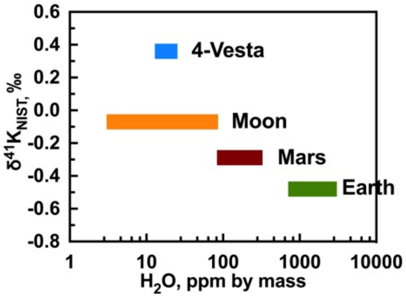

Fig. 3. Average $\delta^{41}K$ of four parent bodies versus their water content estimates. Data source:[5-9, 16].

On the basis of K isotopes, the volatile content of bulk Mars is lower than that of the Earth, and Mars is unlikely to be habitable as it lies at the size threshold to retain sufficient life-sustaining volatiles. This conclusion is at odds with the reigning paradigm that Mars is more volatile-rich than the Earth based on K/Th. Nonetheless, the apparent high K/Th of Mars could result from sampling the highly-differentiated volatile-rich crust. The new K isotopic composition of BSM and the strong correlation between $\delta^{41}K$ and planet gravity could shed light on habitability of planets, and assist with constraining unknown parent body sizes (*e.g.,* angrite and ureilite parent bodies).

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References: [1] Yoshizaki and McDonough (2020), *GCA*, 273, 137-162. [2] Day and Moynier (2014) *Phil. Trans. R Soc. A*, 372, 20130259. [3] Chen et al. (2019) *J. Anal. At. Spectrom.* 34, 160–171. [4] Bunch and Reid (1975) *Meteoritics* 10, 303-315. [5] Tuller-Ross et al. (2019), *GCA*, 259, 144-154. [6] Tian et al. (2020), *GCA*, 280, 263-280. [7] Wang and Jacobsen (2016) *Nature*, 538, 487-490. [8] Tian et al. (2019), *GCA*, 266, 611-632. [9] Ku and Jacobsen (2020), *Sci. Adv.* [10] Zhao et al. (2019), *MAPS*, 55, 1404-1417. [11] O'Neill and Palme (2008), *Phil. Trans. R Soc. A,* 366, 4205-4238. [12] Siebert et al. (2018), *EPSL*, 485, 130-139. [13] Vollstaedt et al. (2020), *Astrophys. J.* 897. [14] Lodders (1994) *Meteoritics*, 29, 492-493. [15] Hin et al. (2017) *Nature*, 549, 511-515. [16] McCubbin and Barnes (2019), *EPSL*, 526, 115771.