Potassium Isotope Cosmochemistry

Zhen Tian

Washington University in St. Louis

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Potassium Isotope Cosmochemistry

by

Zhen Tian

A dissertation presented to
The Graduate School
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

December 2021
St. Louis, Missouri
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ACKNOWLEDGEMENTS

My memory always flashed back to five years ago, when I firstly stepped on this new continent, half an Earth from where I was born and raised, wondering what kind of journey waits ahead. I was fortunate to have professors and colleagues that helped to transform my own interest in cosmochemistry into a deeper understanding. I would like to express my deepest appreciation to my research advisor, Dr. Kun Wang, for his encouragement, patience, belief in my abilities, and a great amount of support throughout my five years of research. I would also like to extend my deepest gratitude to my research committee, Dr. Bradley L. Jolliff, Dr. Bruce Fegley Jr., Dr. Katharina Lodders, and Dr. Ryan Ogliore. The completion of my dissertation would not have been possible without their support and nurturing. I benefited a lot from their unparalleled knowledge and invaluable insight into cosmochemistry and geochemistry.

I would also like to express my sincere thanks to my collaborators from various universities and research institutions: Dr. Heng Chen, Dr. Jean-Alix Barrat, Dr. James M.D. Day, Dr. Randy L. Korotev, Dr. Tomas Magna, Dr. Klaus Mezger, Dr. Erik E. Scherer, Dr. Remco C. Hin, Dr. Piers Koefoed, and Miss Hannah Bloom. I enjoyed our conversations over various projects and scientific questions, or something more general: how we should do science. I had great pleasure working with all of you and even though I have decided to move to a path in industry, your unwavering guidance and constructive criticism are important treasures for me. I would also acknowledge a fellowship from the McDonnell International Academy for the financial support.
Coping with a foreign culture while still performing my best in academia is hard, yet I am lucky to have relentless support from my friends: Lei Chen, Jiayang Chen, Xuan Jiang, Yuanyuan Liang, Zhengyang Zhou, Jinshu Yan, Xiaochen Mao, Chen Cai, Haotian Wang; and peer classmates: Robert Kupper, Kaushik Mitra, Mike Sly, Maddie Hughes, Tim Hahn, Amanda Price. I will never forget the laughter, the tears, those drunk nights when we dreamed about the future, and those thermodynamic jokes. You all are the best things I have here in St. Louis. Spending my last two years in graduate school under a global pandemic is probably the last thing I could imagine, and it indeed has been rough on everyone, including me. Yet hope and joy remain as we stay tight together.

Above all I would like to thank my fiancé Robert Kupper for keeping me sane over the worst times. Thank you for being my magic the gathering mentor, for proofreading my bad writings, and for being my best friend and the joy of my life. I would also like to thank my parents, grandparents, and the whole extended family for the love and support over the past twenty-seven years. Without you I can never come this far and pursue my dreams. This dissertation is dedicated to all the people who love me, and I love.

Zhen Tian

*Washington University in St. Louis*

*December 2021*
ABSTRACT OF THE DISSERTATION

Potassium Isotope Cosmochemistry

by

Zhen Tian

Doctor of Philosophy in Earth and Planetary Science

Washington University in St. Louis, 2021

Professor Kun Wang, Chair

In Chapter 1, I review the geochemical and cosmochemical properties of potassium (K). Classified as a moderately volatile element, K serves as a robust proxy for understanding the key processes during nebular/planetary evaporation events. I review different mechanisms of volatile depletion among various planetary materials: mass-dependent variations in “nebular” processes; mass-independent variations among different nucleosynthetic sources; or planetary-scale volatile depletion processes. Furthermore, I provide an optimized K purification procedure via ion-exchange chromatography and a high-precision K isotope analysis technique using Neptune plus Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) in both “cold plasma” and “dry plasma” methods. I also conduct an inter-laboratory comparison of δ⁴¹K on various instrumentations on geo-reference materials.

In Chapter 2, I apply the high-precision K isotope measurements onto a suite of howardite–eucrite–diogenite (HED) meteorites. The focus on HED meteorites is driven by the evidence for extreme volatile depletion in K and other moderately volatile elements, which is inferred on the basis of its
low K/U. The results show substantial heavy K isotope enrichments among HED meteorites relative to the bulk silicate Earth (+0.36 ± 0.16‰ versus −0.43 ± 0.17‰ for average HEDs and bulk silicate Earth, respectively). I propose that the average K isotopic composition obtained from HED meteorites is representative of bulk silicate 4-Vesta. The significant depletion of moderately volatile element K and its associated K heavy isotope enrichment can be interpreted as either (1) Precursor: 4-Vesta accreted from volatile-poor materials already depleted in volatiles, either through incomplete condensation from the proto-solar nebula or partial re-evaporation in the nebular environment; (2) Accretion: 4-Vesta acquired its volatile depletion and heavy K isotopic feature from the vapor loss during its accretionary growth; or (3) Magma ocean: 4-Vesta experienced volatile degassing during a global and/or in-situ magma ocean phase.

Previous K stable isotope studies largely focused on placing the collected data into the broad framework of lunar volatile depletion as well as the evolution of the Earth-Moon system. Nevertheless, the distribution of K isotope among different reservoirs in the lunar interior and K isotopic fractionation after the Moon-forming Giant Impact event remain loosely constrained. In Chapter 3, I conduct the high-precision K isotope measurements onto a new suite of lunar samples, covering a range in lunar geochemical and petrological diversity. These new data along with data from previous studies provide a comprehensive evaluation of K isotopic composition of the Moon and the processes of volatile redistribution between major reservoirs. I define the K isotopic composition of the bulk silicate Moon as −0.07 ± 0.09‰ (2SD). Furthermore, I interpret the heavy K isotope enrichment in the (or a portion of the) urKREEP reservoir as a natural consequence of extended degassing of K from the late-stage Lunar Magma Ocean (LMO) as the K chloride species.
The complementary isotopically light K-bearing vapor phases condense back onto the lunar surface, causing substantial K isotope variations in lunar nonmare rocks. Nevertheless, the heterogeneous K isotope distribution should not change the K isotopic composition of the bulk silicate Moon, which is well represented by the lunar mantle.

Using spacecraft data and elemental abundances derived from martian meteorites, earlier studies set a paradigm of a volatile- and water-rich Mars relative to Earth. Nevertheless, inherent difficulty in determining the volatile budget of bulk silicate Mars makes it challenging to directly compare the extents of volatile depletions among differentiated bodies in the Solar System. Moreover, the debate about volatile depletion originating in the solar nebula or on planetary bodies has resurfaced quite strongly recently, calling for new isotope proxies. In Chapter 4, I provide an alternative for evaluating the nature of volatiles on Mars as well as mechanisms for planetary volatile retention using K isotopes. Combining available high-precision K isotope data to-date among differentiated planetary bodies, I reveal the role of fundamental physical properties in dictating the degree of volatile loss during planet formation, and thus the K isotopic variability observed. The new K isotopic composition of bulk silicate Mars and the strong correlation between $\delta^{41}$K and planet mass suggest that the planetary body sizes fundamentally control their ability to retain volatiles. This could further shed light on water content and habitability of planets and assist with constraining unknown parent body sizes.
Chapter 1:

Introduction
1.1. Overview

Potassium (K) is a lithophile, highly incompatible, water-soluble Group IA alkali metal. There are three naturally occurring isotopes of K: \(^{39}\text{K}\) (stable, abundance: 93.26%), \(^{40}\text{K}\) (0.0117%, half-life of \(1.248(3) \times 10^9\) yrs \(\text{[Kossert and Günther, 2004]}\)), and \(^{41}\text{K}\) (stable, 6.73%). Potassium preferentially incorporates into the silicates during core-mantle differentiation. Hence, only a few ppm to ~ 40 ppm of K is present in the Earth’s core, which is negligible relative to that in the bulk silicate Earth. \(\text{[e.g., McDonough and Sun, 1995; Corgne et al., 2007; McDonough, 2014; Watanabe et al., 2014; Xiong et al., 2018]}\); although Lodders (1995) proposed a high estimated value of 550 ± 260 ppm K in the Earth core if highly reducing conditions were assumed \(\text{[Lodders and Fegley, 1995]}\). During igneous processes, potassium tends to be quantitatively removed into partial melts as the major mantle mineral assemblage (i.e., olivine and pyroxene) rejects K owing to its large ionic radius. Therefore, the crust is enriched in K relative to the mantle (2.80 wt.% K\(_2\)O in the upper continental crust \(\text{[Rudnick and Gao, 2013]}\) versus 50 to 60 ppm of K in the upper mantle \(\text{[Salters and Stracke, 2004; Workman and Hart, 2005]}\) and 240 ppm of K in the lower mantle \(\text{[McDonough and Sun, 1995]}\); ~ 70% K resides in Earth’s mantle, and the rest of K is contained in the crust reservoir). Potassium is also mobile during chemical weathering, hydrothermal and aqueous alteration, and metasomatism.

The volatility of elements can be evaluated by either 50% condensation temperature (50% \(T_c\)) under cosmochemical gas pressure \(10^{-4}\) bars \(\text{[Lodders, 2003; Fegley and Schaefer, 2010; Wood et al.]}\).
al., 2019), or 1% evaporation temperature from a ferrobasaltic melt at 1 bar and \( \log fO_2 = -10 \) (Sossi et al., 2019). Highly volatile elements are those with 50% \( T_c < 665 \) K; refractory elements are those with 50% \( T_c > 1335 \) K; major elements are those with 50% \( T_c \) between 1250 K and 1335 K; and moderately volatile elements are those with 50% \( T_c \) between 665 K and 1250 K. Potassium (50% \( T_c = 1006 \) K; [Lodders, 2003]) is one of the more abundant moderately volatile elements both in the Solar System (ranked 20\(^{th}\)) (Palme et al., 2014) and in the Earth crust and seawater (ranked 8\(^{th}\)) (Millero, 2003; Rudnick and Gao, 2013). The potassium to Thorium (Th)/Uranium (U) ratio has been widely used to evaluate the degree of volatile depletion among differentiated parent bodies in the inner Solar System relative to CI chondrites (Figure 1.1).

![Figure 1.1](image.png)

**Figure 1.1.** The K/U among different planetary materials normalized to K/U of CI chondrites. The figure is reproduced from (K. Wang et al., 2021).
It is well acknowledged that terrestrial planets, including Earth, Mars, Moon, 4-Vesta, and Angrite Parent Body (APB), are depleted in volatile elements compared to CI chondrites (representative of the initial Solar System composition) (e.g., Taylor, 1982; Lodders and Fegley, 1998; Arevalo et al., 2009; Peplowski et al., 2011; Barrat et al., 2012; Yoshizaki and McDonough, 2020). Yet the mechanism behind such ubiquitous volatile depletion among inner Solar System rocky bodies is unsettled (e.g., Albarède, 2009; Paniello et al., 2012a; Paniello et al., 2012b; Day and Moynier, 2014; Kato et al., 2015; Wang and Jacobsen, 2016b; Norris and Wood, 2017; Siebert et al., 2018; Sossi and Fegley, 2018). The potassium stable isotope system has two advantages that could potentially shed light on this problem. Firstly, K isotopic composition is insensitive to planetary-scale secondary effects such as impact-induced vaporization (e.g., the formation of tektite; [Jiang et al., 2019]) or eruptive degassing (e.g., volcanic eruptions on the lunar surface, [Ni et al., 2019]). Potassium tends to remain in the silicate melt owing to its low activity coefficient during evaporation compared to some other moderately volatile elements with similar 50% Tc (e.g., Cu and Zn). Such relatively “refractory” behavior is supported by thermodynamic calculations (Jiang et al., 2019; Tian et al., 2019), the volatility trend derived from volatile abundances in orange glass melt inclusions (Ni et al., 2019), and a lack of heavy K isotope enrichment (in contrast to elevated $\delta^{66}$Zn and $\delta^{65}$Cu) in tektites (Rodovská et al., 2016; Jiang et al., 2019; Magna et al., 2021). Therefore, K isotope composition is a robust proxy for understanding the primary signatures that have been imprinted by planetary formation events.

Secondly, the K isotopic composition remains constant during igneous processes. Tuller-Ross et al. (2019b) studied whether igneous processes would introduce systematic K isotopic fractionation
by examining a suite of magmatically differentiated samples from Hekla (basalt to rhyolite). The δ⁴¹K variation within this suite of samples is not resolvable under our current laboratory conditions and the average value agrees with that of the bulk silicate Earth, which is defined by a systematic investigation of Mid-Ocean Ridge Basalts (MORB) and Ocean Island basalts (OIB) (Tuller-Ross et al., 2019a). This conclusion is also supported by a new study by (Hu et al., 2021).

In this contribution, we develop the method for high-precision K isotope measurement and apply it onto a variety of planetary materials. We aim to provide a comprehensive evaluation of K isotopic compositions among bulk silicate planets, and from the data, reveal a mechanism of planetary volatile depletion.
1.2. Mechanisms of Volatile Depletion in Planetary Materials

The debate about volatile depletion originating in the solar nebula or on planetary bodies can be traced back to the 60s (Ringwood, 1966a; Ringwood, 1966b), with some arguing that it occurred during incomplete condensation and/or partial evaporation of planetary precursors in the solar nebula, some suggesting that it occurred during planetary-scale volatile loss during accretionary growth, others proposing it happened during the global magma ocean degassing, or a combination of two/all mechanisms (e.g., Humayun and Clayton, 1995a; Albarède, 2009; Day and Moynier, 2014; Dauphas et al., 2015; Hin et al., 2017; Wang et al., 2019; Day et al., 2020; Fegley et al., 2020 and references therein; W. Wang et al., 2021). This debate seemed to settle in favor of volatile depletion being nebular in origin (e.g., Humayun and Clayton, 1995a), where the marginal δ⁴¹K differences could not be distinguished with ~ 0.5‰ analytical uncertainties at the time. They concluded that the chemical depletion of K occurred during the condensation of precursors in the solar nebula for the lack of K isotopic fractionation among different planetary materials.

Yet, the debate has resurfaced quite strongly in the last few years with the recent development of high-precision isotope measurements. Wang and Jacobsen (2016b) reported a ~ 0.4‰ heavy K isotope enrichment in lunar samples relative to the bulk silicate Earth (Tian et al., 2020). The Moon was formed from a single-stage collision between a Mars-sized “Theia” and the proto-Earth. The Earth and the Moon are “twins” in terms of their refractory element isotopic compositions (e.g., Barr, 2016 and references therein), yet the Moon is overall depleted in moderately volatile elements including K (e.g., Cl, Zn, Ga, and Rb, [Herzog et al., 2009; Sharp et al., 2010; Paniello et al., 2012a; Kato et al., 2015; Kato and Moynier, 2017; Pringle and Moynier, 2017; Potts et al.,
The Moon could potentially go through two distinct stages that shaped its K isotopic composition: vapor loss and isotopic fractionation during the accretions of proto-Earth and Theia, followed by the giant impact event that further depleted volatiles, with the giant impact being unique to the Moon. Furthermore, Hin et al. (2017) modelled the fraction of vapor loss for each mass addition during the accretionary growth of Earth by a N-body collisional accretion simulation to account for the heavy Mg isotope enrichment in the bulk silicate Earth.

Sossi et al. (2019) proposed a nebular-scale volatile depletion mechanism in terms of the elemental and isotopic fractionation observed in differentiated bodies: accretion from a distribution of partially evaporated bodies that either retain all volatiles or lose them completely. Such a “binary” system is consistent with the isotopic similarity between the bulk silicate Earth and enstatite chondrites (presumeable Earth building blocks), as δ⁴¹K of the bulk silicate Earth records the isotopic signature of the materials that went through negligible evaporation. New evidence on the light S isotopic signature of Earth also favored a planetesimal volatile evaporation scenario, where they suggested volatile loss from planetesimals prior to planetary formation might play an important role in establishing the volatile inventories of Earth (W. Wang et al., 2021).

The K isotopic compositions of chondrites have been reported recently in (Ku and Jacobsen, 2020; Bloom et al., 2020; Zhao et al., 2020). As shown in Figure 1.2, the range of K isotopic compositions within chondrites vary by ~ 2‰. A combination of parent body alteration and nebular process on precursors are proposed to account for the wide δ⁴¹K range (i.e., aqueous
alteration, thermal metamorphism, and impact vaporization). Bloom et al. (2020) used a chondrule-matrix mixing model (simplified from Alexander, 2019, who used a four-component mixing model to successfully reproduce K elemental abundances in carbonaceous chondrite groups) to explain the observed $\delta^{41}$K variations. On the contrary, Ku and Jacobsen (2020) proposed that a heterogeneous distribution of now extinct $^{41}$Ca (branched decayed to $\delta^{41}$K with a short half-life of $\sim$ 0.1 Ma) in the protoplanetary disk is responsible for such $\delta^{41}$K differences (and perhaps the carbonaceous chondrite – ordinary chondrite $\delta^{41}$K dichotomy). Nevertheless, there is currently no consensus on what has caused such large variation and it is still very uncertain what would be the “average” K isotopic composition for each chondrite group.

The K stable isotope systematics along with other moderately volatile isotope systems could potentially reveal the mechanism in generating the volatile depletion pattern among chondrite groups and differentiated parent bodies in the inner Solar System. Pringle and Moynier (2017) reported a positive trend between Rb isotopic composition and Rb enrichment (i.e., light Rb isotope enrichments with decreasing Rb/Sr) for bulk carbonaceous chondrites. Such isotope evidence contradicts the expectation from partial evaporation of precursors, and further supports that the mixing of isotopically distinct reservoirs results in the Rb isotope range in carbonaceous chondrites. Zinc isotope systematics of carbonaceous chondrites define a similar volatile-depletion array, where the bulk Earth lies at the isotopically light end of this trend. Such correlation, together with the observation that the bulk Earth also lies on the volatile-depleted end of the Mn/Na vs. Mn/Mg space, was used to indicate that the building blocks of the Earth went through similar chemical fractionation processes as the carbonaceous chondrites group in the
solar nebula at least for moderately volatile elements (Sossi et al., 2018). Similar arguments on the basis of elemental ratios were made earlier by (Allège et al., 2001) as well. Nevertheless, such a trend is not observed in K isotopes, as K isotopic compositions among different carbonaceous chondrites groups, as well as the bulk silicate Earth, are indistinguishable from each other within analytical uncertainty (Figure 1.2). Furthermore, there is a lack of correlation between $\delta^{41}$K and $\delta^{66}$Zn/$\delta^{65}$Cu among carbonaceous chondrites (Figure 7 in Bloom et al., 2020). K behaves differently from other moderately volatiles not only under solar nebular conditions, but also during impact-induced vaporization on the Earth and eruptive degassing on the lunar surface.
**Figure 1.2.** Histogram plot of the K isotopic compositions of differentiated parent bodies Mars, the Earth, Moon, and the asteroid 4-Vesta; and undifferentiated planetary materials ordinary, carbonaceous, and enstatite chondrites. Bins for the histogram are in 0.10‰ increments.
1.3 Ion-exchange Chromatographic Separation for K

We applied a two-step ion-exchange chromatography to separate K from other matrix elements, a detailed protocol is provided in Table 1.1, with elution curves of selected elements shown in Figure 1.2 and 1.3. On the basis of K concentration of the target sample, about 10 to 150 mg of homogeneously pulverized sample was dissolved in a concentrated HF-HNO3 mixture (~3:1 vol/vol) either in Teflon beakers or Parr high-pressure digestion vessels, depending on the sample mineralogy. The fully dissolved sample was dried down and refluxed in 6 M HCl under a heating lamp overnight before completely dried down again and ready for the chemical purification procedure. We ensured > 99% K recovery rate during column chemistry by monitoring the pre- and post-cut for any potential K loss.

Ultrapure water (Milli-Q, 18.2 MΩ*cm) and double-distilled HCl and HNO3 were used in sample dissolution and ion-exchange chromatography to reduce blank levels. The total procedure blank is evaluated as 0.26 ± 0.15 µg (2SD; n = 7), with a distinct K isotopic composition of −1.31 ± 0.05‰. The K isotope drift induced by procedure blanks is negligible for all samples in this thesis (see the Section 2.3. in [Chen et al., 2019]).
Table 1.1. Chemical purification of K

<table>
<thead>
<tr>
<th>Big column (ID = 15 mm, BIO-RAD Econo-Pac, AG50-X8 100–200 mesh cation-exchange resin, volume of 19 mL in milli-Q water medium)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning</td>
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<td>Conditioning</td>
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<tr>
<td>Sample loading</td>
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<tr>
<td>Matrix elution</td>
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<tr>
<td>Pre-cut</td>
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<tr>
<td>Potassium cut</td>
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<tr>
<td>Post-cut</td>
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<tr>
<td>The K cut are completely dried down on a hot plate for the following “small column” step</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Small column (ID = 5 mm, BIO-RAD Glass Econo-Column, AG50-X8 100–200 mesh cation-exchange resin, volume of 2.4 mL in 4 M HCl medium)</th>
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</thead>
<tbody>
<tr>
<td>Cleaning</td>
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<tr>
<td>Conditioning</td>
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<tr>
<td>Sample loading</td>
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<td>Matrix elution</td>
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<tr>
<td>Pre-cut</td>
</tr>
<tr>
<td>Potassium cut</td>
</tr>
<tr>
<td>Post-cut</td>
</tr>
<tr>
<td>The “small column” step is repeated twice to further purify K from matrix elements</td>
</tr>
<tr>
<td>The K cut are completely dried down on a hot plate for analysis</td>
</tr>
</tbody>
</table>


Figure 1.3. “Big” column elution curve using geo-reference material BHVO-2 in 0.7 M HNO₃.

Figure 1.4. “Small” column elution curve using geo-reference material BHVO-2 in 0.5 M HNO₃.
1.4 High Precision K Isotope Measurements on MC-ICPMS

Early attempts at K stable isotope measurements were at relatively low resolution owing to analytical challenges. In the 1970s, analyses of the absolute $^{39}$K/$^{41}$K ratio on Thermal ionization mass spectrometry (TIMS) could only reach a precision of ~ 1‰, at which the marginal $\delta^{41}$K differences among most natural samples are unresolvable. The noticeable exception is lunar soil, the fine-grained fragmental layer of debris on the lunar surface caused by meteoroid bombardment. Previous studies have shown substantial heavy K isotope enrichment in lunar soils compared to lunar basalts and terrestrial igneous rocks (up to ~10‰) (Barnes et al., 1973; Garner et al., 1975; Church et al., 1976). Such extreme K isotopic fractionation can be attributed to kinetic fractionation during the micrometeorite bombardment, which causes lunar soils to preferentially lose light K isotopes.

In the 1990s, Humayun and Clayton (1995a) and Humayun and Clayton (1995b) utilized Secondary Ion Mass Spectrometry (SIMS) to achieve a precision of ~ 0.5‰ on K stable isotope measurements. They surveyed a variety of planetary materials with different degrees of volatile depletion relative to CI chondrites (the representative of initial Solar System composition). Nevertheless, they reported that there is no isotopic fractionation of K among planetary bodies within analytical uncertainty, with the exception of lunar soils and one lunar feldspathic rock.

For the past two decades, analytical advances on Multiple-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) have brought the K stable isotope system back to the spotlight, as an order of magnitude of precision improvement relative to those of TIMS and SIMS was
achieved in K stable isotope measurements (from ~ 0.5 to 1‰, to ~ 0.05‰, two standard errors). It enables us to distinguish the subtle K isotope fractionation in the natural system, which demonstrates the strength of K stable isotope system in tracing various geochemical and cosmochemical processes (Li et al., 2016; Hu et al., 2018; Morgan et al., 2018; Chen et al., 2019; Huang et al., 2019; Xu et al., 2019; Chen et al., 2021; Moynier et al., 2021).

The major challenge in using MC-ICPMS on K isotope measurements is the large argon-based isobaric interference ($^{38}$Ar$^1$H$^+$ on $^{39}$K$^+$; $^{40}$Ar$^1$H$^+$ on $^{41}$K$^+$). There are three common ways to eliminate the problem. (1) The “cold plasma” method, which limits the generation of argides by lowering the RF generator power to ~ 500 to 600 W (i.e., lower plasma temperature); (2) the “dry plasma” method, which utilizes an Elemental Scientific Apex Omega desolvating nebulizer system to suppress the formation of argon hydrides under normal RF generator power (~ 1350 W); (3) the “collision cell” method, which introduces a neutral (He) or reactive gas (H$_2$/D$_2$) to dissociate the charged argides. It is noteworthy that the interference of $^{40}$Ar$^1$H$^+$ on $^{41}$K still needs to be resolved by conducting the measurements on the low mass “shoulder” of the peak with the instrument’s high-resolution mode (m/Δm > 10,000) for both “cold plasma” and “dry plasma” methods.
During the course of my Ph.D. research, I used both “cold plasma” and “dry plasma” methods on a Thermo Scientific Neptune Plus MC-ICPMS and an Elemental Scientific APEX omega desolvating nebulizer to achieve high-precision K isotope measurements. Typical instrumental settings are shown in Table 1.2. The parameters are optimized before the analytical session to achieve the best performance. An elemental concentration measurement is performed on the K-cut after ion-exchange chromatography using a Thermo Scientific iCAP Q Quadrupole ICP-MS with a typical uncertainty of 5% (2 relative standard deviations, 2RSD) to eliminate the matrix effect. This is because the presence of matrix (elements other than K) would potentially induce analytical artifacts. The matrix effect is tested by doping different amounts of matrix elements into K. The results show that there is no resolvable matrix effect when the ratio of concentration of all matrix elements other than K to that of K is limited within 2%.
Table 1.2. Instrument settings on a *Thermo Scientific* Neptune Plus MC-ICPMS and an *Elemental Scientific* APEX omega desolvating nebulizer

<table>
<thead>
<tr>
<th>Neptune Plus MC-ICPMS parameters</th>
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<tr>
<td>RF power</td>
<td>600 W</td>
</tr>
<tr>
<td>Cooling gas flow rate</td>
<td>15 L min⁻¹</td>
</tr>
<tr>
<td>Intermediate gas flow rate</td>
<td>1.0 L min⁻¹</td>
</tr>
<tr>
<td>Sample gas flow rate</td>
<td>1.15 L min⁻¹</td>
</tr>
<tr>
<td>Focus quad</td>
<td>− 5.5 V</td>
</tr>
<tr>
<td>Dispersion quad</td>
<td>0.00 V</td>
</tr>
<tr>
<td>Integration time</td>
<td>8.389 s</td>
</tr>
<tr>
<td>Number of integrations</td>
<td>1</td>
</tr>
<tr>
<td>Number of cycles</td>
<td>25</td>
</tr>
<tr>
<td>Number of blocks</td>
<td>1</td>
</tr>
<tr>
<td>Cup configuration</td>
<td>L2 (³⁹K), L1 (⁴⁰Ar), Center (⁴¹K), H3 (⁴⁴Ca)</td>
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</tbody>
</table>

<table>
<thead>
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<th>APEX omega desolvating nebulizer parameters</th>
<th></th>
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<tr>
<td>H₂ flow rate</td>
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</tr>
<tr>
<td>Ar (sweep gas) flow rate</td>
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</tr>
<tr>
<td>Sample uptake rate</td>
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<td>Peltier cooler temperature</td>
<td>3 °C</td>
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<tr>
<td>Desolvator temperature</td>
<td>155 °C</td>
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</tbody>
</table>

The analytical session typically contains ten analytical cycles. Each analytical cycle typically contains six samples and one geo-reference material using the sample-standard-sample bracketing technique. The within-run reproducibility (two standard errors, 2SE) is calculated by averaging the ~ 10 analyses in one analytical session for each sample (~ 0.05‰). A parallel comparison among the same geo-reference material (BHVO-2) in different analytical sessions allows us to monitor potential instrumental drift on different days. The long-term reproducibility is calculated on the basis of the two standard deviations (2SD) of the same geo-reference material in different analytical sessions over ~ 20 months (~ 0.11‰). Within one analytical session, the internal reproducibility for both samples and geo-standards is comparable to each other. The conservative
estimate for K isotope measurement precision conducted in our lab setting would be \(\sim 0.11\%\), which is usually larger than the within-run uncertainty.
Figure 1.6. Potassium isotopic composition of geo-reference material BHVO-2 routinely measured in 90 days over 20 months (from Jan. 2017 to Aug. 2018, n = 890). Each data point represents the average $\delta^{41}$K of BHVO-2 in an overnight analytical session (typically 5 to 15 repeated measurements) with 95% confidence interval. The shaded area stands for the K isotopic composition of the bulk silicate Earth (BSE) defined by (Wang and Jacobsen, 2016a), which cannot be differentiated from the average $\delta^{41}$K of BHVO-2. This figure is reproduced from (Chen et al., 2019).

Figure 1.7. Inter-laboratory comparison of K isotopic compositions of common geo-reference materials. The error bars for each sample represent two standard deviations (2SD). The dotted line stands for the average K isotopic composition of oceanic basalts defined by (Tuller-Ross et al., 2019a). The figure is reproduced from (K. Wang et al., 2021).
References


Chapter 2:

Potassium isotopic compositions of howardite-eucrite-diogenite meteorites

Abstract

We report new high-precision stable K isotope data for three martian meteorites, one lunar meteorite, one ordinary chondrite, four terrestrial igneous United States Geological Survey (USGS) reference materials, and twenty howardite–eucrite–diogenite [HED] meteorites. The three martian meteorites define a relatively narrow $\delta^{41}$K range with an average of $-0.36 \pm 0.12\%$ (2 SD) that is slightly heavier than the Bulk Silicate Earth (BSE) K isotopic composition ($-0.48 \pm 0.03\%$). Except for the four Northwest Africa samples which were terrestrially contaminated, all HED meteorites reveal substantial $^{41}$K enrichment compared to BSE, lunar samples, martian meteorites, and chondrites. We propose that the average $\delta^{41}$K ($+0.36 \pm 0.16\%$) obtained from HED meteorites is representative of Bulk Silicate 4-Vesta. The coupled volatile depletion and heavy K isotope enrichment in 4-Vesta could be attributed to both nebula-scale processes and parent-body events. The asteroid 4-Vesta is likely to either have accreted from planetary feedstocks that have been significantly volatile-depleted prior to the major phases of planetary accretion in the early Solar System, or go through K loss during accretionary growth, or a combination of both.
2.1. Introduction

Volatile inventories, including their abundances, distributions and sources of planetary bodies are useful for understanding how those bodies formed. The volatilities of elements can be defined according to their 50% condensation temperatures (50% $T_c$) under cosmochemical gas pressure (e.g., $10^{-4}$ bars; e.g., Larimer, 1967; Lewis, 1972; Grossman, 1994; Lodders, 2003). Highly volatile elements are those with $50\% T_c < 665$ K (the 50% $T_c$ of S), whereas moderately volatile elements are those with $50\% T_c$ setting between 665 K to 1335 K (the 50% $T_c$ of Mg, Fe, Si; Lodders, 2003). In the early 1960, studies of Earth’s upper mantle and crust identified a depletion in moderately volatile elements compared to CI chondrites (Gast, 1960; Wasserburg et al., 1964). Later studies showed that the terrestrial planets, including Earth, the Moon, Mars and Mercury, and asteroids, such as 4-Vesta, are all more depleted in potassium (K) than the bulk Solar System composition, represented by CI chondrites (Wolf and Anders, 1980; Taylor, 1992; Palme et al., 1993; Peplowski et al., 2011). Depletion of volatile elements is therefore a ubiquitous process that influences the chemical compositions of all the inner Solar System bodies. The mechanisms of this volatile depletion, however, are debated, with models of volatile loss through either nebular or planetary processes (e.g., Albarède, 2009; Paniello et al., 2012b; Day and Moynier, 2014; Palme et al., 2014; Kato et al., 2015; Wang and Jacobsen, 2016b; Norris and Wood, 2017; Sossi and Fegley, 2018).

Potassium is a moderately volatile element (50% $T_c \sim 1006$ K; Lodders, 2003), and is a robust proxy for understanding the primary signatures that have been imprinted by planetary formation events (e.g., Humayun and Clayton, 1995a; Wang and Jacobsen, 2016b). The K/U ratio has been widely used as an indicator of the degree of the volatile depletion in planetary materials as K and
U have similar geochemical affinity (both incompatible lithophile) but contrasting volatility (volatile K versus refractory U), making this ratio insensitive to magmatic differentiation but sensitive to volatile loss. The CI-chondrite K/U ratio is ~71,000 based on the rigorous survey on the Orgueil meteorite (Barrat et al., 2012), whereas the Bulk Silicate Earth shows a depletion in K, with a K/U ratio of 13,800 (~20% that of the CI chondritic value, see Fig. 2.1(b)) (Arevalo et al., 2009). Additionally, the K/U estimates for Mercury, Venus, and Mars, are similar to that of the Bulk Silicate Earth (Lodders and Fegley, 1998; Lodders, 1998; Peplowski et al., 2011; Mittlefehldt, 2014). The Moon and 4-Vesta show an even greater depletion in K, with K/U ratios being approximately twenty-five times lower than the CI chondrites (Taylor, 1982; Kitts and Lodders, 1998). This variation in K and other volatile elements by more than an order of magnitude among inner Solar System planetary bodies requires a fundamental mechanism(s) to explain such planetary-wide volatile loss.

Potassium has three isotopes: $^{39}$K (abundance: 93.26%), $^{40}$K (0.0117%, half-life of $1.251\times10^9$ yrs), and $^{41}$K (6.73%). Although K and its stable isotopes ($^{41}$K/$^{39}$K) are important for understanding processes of volatile depletion among the terrestrial planets, early studies of K isotopes were at relatively low resolution due to analytical challenges. It was initially reported that there is no isotopic fractionation of K among planetary bodies (Kendall, 1960; Garner et al., 1975; Herzog et al., 2008; Humayun and Clayton, 1995a, 1995b; Humayun and Koeberl, 2004). Recently, analytical advances have led to an order of magnitude improvement in the precision on the $^{41}$K/$^{39}$K ratio from 0.5‰ to 0.05‰ (two standard errors). These advances have made it possible to distinguish smaller isotopic differences between materials (Li et al., 2016; Morgan et al., 2012,
2013, 2018, Wang and Jacobsen, 2016a, 2016b). In particular, the average composition of lunar Apollo samples (basalts, breccias, and an impact melt) are significantly heavier than the average of terrestrial igneous rock standard reference materials (basalts, andesites, and granites) and this difference has been attributed to volatile-loss during the formation of the Moon (Wang and Jacobsen, 2016b). This observation followed Zn isotope evidence for volatile depletion of the Moon (Paniello et al., 2012a), demonstrating the powerful application of high-precision K isotopes and other moderately volatile elements.

The DAWN mission has provided additional evidence that the asteroid 4-Vesta (and associated vestoid asteroids) is the HED parent body as was widely believed prior to the mission (McSween et al., 2013, Binzel and Xu, 1993, and references therein). Our focus on HED meteorites is driven by the evidence for extreme volatile loss inferred for this body based both on Rb/Sr and K/U ratios (e.g., Halliday and Porcelli, 2001; Day and Moynier, 2014), as well as previous evidence for volatile depletion from Zn and Cl isotope measurements (Paniello et al., 2012b; Sarafian et al., 2013; Sarafian et al., 2017). In this contribution, we apply a high precision K isotope determination method to investigate howardite–eucrite–diogenite (HED) meteorites. Meanwhile, we compare the results for the HED samples with published values for Earth, Moon, Mars, and chondrites.
Figure 2.1 (a). The K isotopic compositions of chondrites, terrestrial basalts, martian meteorites, Apollo lunar rocks and lunar meteorites, and HEDs. The shaded area is the Bulk Silicate Earth (BSE) $\delta^{41}$K value ($-0.48 \pm 0.03$‰, 2 SD) (Wang and Jacobsen, 2016a). The K isotopic compositions of Apollo lunar samples and chondrites are reported in (Wang and Jacobsen, 2016b) and are normalized to NIST SRM 3141a via $\delta^{41}$K$_{\text{NIST}} = 1.000479 \times \delta^{41}$K$_{\text{Suprapur}} + 0.479$. The error bar for each sample represents two standard error (2 SE).

(b). The K/U ratio versus the K isotopic compositions among different planetary materials. The K isotope data and errors are compiled from (Zhao et al., 2019) for enstatite (both EH and EL), (Wang and Jacobsen, 2016b) for CI chondrite and the Moon, and from this study for BSE, Mars, and asteroid 4-Vesta. The vertical shaded area represents the $\delta^{41}$K for BSE. The K/U ratios of various planetary materials are a compilation of previous literatures: CI (Barrat et al., 2012); BSE (Arevalo et al., 2009); Mercury (Peplowski et al., 2011); Venus, OC and CC group (Lodders and Fegley, 1998); Moon (Taylor, 1982); Mars (Lodders, 1998), and asteroid 4-Vesta (Kitts and Lodders,
2.2. Samples and Method

2.2.1. Sample descriptions

We analyzed twenty HED meteorites (twenty-five aliquots), three martian meteorites (four aliquots), one lunar meteorite, and one chondrite. In addition to extraterrestrial samples, we also measured four terrestrial igneous rocks from the collection of United States Geological Survey (USGS) geo-reference materials (BHVO-2, BCR-1, AGV-1, and G-2, seven aliquots in total). The terrestrial standards, a L6 ordinary chondrite (Allan Hills A76001) and a lunar low-Ti mare basalt meteorite (La Paz Icefield 02224) are reported for direct comparison with the eucrite and martian meteorite data analyzed in the same analytical sessions, and to compare with previous literature data (Wang and Jacobsen, 2016a, b) (Tables 2.1-2.3).

Howardites are polymict breccias. Eucrites are basaltic or accumulative rocks that are typically brecciated, and diogenites are intrusive orthopyroxenites and harzburgites. Basaltic eucrites can be sub-divided into three groups according to their Mg#, TiO$_2$ content, and incompatible trace element abundances: Main Group Nuevo Laredo-trend (MG-NL trend) eucrites, Stannern-trend eucrites and the residual eucrites (e.g., Warren and Jerde, 1987; Yamaguchi et al., 2009; McSween et al., 2013). Five of the eucrite meteorites that we measured are hot desert (Northwest Africa) finds (Table 2.3), seven HED samples (eleven aliquots) are Antarctic finds, and eight samples (nine aliquots) are falls. Of the cold desert finds and falls, seven are Main Group-Nuevo Laredo trend eucrites (two separate fragments of Bereba and Haraiya, three separate fragments of Juvinas, Millbillillie, Sioux County, Nuevo Laredo, and EET 87542), two are Stannern trend eucrites (two
separate fragments of Bouvante, two fragments of Stannern), two are residual eucrites (DaG 945 and EET 90020), and one is an ungrouped eucrite (Pasamonte) (*Table 2.2*). We also measured three Antarctic howardite meteorites (EET 87503, LAP 10018, and QUE 97001).

The martian meteorites have been linked to the planet Mars since the late 1970’s based on noble gas compositions, young ages, and their unique O isotope compositions (*e.g.*, Stolper and McSween, 1979; McSween and Stolper, 1980; Bogard and Johnson, 1983; McSween, 2002). Martian meteorites can be divided into shergottites (in one classification, either basaltic, lherzolitic, or olivine-phyric), nakhlites (clinopyroxene-rich basalts), chassignites (dunites), an orthopyroxenite (ALH 84001) and a basaltic regolith breccia (NWA 7034/7533 and associated pairings) (Krot et al., 2013). In this study we present high-precision K isotope data for three martian meteorites (*Table 2.2*), including two shergottites (two fragments of EETA 79001 lithology A, and Tissint [Fall] Chennaoui Aoudjehane et al., 2012) and one nakhlite with a vitrophyric mesostasis (MIL 03346; Day et al., 2006).
<table>
<thead>
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<th>Sample</th>
<th>Description</th>
<th>Location</th>
<th>Weight [mg]</th>
<th>[K] ppm</th>
<th>δ⁴¹K_{NIST}/‰</th>
<th>2SE*</th>
<th>n**</th>
<th>Literature Values</th>
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<td>G-2</td>
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<td>Rhode Island</td>
<td>37200</td>
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<td>Oregon</td>
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</tbody>
</table>

* Standard errors (SE = standard deviation divided by the square root of the total number of measurements)
** Number of measurements

a. Wang and Jacobsen, 2016a
b. Wang and Jacobsen, 2016b
Table 2.2. Potassium isotopic compositions of extraterrestrial samples (chondrites, martian meteorites, lunar meteorites, and HEDs)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Type</th>
<th>Fall/Find</th>
<th>Breccia</th>
<th>Mass [mg]</th>
<th>K [ppm]</th>
<th>K [ppm] literature Value</th>
<th>$\Delta^{41}K_{NIST}$ [%]</th>
<th>2SE*</th>
<th>n**</th>
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<td>Fall</td>
<td>Monomict</td>
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<td>330&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>Monomict</td>
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<td>Find</td>
<td>Monomict</td>
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<td>Monomict</td>
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<td>Find</td>
<td>Monomict</td>
<td>41.5</td>
<td>553</td>
<td>565&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.31</td>
<td>0.11</td>
<td>8</td>
<td>Prof. Barrat</td>
</tr>
<tr>
<td>SiouxBouvante, b</td>
<td>Stannern Trend</td>
<td>Find</td>
<td>Monomict</td>
<td>208.1</td>
<td>568</td>
<td>646&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.31</td>
<td>0.03</td>
<td>23</td>
<td>Narodni Muzeum Prague, 2-4-98</td>
</tr>
<tr>
<td>Stannern, a</td>
<td>Stannern Trend</td>
<td>Fall</td>
<td>Monomict</td>
<td>39.7</td>
<td>672</td>
<td>646&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.40</td>
<td>0.02</td>
<td>11</td>
<td>Prof. Barrat</td>
</tr>
<tr>
<td>DaG 945</td>
<td>Residual</td>
<td>Find</td>
<td>Brecciated</td>
<td>250</td>
<td>498</td>
<td>646&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.72</td>
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<td>13</td>
<td>Prof. Barrat</td>
</tr>
<tr>
<td>Stannern, b</td>
<td>Stannern Trend</td>
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<td>Monomict</td>
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<td>232</td>
<td>268&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>0.02</td>
<td>10</td>
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<tr>
<td>EET 87503, 202</td>
<td>Howardite</td>
<td>Find</td>
<td>Unbrecciated</td>
<td>93.1</td>
<td>154</td>
<td>220&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.68</td>
<td>0.06</td>
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<td>LAP 10018, 15</td>
<td>Howardite</td>
<td>Find</td>
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<td>275.9</td>
<td>90</td>
<td>91&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.44</td>
<td>0.04</td>
<td>9</td>
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<td>QUE 97001, 82</td>
<td>Howardite</td>
<td>Find</td>
<td>Unbrecciated</td>
<td>279.1</td>
<td>63</td>
<td>91&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.44</td>
<td>0.08</td>
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</tr>
<tr>
<td>Pasamonte</td>
<td>Ungrouped</td>
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<td>Polymict</td>
<td>298.5</td>
<td>338</td>
<td>358&lt;sup&gt;a&lt;/sup&gt;</td>
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<td><strong>Martian</strong></td>
<td><strong>Meteorites</strong></td>
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<td>EETA 79001, 668</td>
<td>Shergottite</td>
<td>Find</td>
<td>Unbrecciated</td>
<td>82.8</td>
<td>448</td>
<td>415&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-0.31</td>
<td>0.05</td>
<td>8</td>
<td>Prof. Barrat</td>
</tr>
<tr>
<td>EETA 79001, 139</td>
<td>Shergottite</td>
<td>Find</td>
<td>Unbrecciated</td>
<td>137.6</td>
<td>213</td>
<td>332&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-0.42</td>
<td>0.03</td>
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<td>MIl 03346, 245</td>
<td>Nakhlite</td>
<td>Find</td>
<td>Unbrecciated</td>
<td>43.1</td>
<td>677</td>
<td>1660&lt;sup&gt;i&lt;/sup&gt;</td>
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<td>0.02</td>
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<tr>
<td>Tissint</td>
<td>Shergottite</td>
<td>Fall</td>
<td>Unbrecciated</td>
<td>114.8</td>
<td>1058</td>
<td>897&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-0.30</td>
<td>0.03</td>
<td>8</td>
<td>Prof. Barrat</td>
</tr>
<tr>
<td><strong>Chondrites</strong></td>
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<tr>
<td>ALH A76001, 30</td>
<td>OC-L6</td>
<td>Find</td>
<td></td>
<td>41.2</td>
<td></td>
<td>897&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-0.80</td>
<td>0.03</td>
<td>15</td>
<td>NASA-ANSMET</td>
</tr>
</tbody>
</table>
Lunar Meteorite

LAP 02224, 44 Low-Ti Mare Find unbrecciated 126.7 1038 913\(^k\) -0.01 0.03 17 NASA-ANSMET Basalt

†The K concentrations in this study is obtained on the Thermo Scientific iCAP Q quadrupole ICP-MS before being measured on the MC-ICP-MS. The typical error for iCAP Q on these data is ~10%.

*Standard errors (SE = standard deviation divided by the square root of the total number of measurements)

** Number of measurements
a. (Kitts and Lodders, 1998)
b. (Mittlefehldt and Lindstrom, 2003)
c. (Usui et al., 2010)
d. (Yamaguchi et al., 2009)
e. (Wetten et al., 2016)
f. (Mittlefehldt et al., 2013)
g. (Barrat et al., 2014)
h. Sample list provided by NASA
i. (Day et al., 2006)
j. (Zhong et al., 1995)
k. (Joy et al., 2006)
Table 2.3. Potassium isotopic compositions of hot desert HED finds

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Type</th>
<th>Breccia</th>
<th>Mass [mg]</th>
<th>$\delta^{41}\text{K}_{\text{NIST}}$ bulk</th>
<th>2SE</th>
<th>n</th>
<th>$\delta^{41}\text{K}_{\text{NIST}}$ residual</th>
<th>2SE</th>
<th>n</th>
<th>$[\text{K}]_{\text{residual}}$ µg</th>
<th>$\delta^{41}\text{K}_{\text{NIST}}$ supernatant</th>
<th>2SE</th>
<th>n</th>
<th>$[\text{K}]_{\text{supernatant}}$ µg</th>
<th>Contamination portion [%] ***</th>
<th>Calculated $\delta^{41}\text{K}_{\text{NIST}}$ bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWA 049</td>
<td>Main Group-Nuevo</td>
<td>Laredo trend</td>
<td>Polymict</td>
<td>68.0</td>
<td>0.08</td>
<td>0.03</td>
<td>14</td>
<td>0.38</td>
<td>0.04</td>
<td>12</td>
<td>21.2</td>
<td>-0.95</td>
<td>0.03</td>
<td>7</td>
<td>8.2</td>
<td>28</td>
</tr>
<tr>
<td>NWA 999</td>
<td>Main Group-Nuevo</td>
<td>Laredo trend</td>
<td>Monomict</td>
<td>61.9</td>
<td>0.08</td>
<td>0.02</td>
<td>12</td>
<td>0.24</td>
<td>0.06</td>
<td>12</td>
<td>20.7</td>
<td>-0.65</td>
<td>0.02</td>
<td>10</td>
<td>15.0</td>
<td>42</td>
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<td>NWA 2061</td>
<td>Stannern Trend</td>
<td>Unbrecciated</td>
<td>38.8</td>
<td>-0.26</td>
<td>0.04</td>
<td>9</td>
<td>-0.07</td>
<td>0.05</td>
<td>14</td>
<td>44.1</td>
<td>-1.23</td>
<td>0.03</td>
<td>5</td>
<td>6.3</td>
<td>12</td>
<td>-0.22</td>
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<tr>
<td>NWA 2362</td>
<td>Residual</td>
<td>Unbrecciated</td>
<td>74.3</td>
<td>-0.20</td>
<td>0.02</td>
<td>11</td>
<td>6.9</td>
<td>7.0</td>
<td>51</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NWA 4523</td>
<td>Stannern Trend</td>
<td>Polymict</td>
<td>35.2</td>
<td>0.29</td>
<td>0.06</td>
<td>11</td>
<td>0.34</td>
<td>0.03</td>
<td>11</td>
<td>78.0</td>
<td>2.0</td>
<td>2</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Standard errors (SE = standard deviation divided by the square root of the total number of measurements)

** Number of measurements

*** Contamination portion [%] = $[\text{K}]_{\text{residual}}/([\text{K}]_{\text{residual}}+[\text{K}]_{\text{supernatant}}) * 100
2.2.2. Analytical Methods

Reported concentrations of K from the literature were used to determine the quantity of powder required for K isotope analysis. About 100-500 mg of homogeneously powdered sample material was digested in Teflon Parr Bomb high-pressure digestion vessels at 150°C in a Fisher Scientific Isotemp 500 oven for two days. The samples were dissolved in a concentrated HF/HNO₃ (VHF: VHNO₃~3:1) mixture and then dried down completely under heat lamps. The samples were then re-digested in 6 N HCl for one day. Fully digested samples were then dried and dissolved in 0.7 N HNO₃ before being loaded onto columns for K purification.

The column separation procedure involves three steps (Chen et al., 2019). The first step uses large columns (ID = 1.5 cm, BIO-RAD Econo-Pac, resin volume of 17 mL) to separate K from much of the matrix elements. Smaller columns (ID = 0.5 cm, BIO-RAD Glass Econo-Column, resin volume of 2.4 mL) are used in the second and third step to further purify K using the same separation technique. Columns are filled with AG50-X8 100-200 mesh cation-exchange resin and the method is calibrated to achieve > 99% recovery of K. Pre-cut and post-cut fractions of all samples are monitored for any possible K loss during column chemistry. Total procedural blanks are 0.21 μg K, and in all cases, this was found to be negligible.

There are currently two techniques to measure K isotopic ratios at high precision: (1) a cold plasma technique (e.g., Morgan et al., 2012; Morgan et al., 2013; Hu et al., 2018; Morgan et al., 2018; Chen et al., 2019) and (2) a collision gas cell technique (e.g., Bourg et al., 2010; Richter et al.,
Here we used the cold plasma method with a *Thermo Scientific* Neptune Plus MC-ICP-MS. High-resolution mode (m/Δm > 10,000) was used to resolve the subtle difference (~0.005 a.m.u.) between the peaks of $^{40}$Ar$^+\cdot$H$^+$ and $^{41}$K$^+$ (Chen et al., 2019). The measurement has been done on the low-mass side shoulder of the peak of $^{41}$K$^+$, which is not affected by the $^{40}$Ar$^+\cdot$H$^+$ interference. Besides, the presence of matrix elements would induce analytical artifacts when applying the “cold plasma” technique, namely “matrix effects” (Chen et al., 2019). For each sample, the ratio of concentration of all matrix elements other than K to that of K is limited within 2% to eliminate potential matrix effects using the Thermo Scientific iCAP Q quadrupole ICP-MS (Chen et al., 2019). In addition to $^{41}$K and $^{39}$K, we also monitored $^{40}$Ar/$^{40}$Ca through $^{44}$Ca to account for potential interferences or contaminations. Samples were introduced into the instrument via an *Elemental Scientific* APEX omega equipped with a desolvation membrane to enhance sensitivity and minimize hydride and oxide generation. A sample-standard bracketing technique was applied, and the concentration mismatches between samples and standards were limited within 2%. The final data is expressed in the delta notation, relative to the NIST SRM 3141a standard solution:

$$\delta^{41}\text{K} = \left(\frac{[^{41}\text{K}/^{39}\text{K}]_{\text{sample}}}{[^{41}\text{K}/^{39}\text{K}]_{\text{NIST SRM 3141a}} - 1}\right) \times 1000 \quad (2.1)$$

In all cases, the internal (within-run) uncertainty of ~10 analytical cycles in one analytical session is ~±0.05‰ (2 SE), which is comparable to previous studies (Li et al., 2016; Morgan et al., 2012, 2013, 2018; Wang and Jacobsen, 2016a, 2016b). The external reproducibility has been reported in
Chen et al. (2019), which is evaluated by six aliquots of the same reference rock materials BHVO-2 and G-2, yielding a 2-standard deviation (2SD) of ±0.08‰. The long-term reproducibility of this method was evaluated as ±0.11‰ in over 20 months (Chen et al., 2019). We decide two samples are different in terms of K isotope compositions if their δ⁴¹K difference exceeds this long-term reproducibility (0.11‰).

Up to date, no certified isotopic standard for K is available, which is a hindrance to data comparisons among different laboratories. Wang and Jacobsen (2016b) previously reported high-precision K isotope data for chondrites and Apollo lunar samples normalized to Bulk Silicate Earth via \( \delta^{41}K_{\text{BSE}} = 1.000479 \times \delta^{41}K_{\text{Suprapur}} + 0.479 \). Chen et al. (2019) further suggested a lack of difference between Merck KGaA Suprapur 99.995% KNO₃ and NIST SRM 3141a in terms of K isotopic composition (i.e. \( \delta^{41}K_{\text{Suprapur}} = \delta^{41}K_{\text{NIST SRM 3141a}} \)). Together they facilitated a direct inter-laboratory comparison with previous high-precision K isotope measurements (Fig. 2.1).
2.3. Results

2.3.1. Potassium isotope compositions of terrestrial samples, lunar meteorites, martian meteorites and an ordinary chondrite

In order to compare our data with those from other laboratories, we analyzed four reference rock materials (seven aliquots). The results are summarized in Table 2.1 and Figs. 2.1 and 2.2. Despite different igneous rock types (basalt, andesite, granite), all terrestrial samples measured in this study yield the same $\delta^{41}$K value, within error, relative to NIST SRM 3141a. The average value is $-0.46 \pm 0.03$‰ (2SD, standard deviation) and is in agreement with the BSE value of $-0.48 \pm 0.03$‰ defined by Wang and Jacobsen (2016a), as well as with literature data reported by Li et al. (2016) and Morgan et al. (2018).

We studied one ordinary chondrite and one lunar meteorite to compare with literature data (Table 2.2 and Figs. 2.1 and 2.2). To date, high-precision K isotope measurements are only available for four chondrites. We find that the $\delta^{41}$K value for ALHA 76001 (L6) is broadly comparable to chondrite data from a previous study (Wang and Jacobsen, 2016b), but is shifted towards a lighter K isotope composition ($-0.80 \pm 0.03$‰ versus $-0.55 \pm 0.06$‰). Analysis of a lunar meteorite LAP 02224 yields $\delta^{41}$K = $-0.01 \pm 0.03$‰, similar to previously studied Apollo lunar samples (Wang and Jacobsen, 2016b).

The three martian meteorites (four aliquots) define a relatively narrow range in $\delta^{41}$K, with an average of $-0.36 \pm 0.12$‰ (2 SD), resembling K isotopic composition of BSE but with a slight enrichment of $^{41}$K and greater dispersion (Table 2.2 and Figs. 2.1 and 2.2). The two EETA 79001
lithology A replicates yielded two different $\delta^{41}K$ values outside of analytical uncertainty ($-0.32 \pm 0.04\%$, $-0.44 \pm 0.02\%$, respectively).
Figure 2.2. The K isotopic compositions of individual samples measured in this study (including one chondrite, one lunar meteorite, three martian meteorites [four aliquots], and fifteen falls and Antarctic finds [twenty aliquots]; the five hot desert NWA eucrites are excluded here). The shaded area is the Bulk Silicate Earth $\delta^{41}\text{K}$ value ($-0.48 \pm 0.03\%$, 2 SD). Sample names are labeled in the figure. The error bar for each sample represents two standard error (2 SE). Literature data for chondrites and Apollo lunar samples are from (Wang and Jacobsen, 2016b); literature data for terrestrial igneous rocks are from (Wang and Jacobsen, 2016a).
2.3.2. Potassium isotope compositions of HED meteorites

The twenty-five aliquots of eucrite and howardite $\delta^{41}$K values obtained in this study are shown in Tables 2.2 and 2.3. In general, the HED samples are isotopically heavy compared with terrestrial, martian and lunar rocks, and chondrites. A “summed Gaussian” ideogram (see Fig. 2.3) reveals that the majority of the eucrite and howardite samples (excluding Pasamonte, Juvinas, four NWA samples [NWA 049, NWA 999, NWA 2061, NWA 2362] and two residual eucrites DaG 945 and EET 90020, more details in the following section) define a range of K isotopic compositions, varying from +0.24‰ (Sioux County, Bouvante, a) to +0.49‰ (Haraiya). The Juvinas aliquots b and c and the two residual eucrites are offset towards heavier K isotope compositions. The NWA samples we analyzed are likely affected by terrestrial K contamination (see Section 2.3.3). Pasamonte is an anomalous eucrite based on its oxygen isotope composition (Wiechert et al., 2004; Scott et al., 2009).

The $\delta^{41}$K value of the eleven remaining HED meteorites show significant dispersion with an average $\delta^{41}$K of +0.36 ± 0.16‰ (2 SD). These eleven samples are categorized into several subgroups based on different criteria: falls/finds, eucrites/howardites, and Main Group-Nuevo Laredo trend/Stannern trend. The average $\delta^{41}$K value of falls is +0.35 ± 0.16‰ (2 SD), whereas the average $\delta^{41}$K value of Antarctic finds is +0.36 ± 0.18‰ (2 SD). The eucrites give a mean $\delta^{41}$K value of +0.35 ± 0.15‰ (2 SD), whereas the howardites group yields a mean $\delta^{41}$K value of +0.38 ± 0.21‰ (2 SD). Furthermore, the eucrites can be divided into the Main Group-Nuevo Laredo trend and Stannern trend, yielding $\delta^{41}$K values of +0.36 ± 0.10‰ (2 SD) and +0.32 ± 0.13‰ (2 SD), respectively.
Figure 2.3. The “summed Gaussian” ideogram and the overall histogram of the $\delta^{41}\text{K}$ distribution of twenty non-hot desert HED meteorites. Each Gaussian distribution in black line on the bottom represents a single HED meteorite data point. The red line is the sum of Gaussian distributions for 20 HED samples. The distribution histogram is shown as blue stairs and the counts are relative to the right y-axis. Number labeled in the figure stands for the number of samples in each bin. Bins for the histogram are in 0.10‰ increments.
2.3.3. Weak-acid leaching experiments on NWA meteorites

Four out of the five Northwest Africa (NWA) samples (NWA 049, NWA 999, NWA 2061, NWA 2362) have lighter bulk K isotopic compositions compared to the eucrite and howardite falls and Antarctic finds (Table 2.3 and Fig. 2.4). Since all Northwest Africa meteorites are finds and meteorite finds, especially those from Sahara and other hot deserts, have long been recognized to experience terrestrial contamination and weathering (Stelzner et al., 1999; Barrat et al., 1999; Zipfel et al., 2000; Crozaz and Wadhwa, 2001; Al-Kathiri et al., 2005; Hyde et al., 2014), we conducted leaching experiments at room temperature (0.5 hour using 1 N HCl) on sample powders to examine the hypothesis that lighter δ⁴¹K values in the NWA samples were due to terrestrial K contamination. Only NWA 4523 showed a “normal” bulk δ⁴¹K value (+0.29 ± 0.06‰) and the leaching supernatant of NWA 4523 had only trace amount of K, which was insufficient for isotopic analysis. Mass-balance calculations (see Table 2.3) show that 12-51% of soluble K was leached out from the powder. The residual K is presumably in silicate minerals that could not be dissolved. The bulk δ⁴¹K values of the NWA samples ranged from −0.26 ± 0.04‰ (NWA 2061) to +0.08 ± 0.02‰ (NWA 049, NWA 999), whereas the δ⁴¹K values of residues (from the leaching experiments) were consistently shifted towards heavier K isotope values. These δ⁴¹K values approached the average for the ‘non-desert’ eucrites and howardites described in Section 2.3.2. In contrast, the leaching supernatants were consistently light with respect to K isotope composition.
Figure 2.4. Terrestrial contaminations of NWA hot desert eucrites. The shaded area is the average K isotopic composition of non-hot desert HED meteorites (0.36 ±0.16‰, 2 SD, see Section 4.2), the vertical dashed line stands for the Bulk Silicate Earth $\delta^{41}$K value (~0.48‰). The error bar for each sample represents two standard error (2 SE). Note the $^{39}$K enrichments in the leaching supernatants.
2.4. Discussion

2.4.1. Terrestrial contamination of potassium in NWA meteorites

Previous studies have observed substantial K enrichment in desert meteorites and attributed this to terrestrial alteration (Bischoff et al., 1998; Zipfel et al., 2000), presumably from the precipitation of K-bearing salts and sulfates (e.g., sylvite), as well as more insoluble zeolite. The majority of NWA meteorites in this study, with the exception of NWA 4523, display bulk rock δ⁴¹K that is lighter compared to the eucrite and howardite falls and Antarctic finds. Since the terrestrial K isotopic composition is lighter (BSE ~−0.48‰; Wang and Jacobsen, 2016a) compared to that of eucrite and howardite falls and Antarctic finds, the enrichment of lighter K isotopes observed in NWA meteorites can be explained by addition of terrestrial K during residence on Earth’s surface. Leaching experiments indicate that substantial amounts of K in NWA 049, NWA 999, NWA 2061, NWA 2362 were derived from post-addition of terrestrial materials (12% to 51%; Table 2.3). In contrast limited amount of K was leached from NWA 4523 (~2%), demonstrating that our sample was not significantly affected by terrestrial K. For the other four NWA samples, the δ⁴¹K values of leached residues consistently shifted towards heavier K isotopic compositions (Table 3 and Fig. 4).

The leaching supernatants are enriched in lighter K isotopes, even lighter than that of the BSE. Li et al. (2017) recently reported K isotope fractionation factors for eight K-bearing salts equilibrated with the corresponding saturated aqueous solutions at room temperature. They found that the K isotopic fractionations between minerals and saturated solutions span a wide range and suggested that both anion charge and bond length are critical for controlling the K isotopic fractionation.
factors. Their results, along with the light $\delta^{41}$K values for leachates in our work, imply that some low-temperature K isotope fractionation process(es) may be involved when the K-bearing phases were precipitated during the meteorites’ terrestrial residence. The $\delta^{41}$K values for the NWA 999 and NWA 2016 residues are still offset compared to other HED falls and Antarctic finds, possibly because of incomplete leaching during the short half hour treatments. Thus, the $\delta^{41}$K values for the residues of the four NWA samples may not reflect their “true” initial K isotopic compositions, but rather some mixing between potassium from HED meteorites and more insoluble terrestrial contaminants (e.g., zeolite, clay, or other hot desert secondary phases). For this reason, we do not include NWA samples in estimations of the K isotopic composition of ‘Bulk Silicate Vesta’.

2.4.2. An estimate of the average K isotopic composition of Bulk Silicate Vesta

Except for the four NWA samples, all other HED meteorites studied are isotopically heavier than that in the BSE, Apollo lunar samples, martian meteorites, and chondrites in terms of K isotopes (see Figs. 2.1 and 2.2). Within the non-hot desert HED group, no resolvable variation among different samples is observed except for four aliquots (two Juvinas replicates and two residual eucrites), which will be discussed in more detail in the next section. The eleven HED samples (fourteen aliquots) define an average $\delta^{41}$K value of +0.36 ± 0.16‰ (2 SD). Howardites are mechanical mixtures of eucrites and diogenites derived by impacts (e.g., Mittlefehldt, 2014). No diogenite samples are included in this study, but diogenites are orthopyroxenites that contain much less K than eucrites. Also, the similarity between $\delta^{41}$K values of eucrites and howardites indicates that impact gardening does not alter significantly the K isotopic compositions of howardites. Thus,
the K isotopic compositions of howardites are controlled by the K isotopic compositions of their eucritic component.

We propose that the average $\delta^{41}\text{K} (+0.36 \pm 0.16\%)$ obtained from HED meteorite clan is representative of Bulk Silicate Vesta. The large number of characterized HED meteorites, with their diverse geochemical and petrological features, is believed to be broadly representative of lithological variations of Vesta’s crust (McCord et al., 1970; Kitts and Lodders, 1998; McSween et al., 2013; Lunning et al., 2016). A layered model involving a metallic core, an ultramafic mantle, and a basaltic crust is widely accepted for 4-Vesta’s interior structure. The crust, and to a lesser extent the ultramafic mantle are probably the major reservoirs of K. Potassium is an incompatible element, and it tends to quantitatively enter melts during partial melting processes (Refer to Table A1 in Laneuville et al., 2018 and reference therein for the low partitioning coefficients of K in basaltic systems). Thus, during partial melting, K isotopic compositions of melts are unlikely to be fractionated from those of their sources and no significant isotopic fractionation should thus be expected between the Vesta crust and its mantle source (under the assumption that the Vesta crust was the product of partial melting of a mantle source). Previous K isotope studies of terrestrial igneous rocks showed no variation of K isotopes and indicate limited isotopic fractionation during magmatic processes (Wang and Jacobsen, 2016a; Tuller-Ross et al., 2019b). In addition, the two sub-groups (Main Group-Nuevo Laredo [MG-NL] trend and Stannern trend) of eucrites do not show any resolvable K isotopic differences. The MG-NL trend can be explained by fractionation crystallization (Stolper, 1977; Warren and Jerde, 1987), whereas the Stannern trend can be explained by contamination of MG-NL eucrite melts with crustal partial melts (Barrat et al., 2007).
Furthermore, incompatible lithophile trace element Hf as well as Mg# (100Mg/(Mg+Fe) by atomic ratios) both serve as indicators of partial melting/fractional crystallization processes (e.g., Mittlefehldt and Lindstrom, 2003). No clear correlation is shown between Hf concentration/Mg# and corresponding δ⁴¹K for samples (see Fig. 2.5(a) and (b)). With all the evidence above, we conclude there is no K isotopic fractionation during igneous processes on 4-Vesta, and that the δ⁴¹K value for Bulk Silicate Vesta is well defined by the HED samples measured in this study, with an average of +0.36 ± 0.16‰ (2 SD).
Figure 2.5 (a). Hafnium concentrations versus the corresponding K isotopic compositions of the non-hot desert HED meteorites. MG-NL trend is the abbreviation for Main Group-Nuevo-Laredo trend. Juvinas, b and c are two out of three Juvinas aliquots that show $^{41}$K enrichments relative to the K isotopic composition of the Bulk Silicate 4-Vesta, which is discussed in Section 4.3.2. Hafnium concentrations are compiled from Kits and Lodders, 1998; Barrat et al., 2007; Yamaguchi et al., 2009; Mittlefehldt et al., 2013), K isotopic compositions are from this study. The vertical error bar for each sample represents two standard error (2 SE). (b). Mg# (100Mg/(Mg+Fe)) versus the K isotopic compositions of the non-hot desert HEDs. All the data points share the same legend as that in Fig. 2.5(a). The Mg# data are a compilation of Kits and Lodders, 1998; Barrat et al., 2007; Warren et al., 2009; Yamaguchi et al., 2009; Mittlefehldt et al., 2013). Note the lack of correlation between the $^{41}$K and the corresponding [Hf]/Mg#, which is indicative of the deficient isotopic fractionation of K, if any, during the igneous processes.
2.4.3. Isotopic variations within HED meteorites

Isotopic variation within eucrites

Unlike terrestrial igneous rocks sampled from diverse geological settings, HED meteorites exhibit a relatively scattered K isotopic spread. Since igneous crystallization processes apparently do not cause resolvable K isotope fractionation, the observed isotopic compositional range is worth discussing as a function of (1) analytical uncertainties, or (2) evaporation/condensation fractionation mechanisms. As detailed in Section 3, our analytical precision is determined by repeated measurements for each sample and is reported as two standard error (2 SE). Typically for ten analyses, the internal reproducibility is ~±0.05‰. Nevertheless, the total procedural uncertainty is usually larger than the within-run errors when taking both the external error and the long-term reproducibility into account (±0.08‰ and ±0.11‰, respectively. See Section 2.2). Hence, the observed dispersion among the HED meteorites is likely at least partially caused by our long-term analytical uncertainties.

The total variation in δ⁴¹K for the HED meteorites in this study ranges from +0.24‰ to +0.77‰. This range of values cannot be satisfactorily explained by analytical uncertainties alone; thus, it appears to reflect the intrinsic spread within the HED clan. One plausible mechanism to fractionate K isotopes is evaporation during Rayleigh distillation processes (Urey, 1947). As shown in Fig. 6, the K concentration and the corresponding δ⁴¹K of eucrites show a negative correlation. The coupled heavy K isotope enrichment and K depletion most likely indicate evaporation and loss of K since K isotopes do not fractionate during magmatic differentiation of basalts (Tuller-Ross et
al., 2019b; Tuller-Ross et al., 2019a). This volatile loss could occur in several ways: (1) eruptive degassing of silicate melts; (2) impact-induced vaporization (e.g., Day and Moynier, 2014), and (3) loss from a global magma ocean. The fractionation between a vapor and melt can be described via the Rayleigh distillation equation:

$$\delta^{41}K = \delta^{41}K_{\text{initial}} + [(1000 + \delta^{41}K_{\text{initial}}) \times (F^{\alpha - 1} - 1)]$$ (2.2)

where F is the fraction of K remaining in the melt, and $\alpha$ is the fractionation factor between vapor and melt. The subscript initial stands for an assumed unfractionated material. Here we arbitrarily choose 700 ppm (the highest K concentration among all measured HEDs in this study) and 0.24‰ (the lowest delta K value in this study) as the initial K abundance and the initial $\delta^{41}K$ (Fig. 6), respectively. For reference the average K concentration in CI chondrites is 546 ppm (see Table 2.3, Palme et al., 2014). We assume K vaporizes as monoatomic K gas, which should be valid at low total pressure and high temperature (e.g., see pp. 425-431 of Sossi and Fegley, 2018). For the ideal evaporation model, $\alpha$ has often been estimated as the square-root of the mass number of the light isotopologue over the mass number of the heavy isotopologue of involved species (e.g., In the case of K, $\alpha_K = (39/41)^{\beta}$, where $\beta = 0.5$). Nevertheless, Richter et al. (2011) suggested a $\beta$ exponent of 0.43 ± 0.03 that best fitted the Rayleigh isotopic fractionation for both vacuum and low-pressure conditions, corresponding to a $\alpha_K$ of 0.9790 (i.e., $\alpha_K = (39/41)^{0.43}$). Significant heavy K isotope enrichment in residues is predicted in the high-vacuum kinetic processes; however, the observed trend is not consistent with the theoretical fractionation line. Rather, the fractionation is compressed with an empirical $\alpha_K$ value approaching unity (between 0.9996 and 0.9999),
suggesting that the evaporation occurred non-ideally. Mulliken and Harkins (1922) showed theoretically and experimentally that the Rayleigh fractionation factor for Hg vapor approaches unity with increasing ambient pressure. Their theoretical discussion has general applicability and is not limited to mercury. Subsequent work (e.g., Young, 2000; Yu et al., 2003; Wombacher et al., 2004; Wombacher et al., 2008; Estrade et al., 2009; Day et al., 2017; Pringle and Moynier, 2017) confirms this effect for Cd, Hg, K, Rb, and Zn. The reason for this is that the “ideal” Rayleigh fractionation factor only applies to evaporation into a vacuum without any re-condensation taking place (e.g., see pp. 42-44 in Mulliken and Harkins 1922, or Fig. 8 of Estrade et al., 2009). After evaluating the aforementioned causes involved, we could draw a conclusion that the K loss and isotopic fractionation during evaporation, coupling with the analytical artifacts, are the main reasons for the $\delta^{41}$K scattering in HEDs. A nearly-unity empirical fractionation factor further suggests the non-ideality nature of such evaporation process(es).
Figure 2.6. Potassium concentrations (denoted as K) versus the corresponding K isotopic compositions of eucrites. The vertical error bar for each sample represents two standard error (2 SE). The [K] and the K isotopic compositions of the samples are from this study (Table 2.2). The starting composition is $[K]_0 = 700$ ppm and $\delta^{41}K_0 = 0.24\%\text{o}$, which is shown as the black cross in the figure (details in the text). Rayleigh fractionation curves are shown in red lines for three different fractionation factors (0.9996, 0.9998, and 0.9999).
Isotopic variation within an individual meteorite: The case of Juvinas.

The majority of HED samples analyzed in this study exhibit a rather constrained range in terms of K isotopic composition (+0.36 ± 0.16‰, 2 SD). However, one eucrite (two out of three Juvinas aliquots) δ⁴¹K is significantly different from this average and needs further discussion. Juvinas is the only sample that shows variation of δ⁴¹K among different fragments (Table 2.2). The three chips of Juvinas from different sources give δ⁴¹K values of +0.50 ± 0.04‰ (2 SE), +0.66 ± 0.03‰ (2 SE), and +0.77 ± 0.03‰ (2 SE) respectively, whereas the different chips of Bereba, Bouvante, and Stannern all overlap with each other in terms of their K isotopic compositions when taking the long-term reproducibility (~ 0.11‰) into account (see Table 2.2). Two out of three chips of Juvinas are not only different from each other but they also have significantly higher δ⁴¹K values than the average δ⁴¹K (+0.36 ± 0.16‰) of all the other HED meteorites.

Juvinas is a main-group equilibrated (thermal metamorphism degree type 5) basaltic eucrite (Takeda and Graham, 1991). It is a meteorite fall, so the possibility of terrestrial contamination or alteration should be lower than that for a find such as the Sahara Desert meteorites. Contamination and/or weathering can also occur during curation in museums (e.g., Consolmagno S J et al., 1998). Juvinas is a heterogeneous rock and three distinct lithologies can be identified (Kanemaru et al., 2018): (1) the matrix, which is composed of a debris of the clasts; (2) a coarse grained lithology, which displays some olivine veins as a result of iron metasomatism; (3) a fine grained lithology, which could be derived by previous impact melting. The complicated history (impacting, annealing and recrystallization) exhibited by the Juvinas sample is the likely cause for the
heterogeneity of K isotopes among different Juvinas fragments, where $\delta^{41}\text{K}$ values vary within small spatial scales. Pringle and Moynier (2017) reported high precision Rb isotopic compositions of HED meteorites (Juvinas and Stannern) and found that Juvinas is substantially enriched in heavier Rb isotopes compared to Stannern, which is consistent with the K isotope evidence in this study (however, note the very limited Rb isotope data set for HEDs, with only two samples being analyzed). Both Rb and K are moderately volatile elements and the coupled enrichments of heavy Rb and K isotopes in Juvinas relative to other HED meteorites indicate a different in-situ degassing/impacting history of otherwise typical main-group eucrite Juvinas.

The exact reason for the high $\delta^{87}\text{Rb}$ and $\delta^{41}\text{K}$ in Juvinas relative to other HED meteorites remains unclear. However, the heterogeneity during magma ocean degassing, as well as localized evaporation and volatile loss accompanied by the brecciating and mixing processes could all possibly induce the $\delta^{41}\text{K}$ scattering observed in Juvinas. The occurrence of such processes on the Juvinas “precursor” materials would result in the evaporation of K and shift the K isotopic composition. After the sequential brecciation formation, the heavy $\delta^{41}\text{K}$ feature would be preserved in the heterogeneous lithologies of Juvinas.

2.4.4. The origin of the heavy K isotope enrichment in 4-Vesta

Regardless of the intra-clan K isotopic composition scatter in HED meteorites, all HEDs are substantially isotopically heavier than other planetary bodies. The most important question is why 4-Vesta exhibits such a unique K isotopic composition compared to chondrites and other differentiated bodies with varying sizes and thermal histories. 4-Vesta is widely known as one of
the most K (and other moderately volatile elements) depleted bodies (only angrites show a greater depletion). Its K/U ratio is more than one magnitude lower than that of the CI chondrites (Kitts and Lodders, 1998). As discussed previously, coupled volatile depletion and heavy K isotope enrichment in 4-Vesta could not be accomplished only through in-situ igneous processes and must require at least asteroid-scale operations. Three explanations should be taken into account: (1) Magma ocean: 4-Vesta experienced volatile degassing during a global magma ocean and the volatiles escaped to space (Day and Moynier, 2014; Dhaliwal et al., 2018). (2) Accretion: 4-Vesta acquired its volatile depletion and heavy K isotopic feature from the vapor loss during the accretionary growth of planetesimals (Halliday and Porcelli, 2001; Hin et al., 2017; Norris and Wood, 2017). (3) Precursor: 4-Vesta accreted from volatile-poor materials already depleted in volatiles, either through incomplete condensation from the proto-solar nebula or partial re-evaporation in the nebular environment (Hans et al., 2013). The first two mechanisms are associated with planetary processes, whereas the last one involves nebular processes.

**Magma ocean degassing**

Magma ocean degassing is one possible mechanism for the depletion of moderately volatile elements such as Zn on the Moon (Kato et al., 2015). A restrict range of $\Delta^{17}$O in HED meteorites has demonstrated that the equilibration of oxygen happened prior to the igneous fractionation, and that a global-scale melting event (> 50%), which led to the development of magma ocean, is favored on 4-Vesta (Greenwood et al., 2005; Greenwood et al., 2014). Greenwood et al. (2014) also suggested that the transition from global-scale melting events to localized magmatic activities was rapid on 4-Vesta. Furthermore, numerical modeling of magma oceans has been conducted to
understand the early thermal history and geological evolution of 4-Vesta and other planetary bodies (Tonks and Melosh, 1993; Righter and Drake, 1997; Ghosh and McSween, 1998; Gupta and Sahijpal, 2010; Mandler and Elkins-Tanton, 2013; Neumann et al., 2014).

Magma ocean degassing can be used to explain the K isotopic variations seen in the basaltic eucrites (see Section on Isotopic variation within eucrites). Nevertheless, whether it can be used to explain the overall loss of less volatile K and the associated K isotopic fractionation on 4-Vesta needs more investigations if assuming HEDs accreted from materials with CI chondritic $\delta^{41}$K values. With global magma oceans being developed pervasively on small planetary bodies in the early Solar System (Greenwood et al., 2005), magma ocean degassing has been used as a plausible explanation for volatile element losses for Zn, Cl, and Rb not only on asteroid 4-Vesta but also on the Moon (Paniello et al., 2012b; Paniello et al., 2012a; Sarafian et al., 2013; Pringle and Moynier, 2017; Sarafian et al., 2017; Ma and Liu, 2019). Potassium is a moderately volatile element with a nebular 50% condensation temperature ($T_c$) of ~1006 K between Zn (726 K) and Cu (1037 K) (Lodders, 2003). However, this sequence of volatilities, established under solar nebular conditions (Lodders, 2003), is likely to be different from that of volatilities during vaporization of a silicate melt (e.g., magma ocean degassing) (Jochum and Palme, 1990; Norris and Wood, 2017). Jiang et al. (2019) conducted a new thermochemical calculation, aiming at computing the partial vaporization pressures of Cu$_2$O, ZnO, and K$_2$O in a silicate melt on tektites as a function of pressure, temperature, oxygen fugacity, and the presence/absence of chlorine. Their results showed that Cu and Zn are more prone to escape from the silicate melt owing to the positive deviation of their activity coefficients from unity over a wide temperature range (1400-2200 K). To the contrary,
K is lack of escaping tendency from the melt as a consequence of its low activity coefficient. The theoretical calculation meets an agreement with the observed heavy Cu and Zn isotopes enrichments and the dismissal of K isotopic fractionation in tektites (Jiang et al., 2019). Hence, it is rational to expect the deficiency of K being dramatically vaporized and isotopically fractionated during the magma ocean degassing on asteroid 4-Vesta.

For the purpose of simulating the potential K vaporization during magma ocean degassing on 4-Vesta, a comparable thermochemical calculation is conducted in this study with parameters being adjusted to fit conditions of the Vestan magma ocean. We majorly focus on the vaporization behaviors of K and Zn as a parallel comparison and the effect of chlorine on their relative volatility by performing calculations with MAGMA code. Sossi and Fegley (2018) summarized experimental studies showing that evaporation of K₂O and ZnO occurs via congruent dissociation to their constituent elements. The evaporation reactions, their standard Gibbs energy changes (ΔG° from the IVTAN database (Belov et al., 1999) and the JANAF Tables), and equilibrium constants are summarized below. The subscripts K and Zn denote evaporation of K₂O and ZnO.

**Evaporation of K₂O**

\[
K_2O \text{ (liquid)} = 2K \text{ (gas)} + \frac{1}{2}O_2 \text{ (gas)} \tag{2.3}
\]

\[
\Delta G^\circ_K = 493,364 - 277.7407T + 0.01313T^2 \text{ J mol}^{-1} \tag{2.4}
\]
The equation for $\Delta G^\circ_K$ is valid from 1013 ~ 3000 K. The lower limit is the melting point of $K_2O$ (solid), taken from the IVTAN database. The upper limit is the highest temperature at which we did a fit to the tabular data and is arbitrary.

$$K_K = e^{\frac{-\Delta G^\circ_K}{RT}} = \frac{P_{K_2O}^{1/2}}{a_{K_2O}} \quad (2.5)$$

$$\log K_K = 14.5073 - \frac{25.770}{T} - 6.86 \times 10^{-4}T \quad (2.6)$$

Evaporation of ZnO

$$ZnO \; (\text{zincite}) = Zn \; (g) + \frac{1}{2} \; O_2 \; (g) \quad (2.7)$$

$$\Delta G^\circ_{Zn} = 468,175 - 202.9T \; J \; \text{mol}^{-1} \quad (2.8)$$

The equation for $\Delta G^\circ_{Zn}$ is valid from 1000 to 2248 K, the melting point $T_m$ of zincite (Bunting, 1930; Jak et al., 1997). At higher temperatures the vaporization reaction is

$$ZnO \; (\text{liquid}) = Zn \; (g) + \frac{1}{2} \; O_2 \; (g) \quad (2.9)$$

$$\Delta G^\circ_{Zn(\text{liq})} = 413,886 - 178.75T \; J \; \text{mol}^{-1} \quad (2.10)$$

This equation is based on the enthalpy of melting (~54.3 kJ mol$^{-1}$) from Jak et al. (1997). It is revised slightly from that used by Visscher and Fegley (2013) and is valid to 4000 K. The equilibrium constant for ZnO vaporization is
\[
K_{Zn} = \exp \left( -\frac{\Delta G^{\circ}_{Zn}}{RT} \right) = \frac{P_{Zn}^{1/2}}{a_{ZnO}} \quad (2.11)
\]

\[
\log K_{Zn} = 10.596 - \frac{24.454}{T} \quad (2.12)
\]

The symbols “\(a_{K2O}\)” and “\(a_{ZnO}\)” are the thermodynamic activities of \(K_2O\) and \(ZnO\). These are unity for the pure oxides but are less than unity for \(K_2O\) and \(ZnO\) dissolved in molten silicates.

The activity of \(K_2O\) or \(ZnO\) (or another oxide) in a molten silicate is equal to its mole fraction (\(X_i\)) times its activity coefficient (\(\gamma_i\))

\[
a_i = \gamma_i X_i \quad (2.13)
\]

In general, the activity coefficient \(\gamma_i\) is a function of temperature, pressure, and composition. Table 2 of Sossi and Fegley (2018) lists \(\gamma_{ZnO}\) values ~ 0.25–0.58 at 1673–1823 K in CaO–Al\(_2\)O\(_3–\)SiO\(_2\) (CAS) melts and \(\gamma_{K2O}\) values ~ 10\(^{-8.4}\)–10\(^{-6.3}\) for a CAS melt with FeO and KAlSiO\(_4\). The activity coefficients for \(ZnO\) and \(K_2O\) in the binary \(ZnO–SiO_2\) and \(K_2O–SiO_2\) systems and in ternary systems with SiO\(_2\) and other metal oxides are similar (e.g., see Charles, 1967; Plante, 1979; Björkman, 1986; Jak et al., 1997 and discussion and references in Sossi and Fegley, 2018). Thus, \(K_2O\) activity coefficients are many orders of magnitude smaller than those of \(ZnO\) in silicate melts.

The symbol “\(f_{O2}\)” in the equilibrium constant expressions denotes the oxygen fugacity, which is equal to the fugacity coefficient \(\phi\) times the \(O_2\) partial pressure.
The oxygen fugacity $f_{O_2}$ is effectively the same as the $O_2$ partial pressure at the very low oxygen fugacities expected for a magma ocean on Vesta, e.g., $\sim 10^{-13.3}$ bar at 1150 °C (Stolper, 1977), which is 0.7 log unit below that of the iron–wüstite buffer

$$1.90 \text{ Fe (metal)} + O_2 (\text{gas}) = 2 \text{ Fe}_{0.95}O (\text{wüstite}) \hspace{1cm} (2.15)$$

$$\log f_{O_2} (\text{bar}) = 5.2614 - \frac{27.341}{T} + 0.4291 \log T \hspace{1cm} (2.16)$$

O’Neill and Pownceby (1993) derived this equation from their measurements that go from the wüstite eutectoid temperature (833 K) to its melting point (1650 K).

When we rearrange the equilibrium constant expressions, we see that the partial vapor pressures of K and Zn are given by the equations

$$P_{K(g)} = \gamma_{K_2O}^{1/2} \left( K_K X_{K_2O} \right)^{1/2} f_{O_2}^{1/4} \hspace{1cm} (2.17)$$

$$P_{Zn(g)} = \gamma_{ZnO} K_{Zn} X_{ZnO} f_{O_2}^{1/2} \hspace{1cm} (2.18)$$

These equations show the partial vapor pressures of K and Zn are inversely proportional to oxygen fugacity to the 4th or 2nd power, respectively. This has been verified experimentally for ZnO by Truesdale and Waring (1941), and for Na$_2$O, which undergoes dissociative vaporization to...
elements like K₂O, by Sanders (1979). Donaldson (1979) qualitatively showed that more Na₂O and K₂O were lost from basaltic melt heated at lower fO₂ than from heating at higher fO₂ under otherwise constant conditions (his Figure 3 and Table II). But he did not measure Na or K gas partial pressures.

Assuming that the temperature – dependent fO₂ of the putative Vestan magma ocean is that of the IW buffer therefore gives a lower limit to the partial vapor pressures of Zn and K gas above it. Using the thermodynamic data given earlier we derive the following two equations

\[
\log P_K (\text{bar}) = 5.9383 - \frac{6.0498}{T} - 3.429 \times 10^{-4} T - 0.10728 \log T + \frac{1}{2} \log X_{K_2O} + \frac{1}{2} \log \gamma_{K_2O} \quad (2.19)
\]

\[
\log P_{Zn} (\text{bar}) = 7.9653 - \frac{10.783.865}{T} - 0.21455 \log T + \log X_{ZnO} + \log \gamma_{ZnO} \quad (2.20)
\]

We used these two equations to compute the partial vapor pressures of K and Zn above a putative Vestan magma ocean over the 1400 ~ 1900 K temperature range. This temperature range spans the silicate solidus (1425 K) and silicate liquidus (1850 K) in Table 2 of Neumann et al. (2014).

Kitts and Lodders (1998) summarized the bulk compositions for 20 eucrites and we used their values for Juvinas (see their Tables 3 and 4). We also computed an average eucrite composition from the unweighted mean of their data. The activity coefficients for K₂O and ZnO were computed using the MAGMA code (Fegley and Cameron, 1987; Schaefer and Fegley, 2004; Visscher and Fegley, 2013). These papers describe the code in detail and discuss its validation against experimental data.
The results of our calculations are shown in Fig. 2.7, which are indicated by solid lines (Juvinas) and dashed lines (average eucrite). In both cases, the partial vapor pressure of Zn above a magma ocean is about 100–400 times larger than that of K(gas) over the entire temperature range considered (1400–1900 K). These results indicate that Zn is more volatile than K and would be more easily lost from a putative magma ocean on Vesta early in its history.

![Graph](image)

**Figure 2.7.** The partial vapor pressure of K and Zn above a putative Vestan magma ocean over the 1400 to 1900 K temperature range calculated as described in the text. The solid lines stand for the composition of Juvinas (Kitts and Lodders, 1998). The dashed lines stand for an average eucrite composition from the unweighted mean of 20 eucrites summarized in Kitts and Lodders (1998).
Following Hashimoto (1983) we use volatility ($\xi_{ij}$) to quantify the tendency of Zn to be lost relative to K during evaporation from a magma ocean and subsequent atmospheric escape. The volatility ratio of Zn and K is given by his equation (16)

$$\frac{\xi_{\text{Zn}}}{\xi_{\text{K}}} = \frac{a_{\text{Zn}} \gamma_{\text{Zn}}}{a_{\text{K}} \gamma_{\text{K}}} \cdot \frac{P_{Zn}^{\circ}}{P_{K}^{\circ}} \cdot \frac{\bar{M}_{Zn}}{\bar{M}_{K}} = \frac{a_{\text{Zn}} \gamma_{\text{Zn}}}{a_{\text{K}} \gamma_{\text{K}}} \cdot \frac{P_{Zn}^{\circ}}{P_{K}^{\circ}} \cdot 1.08 \ (2.21)$$

The $P_{i}^{\circ}$ values are the vapor pressures of pure ZnO and K$_2$O and the $\bar{M}_{i}$ values are the mean molar mass of the evaporated species. The activity coefficients of ZnO and K$_2$O in silicate melts were discussed earlier and we incorporated them into our partial pressure calculations plotted in Fig. 2.7.

The $\alpha_{i}$ values are the Langmuir coefficients for evaporation of Zn and K from the molten silicate and are equal to the ratio of the observed vapor pressures and the equilibrium vapor pressures. Langmuir coefficients are unity if vaporization is not kinetically inhibited and are less than unity if kinetic inhibition occurs. Typically, evaporation of solids with complex structures and strong bonds has $\alpha_{i}$ values less than unity while evaporation of melts at high temperatures has $\alpha_{i}$ values closer to unity (e.g., see Sossi and Fegley, 2018, section 4.7 of Schaeffer and Fegley, 2004, Paule and Margrave, 1967, and references therein).

Our results in Fig. 2.7 imply
\[
\frac{\xi_{Zn}}{\xi_K} \sim 100 - 400 \ (2.22)
\]

unless

\[
\frac{\alpha_{Zn}}{\alpha_K} \ll 0.01 - 0.0025 \ (2.23)
\]

We think it is unlikely that the ZnO Langmuir coefficient from a molten silicate is much less than that of K$_2$O. Fedkin et al. (2006) derived Langmuir coefficients from their analysis of vaporization experiments by several groups. They give $\alpha_i$ values for vaporization of oxides dissolved in molten silicates into vacuum of ~0.13 for K, 0.26 for Na, 0.14–0.19 for Mg, and 0.23–0.28 for Fe. It has been known for some time that ZnO is less basic than K$_2$O and that its basicity is in the sequence CaO, ZnO, MgO, FeO (Flood et al., 1947; Rey, 1948). Magnesium oxide and FeO–like ZnO–undergo dissociative vaporization (Table 1, Sossi and Fegley, 2018). We assume that the $\alpha_i$ values for MgO, FeO, and ZnO are similar on the basis of their similar vaporization reactions and basicity in silicate melts. The results of Fedkin et al. (2006) support our assumption as their derived $\alpha_i$ values for oxides of similar basicity and similar vaporization reactions (i.e., Na$_2$O and K$_2$O, MgO and FeO) are similar within a factor of two. We derive

\[
\frac{\alpha_{Zn}}{\alpha_K} \sim \frac{\alpha_{Mg}}{\alpha_K} = \frac{0.14-0.19}{0.13} \sim 1.1 - 1.5 \ (2.24)
\]

\[
\frac{\alpha_{Zn}}{\alpha_K} \sim \frac{\alpha_{Fe}}{\alpha_K} = \frac{0.23-0.28}{0.13} \sim 1.8 - 2.2 \ (2.25)
\]

We conclude that the $\alpha_{Zn}/\alpha_K$ ratio is ~ 1 – 2 and that Zn is significantly more volatile than K and is lost much easier than K from a magma ocean on Vesta.
Potassium and Zn both form chloride gases and we also studied the effect of chlorine on their relative volatility by performing calculations with the MAGMA code. Koster van Groos and Wyllie (1969) measured 2.5 wt% NaCl solubility in molten albite at 1020 °C (1293 K). The corresponding NaCl mole fraction is ~0.028 and the activity coefficient is ~36. Bateson and Turner (1939) measured $\gamma_{\text{NaCl}} \sim 43$ at 1673 K in soda–lime glass and Tanimoto and Rehren (2008) measured similar values for the NaCl and KCl activity coefficients in soda–lime glass at 1323 K. In the absence of data for melts with eucritic composition we use a KCl activity coefficient of 40 in our calculations. We used average Cl and Zn contents of 18.4 and 2.9 ppm (calculated from data in Kitts and Lodders, 1998) in our calculations, which were done at 1650 K, approximately halfway between the silicate solidus and liquidus of Neumann et al (2014).

Our results are plotted in Fig. 2.8 as the log mole fraction of an oxide remaining in the magma ocean versus the total mass fraction of the magma ocean that has been vaporized. The presence of chlorine does not change our conclusion that Zn is significantly more volatile than K and is lost much easier than K from a magma ocean on 4-Vesta. The reason is that most chlorine is lost as Zn chloride gases and its depletion trend on Fig. 2.8 is roughly similar to that of Zn – both elements are completely lost prior to 0.01% total vaporization of the magma. In contrast the K$_2$O mole fraction in the magma ocean remains unchanged until ~0.6% of the magma ocean is vaporized. Potassium depletion begins at this point and is complete ($X_{\text{K}_2\text{O}} = 10^{-9}$) by ~1.8% vaporization of the total mass. Note that Na vaporization is similar to that of K.
Our major conclusion from modeling is that Cl and Zn can be completely or almost completely lost by vaporization from a magma ocean early in 4-Vesta’s history without altering the K and Na inventory. Consequently, modeling based on isotopes of these two highly volatile elements (Zn and Cl) may not necessarily constrain loss of K from 4-Vesta.

Further evidence against the magma ocean degassing, which could cause the K isotopic fractionation, can be seen from the lack of K isotopic variation among different chemical subgroups in HEDs. If magma degassing causes all of the K loss observed in HED samples, and if
degassing and crystallization took place simultaneously, the crystallization sequence in the magma ocean solidification timeline is expected to record different isotopic values (i.e., any rocks crystallized in a later stage have endured longer degassing time, and are expected to be more depleted in lighter isotopes; whereas the early-formed cumulates tend to preserve their original isotopic feature) (Day and Moynier, 2014). This prediction is supported by the measurements of Cl isotopes (Sarafian et al., 2017). However as shown in Fig. 2.5(a) and (b), no correlation is observed between $\delta^{41}$K and both Hf concentrations and Mg#, indicating that during the igneous processes both the more evolved and the less evolved HEDs yield the same $\delta^{41}$K values. Sarafian et al. (2017) used the magma ocean metal-chloride (e.g., ZnCl$_2$, CuCl) degassing hypothesis to explain the Cl isotopic composition on 4-Vesta and found a correlation between Cl and Zn isotopes, albeit in only four samples. Such a correlation is not observed in the K isotopes of HED meteorites in this study, but this is not surprising. Models of the eucrite parent body (EPB) predict that the K/Cl molar ratio was $\gg$ unity (e.g., Dreibus et al., 1997; also see Table 4.6 of Lodders and Fegley, 2011); thus, only a small fraction of total potassium could be degassed as KCl gas, and a correlation between K and Cl isotopes is not expected. Conversely Zn/Cl and Cu/Cl molar ratios less than unity are predicted for the EPB.

In summary, although magma oceans are widely expected on early-formed asteroidal bodies in the Solar System (Greenwood et al., 2005), global-scale magma ocean degassing is not likely to generate the substantial K depletion and K isotopic fractionation observed in this study. Rather, this global- or in situ-scale degassing process(es) is contributed to the K isotopic compositional scattering among the HED clan.
Accretion

Vapor loss during the accretionary growth of planetesimals has been proposed to be another viable way to explain the volatile depletion in planetary materials compared to chondrites (e.g., Hin et al., 2017). Two scenarios have been quantitatively evaluated in the past: (1) shock waves induced vaporization (Dauphas et al., 2015); (2) direct vapor loss from shock generated melts/magma ponds (Hin et al., 2017). In the first scenario, the vapor generation mechanism is extremely inefficient for bodies smaller than 0.2 M_{Earth} due to the low impact velocities of colliding planetesimals (Dauphas et al., 2015) and cannot produce the large volatile depletion observed in HED meteorites. In the second scenario, the vapor produced in planetary bodies is significantly more abundant than that in the first scenario. For example, Hin et al. (2017) showed that the Earth is slightly heavier in Mg isotopes than chondrites as a result of the accretional vapor-melt fractionation. Their model, if correct, predicted >99.9% K loss via shock-generated evaporation during the Earth formation and required 20% re-accretion of chondritic materials in order to match the K concentration of BSE. In the second scenario, the vapor which outgasses from silicate melts generated by impacts is essentially identical to the degassing of magma ocean and later local-scale magmatism generated by $^{26}$Al decay on 4-Vesta, which we have briefly discussed in the section ‘Magma Ocean Degassing’. The difference however is that the temperatures of the silicate melts generated by impacts (1400-3500 K) are potentially higher than those of the magma ocean of 4-Vesta (~1637 K estimate of the magma ocean). Although we have argued in the ‘Magma Ocean Degassing’ Section that the substantial K depletion of 4-Vesta cannot be achieved through
degassing at magmatic temperatures, it is possible to lose K via vapor outgassing from silicate melts at high temperatures generated by impact melting (see “Isotopic variation within eucrites”).

**Precursor depletion**

As discussed above, the K depletion and isotopic fractionation during magma ocean degassing fail to completely explain the K isotope fractionation observed. Another remaining option is that 4-Vesta accreted from materials that were already depleted in volatiles prior to accretion and simply inherited its heavy K isotopic composition. Such a suggestion regarding the volatile-depleted precursor materials that accreted to form 4-Vesta was first proposed by Palme (2000). It is further supported by the recently reported K isotopic compositions of various carbonaceous and ordinary chondrites by Bloom et al. (2018) and Ku and Jacobsen (2019). This data set shows $\delta^{41}$K variations in chondritic components and demonstrates vast K isotopic heterogeneity in the early Solar System. Particularly, some volatile-depleted chondrites (e.g., CV, CM) show enrichments in heavy K isotopes relative to CI (Ku and Jacobsen, 2019) (yet we are not suggesting that asteroid 4-Vesta originated from such chondrites owing to the chemical infeasibility, e.g., oxygen isotopes). Therefore, our suggestion that the HED precursor may have had a heavy K isotopic composition is viable. One possible candidate for the parent material of 4-Vesta is a volatile-depleted chondrule-rich precursor. Chondrules could possibly obtain their enriched heavy K isotopes by incomplete condensation/re-evaporation in the early hot solar nebula (Grossman, 1972; Cassen, 1996; Davis, 2006; Davis and Richter, 2013). Indeed, the K isotopic compositions of individual chondrules have been previously measured and significant K isotopic fractionation has been observed, with a striking range of $-10 \sim +18\%$ (Alexander and Grossman, 2005). It has been
proposed that thermally processed and volatile-depleted chondrules are the building blocks of volatile-depleted planetary bodies (Bollard et al., 2017) and a recent model has shown that the large (>100 km) asteroids such as 4-Vesta grow primarily through chondrule accretion (Johansen et al., 2015).

2.4.5. The Moon-4-Vesta analogy

A considerable amount of evidence has shown that the Moon shares some overall compositional similarities with the HED parent body (e.g., Ruzicka et al., 2001 and references therein; Tera et al., 1970). The high degree of resemblance in moderately volatile and volatile-lithophile elements (e.g., Na, K, Rb, and Cs), ferromagnesian elements (e.g., Mg, Fe, Cr, and V) and many siderophile elements (e.g., Ni, Co, Ga, and Ir) between lunar mare basalts and non-cumulate eucrites has been long recognized (Tera et al., 1970; Anders, 1977; Dreibus et al., 1977; Morgan et al., 1978; Taylor, 1986; Taylor and Esat, 1995; Ruzicka et al., 2001). Average eucrites along with both low-Ti and high-Ti mare basalts reveal a progressive depletion sequence in alkali elements (Na, K, Rb, and Cs) relative to CI chondrites with regard to their volatilities; whereas terrestrial basalts and martian meteorites are relatively more volatile-rich (Lodders and Fegley, 2011). Such analogy is further strengthened by the newly-revealed heavy potassium isotopic composition in both Apollo lunar samples and HED meteorites (Wang and Jacobsen, 2016b, this study).

Among the limited measured K isotope data for different parent bodies, 4-Vesta and the Moon are the only two differentiated bodies exhibiting a heavy K isotope enrichment. Previously, Wang and Jacobsen (2016b) reported that the Moon is also significantly enriched in heavy K isotopes relative
to the Earth and chondrites. They explained that the $\sim0.4\%$ K isotopic difference between the Earth and Moon is a result of partial condensation of silicate droplets from the Bulk Silicate Earth vapor which formed during the Moon forming impact. This interpretation relies on the extrapolation of the previous experimental data of K isotopic fractionation (Yu et al., 2003; Richter et al., 2011) and is still controversial (Dauphas et al., 2018). Although to settle the debate, theoretical calculation and experimental calibration of equilibrium isotopic fractionation factors of K between melt and vapor are needed, here we can still discuss the implications of the K isotopes of HEDs and martian meteorites from this study.

The alternative explanation proposed for the K isotopes of the Moon is that the heavy K isotope enrichment was inherited from its precursor (Dauphas et al., 2018). The canonical Giant Impact model for the origin of Moon predicted a disc derived primarily from the Mars-size impactor’s mantle (e.g., Canup, 2014, and reference therein). If the impactor had already been depleted in volatiles and experienced K isotope fractionation prior to the Giant Impact, the Moon may simply inherit the heavy K isotopic composition from the impactor. The issue with this alternative explanation is that the impactor has to bear a close genetic relationship with the Earth according to the mass-independent isotope systems (e.g., Akram and Schönbächler, 2016; Dauphas, 2017), and the impactor and Earth have to accrete from the same building-block materials at the same locality in the solar nebula. Thus, this “precursor” scenario is unlikely to explain the $\sim0.4\%$ K isotopic difference between Earth and Moon. A more likely scenario to explain this difference is through the process of Giant Impact total-vaporization and partial-condensation (Greenwood et al., 2018; Lock et al., 2018).
In contrast, 4-Vesta was not formed as the result of a Giant Impact and cannot be explained with the same mechanism proposed for the Moon (i.e., partial condensation of silicate droplets from a BSE vapor; Wang and Jacobsen, 2016b). As discussed in former sections, the unique $\delta^{41}K$ feature of 4-Vesta could be indigenous and inherited from the building-block materials. 4-Vesta accreted with precursor materials at a different locality from that of the Earth, Moon and Mars. Nebula processes at different localities in the solar nebula naturally generate different amount of volatile depletion (e.g., different groups of chondrites) and isotopic fractionation through either incomplete condensation or partial re-evaporation. Such a process is a viable way to generate small (e.g., 0.4 or 0.8‰ depending on the condensation temperature) K isotopic fractionation observed in this and previous studies. Furthermore, as supported by the K isotope similarities between 4-Vesta and the Moon, this incomplete condensation or partial re-evaporation from a hot solar nebular setting for the 4-Vesta precursors resembles, to some degree, the partial condensation of silicate droplets from a Bulk Silicate Earth vapor.
2.5. Conclusions

The K isotopic compositions of four terrestrial igneous rocks (seven aliquots), one ordinary chondrite, and one lunar meteorite are all comparable to published literature data. The martian samples define a relatively narrow $\delta^{41}$K range with an average of $-0.36 \pm 0.12\%$ (2 SD), resembling the BSE K isotopic composition with a slightly $^{41}$K enrichment. The non-hot desert HED samples are extremely enriched in heavy K isotopes compared to terrestrial igneous rocks, martian meteorites, lunar samples, and chondritic samples. Based on the homogeneous $\delta^{41}$K between MG-NL trend and Stannern trend as well as the lack of correlations between $\delta^{41}$K and their corresponding [Hf]/Mg# in HEDs, we infer that there is no K isotopic fractionation observed during igneous processes on 4-Vesta, and the average $\delta^{41}$K ($+0.36 \pm 0.16\%$) obtained from the HED meteorites clan is representative of the ‘Bulk Silicate Vesta’.

The enrichment of $^{39}$K observed in hot desert NWA meteorites can be well explained by simple addition of terrestrial K during residence on Earth. The $\delta^{41}$K values of supernatants, which are similar and slightly lighter than the BSE value, may suggest some low-temperature K fractionation processes on Earth. Potassium isotopic compositional scattering among the HED meteorites suggests that Rayleigh distillation processes, including localized evaporation and volatile loss owing to volcanic degassing or impacts did occur, with an empirical fractionation factor between 0.9996 and 0.9998.

In order to explain the enrichment of heavy K isotopes in Bulk Silicate Vesta compared to Earth, Mars, Moon, and chondritic parent bodies, we considered three major mechanisms: inheriting K
elemental and isotopic signatures from “precursor” materials through nebular-scale processes, accretional volatile loss, and magma ocean degassing. We suggest that it is unlikely, although not impossible, for 4-Vesta to loss K and to generate substantial K isotopic fractionation during magma ocean degassing alone.
Acknowledgments

We thank the Guest Editor Dr. Yang Liu for handling and editing of this manuscript. We also thank four anonymous reviewers for their detailed and constructive comments. We are grateful to the ANSMET (Antarctic Search for Meteorites), NASA Johnson Space Center, Smithsonian National Museum of Natural History, The American Museum of Natural History, Western Australia Museum, The Monnig Meteorite Collection at Texas Christian University, National Museum in Prague and the British Museum for providing samples. US Antarctic meteorite samples are recovered by the ANSMET program which has been funded by NSF and NASA and characterized and curated by the Department of Mineral Science of the Smithsonian Institution and Astromaterials Acquisition and Curation Office at NASA Johnson Space Center. B. Fegley and K. Lodders were supported by NSF Grants AST-1517541 and AST-1517541. Z. Tian acknowledges the fellowship from the McDonnell International Academy. We are grateful for financial support from the McDonnell Center for the Space Sciences. We thank Dr. Piers Koefoed for proofreading the manuscript.
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Chapter 3:

Potassium isotopic composition of the Moon

Abstract

The Moon is depleted in water and other volatiles compared to Earth and the bulk solar composition. Such depletion of volatile elements and the stable isotope fractionations of these elements can be used to better understand the origin and early differentiation history of the Moon. In this study, we focus on the moderately volatile element, potassium, and we report the K elemental abundances and isotopic compositions ($\delta^{41}$K relative to NIST SRM 3141a) for nineteen Apollo lunar rocks and lunar meteorites (twenty-two subsamples), spanning all major geochemical and petrologic types of lunar materials. The K isotopic compositions of low-Ti and high-Ti basalts are indistinguishable, providing a lunar basalt average $\delta^{41}$K of $-0.07 \pm 0.09$‰ (2SD), which we also consider to be the best estimate of the lunar mantle and the bulk silicate Moon. The significant enrichment of K in its heavier isotopes in the bulk silicate Moon, compared with the bulk silicate Earth ($\delta^{41}$K = $-0.48 \pm 0.03$‰), is consistent with previous analyses of K isotopes and other moderately volatile elements (e.g., Cl, Cu, Zn, Ga, and Rb). We also report the first analyses of K isotopes for lunar nonmare samples, which show large variations of K isotopic ratios compared to lunar basalts. We interpret this large K isotopic fractionation as the result of late-stage magma ocean degassing during urKREEP formation, which is also coupled with Cl isotope fractionation. Degassing of urKREEP likely triggered redistribution of K isotopes in the Moon, enriching the urKREEP reservoir in heavy K isotopes while implanting the light K isotopic signatures onto the lunar surface. This scenario suggests a heterogeneous distribution of K isotopes in the Moon as a consequence of its magmatic evolution.
3.1. Introduction

The origin of the Moon has been the subject of intense scientific debate for centuries. The Giant Impact hypothesis has been the leading scenario since the mid 1970’s (Hartmann and Davis, 1975; Cameron and Ward, 1976). For decades, numerous efforts and refinements have been made to lunar formation models in attempts to reconcile the thermal, chemical, physical, and dynamical properties (e.g., Lugmair and Shukolyukov, 1998; Canup and Asphaug, 2001; Wiechert et al., 2001; Canup, 2004; Pahlevan and Stevenson, 2007; Touboul et al., 2007; Canup, 2008; Armatge et al., 2012; Canup, 2012; Ćuk and Stewart, 2012; Zhang et al., 2012; Canup, 2014; Ćuk et al., 2016; Young et al., 2016; Mougel et al., 2018; Lock et al., 2018; Hosono et al., 2019). Yet, the origin of the Moon still remains unresolved (e.g., Barr, 2016 and references therein).

The volatile depletion pattern of the Moon, including for elements such as Na, K, Cu, Zn, and Rb, relative to that of the Earth, is of particular importance in the lunar formation debate (e.g., Tera et al., 1970; Taylor et al., 2006). Early observations were that these elements are more depleted in the Moon than in the Earth, implying significant volatile element loss from the Moon during its formation. Potassium (50% Tc ~1006 K [Lodders, 2003]) is a promising candidate among moderately volatile elements (MVEs) to shed light on the mechanisms of such volatile depletion. Potassium (K) is one of the more abundant moderately volatile elements in the Solar System and has three naturally occurring isotopes: $^{39}$K (abundance: 93.26%), $^{40}$K (0.0117%, half-life of $1.248(3) \times 10^9$ yrs, [Kossert and Günther, 2004]), and $^{41}$K (6.73%). Using K stable isotopic ratios (i.e., $^{41}$K/$^{39}$K) to interrogate volatile depletion processes among the terrestrial planets and during
the formation of the Moon can be traced back to Humayun and Clayton (1995), who reported that there was no distinguishable isotopic fractionation within their ~ 0.5‰ uncertainty among most planetary materials, and who further used such K isotopic uniformity to eliminate the possibility of partial evaporation for the observed volatile abundance depletions. Recent developments in K isotope analysis have led to a precision improvement of an order of magnitude and have enabled measurements of K isotopic compositions ($^{41}\text{K}/^{39}\text{K}$) at a precision better than 0.05‰ (Li et al., 2016; Wang and Jacobsen, 2016a; Wang and Jacobsen, 2016b; Morgan et al., 2018). With this improved precision, Wang and Jacobsen (2016b) reported a ~ 0.4‰ heavy K isotope enrichment in lunar samples relative to the bulk silicate Earth (BSE) value. Such K isotope differences between the BSE and the Moon have been attributed to a high-energy, high-angular-momentum Giant Impact Moon-forming event (Lock et al., 2018); or, alternatively, to an incomplete accretion of volatile-poor melt to the Moon within an impact-generated disk (Canup et al., 2015). Nevertheless, there is still debate regarding such explanations owing to the uncertainties of vapor-melt isotopic fractionation factors (Zeng et al., 2019) and alternate models of volatile losses for the Moon (Day and Moynier, 2014).

Previous K isotopic studies have largely focused on placing the collected data into the broad framework of lunar volatile depletion, and the origin and subsequent evolution of the Earth-Moon system (Wang and Jacobsen, 2016b). For this reason, the distribution of K and the fractionation of K isotopes among different major lunar reservoirs remain unconstrained. Inhomogeneous distribution of potassium and its isotopic fractionation between major reservoirs would reveal important information on the processes of volatile redistribution within the Moon. The Moon is
known to have a chemically and compositionally stratified structure, revealed by the Apollo and Luna returned samples and remote sensing data such as Clementine, Lunar Prospector (LP), Lunar Reconnaissance Orbiter (LRO), and the Gravity Recovery and Interior Laboratory (GRAIL) (e.g., Zuber et al., 1994; Lawrence et al., 1998; Tompkins and Pieters, 1999; Jolliff et al., 2000; Prettyman et al., 2006; Taylor and Wieczorek, 2014).

Recognition of anorthosite clasts in the first returned Apollo regolith samples led to the concept of the lunar magma ocean (LMO) (Smith et al., 1970; Wood et al., 1970), which is now a paradigm for early lunar differentiation. In the LMO model, the Moon underwent wholesale melting after a high energy accretion process (presumably the giant impact Moon formation event). Progressive fractionation then took place, with crystallization of ultramafic to mafic cumulates to form the lunar mantle (Snyder et al., 1992). After ~75% lunar magma ocean crystallization, melts reached plagioclase saturation and low-density plagioclase would float in the residual melt, resulting in a primary lunar upper crust. At ~90% LMO crystallization, dense Fe-Ti oxides (i.e., ilmenite) began to precipitate and may have led to mantle overturn owing to gravitational instability (e.g., Elkins Tanton et al., 2002). The LMO model also predicts a layer or concentration as the last residual melt at the crust-mantle boundary, named urKREEP: KREEP for potassium, rare earth element, and phosphorous, and “ur” meaning original or earliest (Warren and Wasson, 1979). The urKREEP layer or segregations, laterally concentrated at depth in the Procellarum KREEP Terrane (e.g., Haskin et al., 2000; Jolliff et al., 2000; Wieczorek and Phillips, 2000; Laneuville et al., 2018), would have been enriched in incompatible elements as well as heat-producing elements (e.g.,
radioactive U, Th, and $^{40}\text{K}$), and can be potentially linked to Apollo KREEP-rich samples (e.g., Korotev, 2000).

Extreme asymmetric distribution of K and other heat-producing elements (Th, U) has been observed from data obtained by the Lunar Prospector and Kaguya gamma-ray spectrometers (Jolliff et al., 2000; Lawrence et al., 2000; Lawrence, 2003; Kobayashi et al., 2012). On the basis of global FeO and Th distributions, the lunar crust can be characterized as exhibiting distinct geologic terranes (i.e., Procellarum KREEP Terrane [PKT], Feldspathic Highlands Terrane [FHT], and South Pole-Aitken Terrane [SPAT], Fig. 3.1) that have undergone different histories and that exhibit broad litho-chemical variations (Jolliff et al., 2000). Further, three compositionally distinct crustal layers with differing [K] (and excluding mare basalts) can be defined as follows: (1) an uppermost layer, corresponding to megaregolith; (2) an anorthosite layer (prominent in FHT); and (3) a mafic lowermost layer (exposed as basin impact ejecta in the PKT and SPAT). The thickness and presence or absence of these layers in each terrane vary and interpretations of their thickness and occurrence vary (Hawke, 2003; Taylor and Wieczorek, 2014). The crust, owing to the KREEP enrichments in the crust, and the mantle, owing to its large volume, are the major reservoirs for K and other incompatible elements (e.g., Th, U) in the Moon (e.g., Taylor and Wieczorek, 2014; Laneuville et al., 2018). The complex distribution and variety of materials in the lunar crust affect the K distribution (elementally and isotopically, and horizontally and vertically) in the Moon. In a previous study, Wang and Jacobsen (2016b) analysed only a limited set of lunar samples (n = 7), spanning a limited range of lithologies. To better evaluate the whole-Moon K isotope composition, we have conducted a more systematic investigation of different lunar rock types.
A new suite of samples, including Apollo samples and lunar meteorites from Antarctica and Northwest Africa (feldspathic and KREEP-bearing) were analyzed, covering a range in lunar geochemical and petrological diversity. These new samples, along with the previously measured Apollo lunar samples (Wang and Jacobsen, 2016b), provide the most comprehensive evaluation to date of K isotopic fractionation within the Moon, and from the data, we derive an estimate of the K isotopic composition of the bulk silicate Moon.

Figure 3.1. Schematic diagram of the compositional stratigraphy of different geological terranes in the lunar interior. The thicknesses and surface areas of major lunar geological terranes are adapted from Taylor and Wieczorek (2014). Note the surface areas and the thicknesses of each layer are demonstrative and not to scale. Here we ignore mare volcanics for its volumetrically minor contribution to the crust.
3.2. Samples and Method

3.2.1 Sample description

Nineteen samples were investigated, which represent a geologically and petrologically diverse set of samples from the Moon, including thirteen Apollo lunar samples (low/high-Ti mare basalts, two anorthosites, a norite, two impact melt breccias, and two pyroclastic glasses), three Antarctic meteorite finds (a low-Ti mare basalt, a feldspathic regolith breccia, and a KREEP-bearing nonmare breccia), as well as three hot desert meteorite finds (all KREEP-bearing nonmare breccias). Detailed studies of the petrology, mineralogy, major and trace elemental abundances are described in the lunar sample compendium and elsewhere (e.g., Korotev et al., 2009; Meyer, 2011; Korotev, 2012; Calzada-Diaz et al., 2017). One sample measured in this study, high-Ti mare basalt 10017, was analyzed previously with comparable precision using a different method on a different instrument (Wang and Jacobsen, 2016b). In addition to lunar samples, we measured the standard rock powder BHVO-2 (Basalt, Hawaiian Volcanic Observatory) from the collection of United States Geological Survey (USGS) geo-reference materials (Table 3.1). The value of BHVO-2 measured in this study is comparable with previous work (Li et al., 2016; Wang and Jacobsen, 2016a; Hu et al., 2018; Morgan et al., 2018; Chen et al., 2019).
Table 3.1. Potassium isotopic compositions of geo-reference material BHVO

<table>
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<tr>
<th>Sample Name</th>
<th>Type</th>
<th>Location</th>
<th>$\delta^{41}$K$_{NIST}$, ‰</th>
<th>2SE$^a$</th>
<th>n$^b$</th>
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a. Standard errors (SE = standard deviation divided by the square root of the total number of measurements)
b. Number of measurements
c. USGS = U.S. Geological Survey
d. Error reported as 2SD (SD = standard deviation)
e. The K data is reported relative to Merck KGaA Suprapur 99.995% KNO$_3$ standard and is identical to the value relative to NIST SRM 3141a (see Section 2.2)
f. Error reported as 95% C.I. (confidence interval)
g. The K data is reported relative to NIST SRM 999b
1. this study
2. Li et al. (2016)
3. Wang and Jacobsen (2016a)
5. Chen et al. (2019)
Mare volcanic rocks are derived from partial melting of the lunar mantle, followed by eruption onto the lunar surface. Two major types of ‘basaltic’ volcanic materials from the Moon include (1) mare basalts, and (2) pyroclastic deposits. Mare basalts cover ~17% of the lunar surface (Head, 1976), and can be subdivided into high-Ti basalts (HT, > 6 wt.% TiO$_2$), low-Ti basalts (LT, 1 – 6 wt.% TiO$_2$), and very low-Ti basalts (VLT, < 1 wt.% TiO$_2$) (Neal and Taylor, 1992). Basalts collected from the Apollo 11 and 17 sites are dominated by high-Ti mare basalts. Furthermore, high-Ti basalts sampled at Apollo 11 can be classified into low-K (< 2000 ppm K) and high-K (> 2000 ppm K) groups. The high-Ti basalts measured in this study are from Apollo 11 (10017) and from Apollo 17 (70215 and 74275). Previously, Wang and Jacobsen (2016b) analyzed two high-K and high-Ti basalts from Apollo 11 (10017 and 10071). A variety of low-Ti basalts were obtained from the Apollo 12 and 15 collections. The Apollo 12 low-Ti basalts consist of three subtypes: olivine basalts, pigeonite basalts, and ilmenite basalts (Neal and Taylor, 1992). All the low-Ti basalts measured in this study are from Apollo 12, including one each of the olivine (12018), pigeonite (12065), and ilmenite (12063) types. Only one low-Ti basalt LAP 02224 has been previously analyzed at high precision for K isotopes (Tian et al., 2019). In addition to the mare basalts, one Apollo 15 green glass clod (15426) and one Apollo 17 orange glass soil (74220) were analyzed. The green glass clod and orange glass soil contain pyroclastic glass beads that were derived from the eruption of volcanic fire-fountains and are crucial for understanding the primitive signature of the lunar mantle (Shearer and Papike, 1993). The green glass clod and orange glass soil were measured as bulk samples (containing soil components).
To first order, highland rocks can be subdivided into (1) highland igneous rocks that include monomict breccias and (2) polymict breccias. Highland igneous rocks can be divided into ferroan anorthosites (FAN) and rocks with a range of Mg/(Mg+Fe) and An contents of plagioclase (including Mg-suite, alkali-suite, and KREEP basalts); whereas polymict breccias are further textually and compositionally defined (Stöffler et al., 1980; Papike et al., 1998). Humayun and Clayton (1995) reported a substantial deviation in terms of K isotopic composition in anorthosite sample 60015 relative to the restricted lunar mare basalts values (Wang and Jacobsen, 2016b), indicating a heterogeneous distribution of K isotopes on the lunar surface. Hence, we considered different types of lunar highland rocks (namely nonmare rocks here) to gain a more complete understanding of the K isotope distribution in and on the Moon. Samples in this study include two anorthosites (60015 and 62255) and one magnesian suite sample (norite from 77215), which are considered pristine on the basis of low concentrations of highly siderophile elements (Day et al., 2010). The three polymict breccias examined in this study consist of different proportions of materials from different lithologies, having formed by impact (64435, 65015, MIL 090070). We also chose four lunar meteorite breccias rich in KREEP components, NWA 4485, SaU 169 (impact melt breccia [IMB], and regolith breccia [RB] components), and MIL 09003 to study the KREEP K isotope composition. Wang and Jacobsen (2016b) also reported K isotopic values for lunar brecciated rocks and these are used for comparison.

### 3.2.2 Analytical procedures

The high-precision K isotope analytical procedures are adapted from Chen et al. (2019). On the basis of reported K concentrations from the literature, about 3 to 180 mg of homogeneously pulverized subsamples of each sample were dissolved in concentrated HF/HNO₃ (VHF: VHNO₃~3:1)
in Parr high-pressure digestion vessels at 150°C in a Fisher Scientific Isotemp 500 oven for over two days. The samples were then completely dried down under heating lamps before refluxed with 6 N HCl. The fully digested samples were again evaporated to complete dryness and re-dissolved into 0.7 N HNO₃ before loading onto purification columns.

The purification column chemistry involved three steps, including one “big column” (ID = 1.5 cm, BIO-RAD Econo-Pac, resin volume of 17 mL), and two repeated “small column” (ID = 0.5 cm, BIO-RAD Glass Econo-Column, resin volume of 2.4 mL). All columns were filled with pre-cleaned AG50-X8 100-200 mesh cation-exchange resin and were conditioned in 0.7 N HNO₃ and 0.5 N HNO₃ for the “big column” and the “small column”, respectively. Samples were re-dissolved in 0.7 N HNO₃ and loaded on the “big column” to separate K from most of the matrix elements. The samples were then fully dried down under the heating lamps before being re-dissolved in 0.5 N HNO₃ for the following “small column” steps. Repeated “small columns” ensure purification of K from other matrix elements. The K collecting volume has to be ~100% yield to avoid any possible K isotopic fractionation during ion exchange chromatography. Hence, we monitored the pre-cut and post-cut (fractions collected before and after the K-collecting volumes) in all samples to back-calculate the K recovery rates. Potassium yields for all measured samples are > 99%, and thus the K losses during column chemistry are negligible (Chen et al., 2019). Furthermore, the ratios of concentrations of all other matrix elements to the concentration of K were measured using a Thermo Scientific iCAP Q quadrupole ICP-MS (Inductively Coupled Plasma Mass Spectrometer) to ensure the matrix elements are below 2% of the total K inventory of the sample (Chen et al., 2019).
Potassium isotopic analyses were performed with a *Thermo Scientific* Neptune Plus Multiple-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). The interference of $^{40}\text{Ar}^+\text{H}^+$ on $^{41}\text{K}$ was resolved by conducting the measurements on the left “shoulder” of the peak with the instrument’s high-resolution mode ($m/\Delta m > 10,000$) to resolve the subtle difference (~0.005 a.m.u.) between the peaks of $^{40}\text{Ar}^+\text{H}^+$ and $^{41}\text{K}^+$ (Chen et al., 2019). An *Elemental Scientific* APEX omega equipped with a desolvation membrane was used as the sample-introducing system to enhance sensitivity and minimize hydride and oxide generation. All analyses were performed based on the sample-standard bracketing technique. The concentration mismatches between our samples and the standards were less than 3% to avoid any potential concentration effects. We used NIST SRM 3141a for the K standard solution. The final results are expressed in the delta notation:

$$\delta^{41}\text{K} (\text{‰}) = \left(\frac{[^{41}\text{K}/^{39}\text{K}]_{\text{sample}}}{[^{41}\text{K}/^{39}\text{K}]_{\text{NIST SRM 3141a}}} - 1\right) \times 1000 \ (3.1)$$

We measured each sample approximately 10 times and reported its average along with the within-run reproducibility (2SE, 2 standard error). Our typical internal precision is ~0.05‰, which is comparable with previous studies (Li et al., 2016; Wang and Jacobsen, 2016a; Wang and Jacobsen, 2016b; Hu et al., 2018; Morgan et al., 2018; Chen et al., 2019; Tian et al., 2019). The long-term reproducibility is reported as ~0.11‰ (2SD, 2 standard deviation) over 20 months by routinely measuring the same georeference materials in different analytical sessions (Chen et al., 2019).

To date, the only available high precision $\delta^{41}\text{K}$ data for lunar basalts were measured by two different laboratories: either by Neptune Plus MC-ICP-MS relative to the NIST SRM 3141a standard solution (Tian et al., 2019, this study), or using a GV Instruments IsoProbe P MC-ICP-
MS relative to Merck KGaA Suprapur 99.995% purity potassium nitrate (Wang and Jacobsen, 2016b). Chen et al. (2019) previously measured the K isotopic compositions of both Merck KGaA Suprapur 99.995% KNO₃ and NIST SRM 3141a. They found that the two standards have identical K isotope ratios and hence are indistinguishable from each other within current analytical uncertainty. Therefore, all literature can be directly converted to values relative to NIST SRM 3141a via (Chen et al., 2019):

\[ \delta^{41}K_{\text{Suprapur}} = \delta^{41}K_{\text{NIST SRM 3141a}} \]  

Furthermore, the potential systematic deviation among different laboratories in K isotope measurements can be alleviated by analyzing the same terrestrial reference materials (e.g., USGS BHVO, BCR, AGV, GSP, and G2; Chen et al., 2019). Wang and Jacobsen (2016b), Tian et al. (2019) and this study all report identical K isotopic values for terrestrial igneous rocks, within analytical uncertainties.
3.3. Results

3.3.1 Mare basalts

In total, seven lunar mare basalts (six Apollo samples and one lunar meteorite) were analyzed, including three high-Ti basalts and four low-Ti basalts (Table 3.2, Fig. 3.2). Generally, all lunar basalts cluster in a constrained $\delta^{41}$K range, varying from $-0.15 \pm 0.04\%$ (2SE; 10017, high-K, high-Ti ilmenite basalt) to $-0.04 \pm 0.04\%$ (2SE; 12063, low-Ti ilmenite basalt and 70215, high-Ti ilmenite basalt). The measured lunar basalts yield an average of $-0.08 \pm 0.09\%$ (2SD), which agrees well with the average K isotopic composition of seven lunar rocks previously reported ($-0.04 \pm 0.16\%$; 2SD; Wang and Jacobsen, 2016b). The new average is consistent with a $\sim 0.4\%$ heavy K isotope enrichment in lunar rocks relative to bulk silicate Earth (BSE, $-0.48\% \pm 0.03\%$, 2SD) (Wang and Jacobsen, 2016a; Tian et al., 2019). Notably, data for the same high-K, high-Ti ilmenite basalt 10017 (different chips) reported in this study and in (Wang and Jacobsen, 2016b), give a $\delta^{41}$K value of $-0.15 \pm 0.04\%$ (2SE) and $-0.11 \pm 0.06\%$ (2SE), respectively. The consistency in both the overall lunar basalt average K isotopic composition and one replicate sample reinforces the robustness of measurements and consistency with prior work.

When considering different chemical groups, the three high-Ti basalts give an average $\delta^{41}$K of $-0.09 \pm 0.11\%$ (2SD), whereas the four low-Ti basalts show an average $\delta^{41}$K of $-0.08 \pm 0.08\%$ (2SD). Despite the distinct TiO$_2$ contents between high-Ti and low-Ti basalts, they display homogeneous K isotopic compositions (Fig. 3.2). Potassium is highly incompatible; during partial melting K quantitatively enters into the melt. There is no K isotopic fractionation during mantle partial melting (Tuller-Ross et al., 2019). Thus, the K isotopic compositions of the basalts can be used to represent those of their mantle sources. Since high-Ti basalts are proposed to be derived
from a distinct mantle reservoir compared to low-Ti basalts (e.g., Lugmair and Marti, 1978; Neal and Taylor, 1992; Snyder et al., 1992, 1994), the lack of $\delta^{41}$K variation suggests an isotopically uniform mare basalt mantle reservoir for K.
Figure 3.2. Potassium isotopic compositions of lunar samples. The shaded area with vertical dashed line represents the bulk silicate Earth $\delta^{41}$K value ($-0.48‰ ± 0.03‰$, 2SD, Wang and Jacobsen, 2016b), whereas all the shaded blocks are the average $\delta^{41}$K values for individual groups ± 2SD. All the sample names are labelled in the figure. The error bars for each sample represent two standard error (2 SE) values. The literature data are compiled from Wang and Jacobsen (2016b) and Tian et al. (2019).
Table 3.2. Potassium isotopic compositions of lunar samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Type</th>
<th>Mass [mg]</th>
<th>[K] ppm this study</th>
<th>[K] ppm literature</th>
<th>δ⁴¹K_{NIST} [%]</th>
<th>2SE*</th>
<th>n**</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low-Ti Basalts</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>12018</td>
<td>Low-Ti olivine basalt</td>
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<td>334</td>
<td>332⁺</td>
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<td>[1]</td>
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<td>12063</td>
<td>Low-Ti Ilmenite basalt</td>
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<td>501</td>
<td>506ᵇ</td>
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<td>0.04</td>
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<td>[1]</td>
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<td>12065</td>
<td>Low-Ti Pigeonite basalt</td>
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<td>510</td>
<td>540ᶜ</td>
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<td>0.03</td>
<td>10</td>
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</tr>
<tr>
<td>MIL 05035</td>
<td>Low-Ti Mare basalt</td>
<td>150.4</td>
<td>407</td>
<td>249ᵈ</td>
<td>-0.11</td>
<td>0.04</td>
<td>16</td>
<td>[1]</td>
</tr>
<tr>
<td>LAP 02224</td>
<td>Low-Ti Mare basalt</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>High-Ti Basalts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>10017</td>
<td>High-Ti Ilmenite basalt (high K)</td>
<td>72.3</td>
<td>2361</td>
<td>2489ᵉ</td>
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<td>0.04</td>
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<td>10017-282†</td>
<td>High-Ti Ilmenite basalt (high K)</td>
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<td>0.06</td>
<td>15</td>
<td>[3]</td>
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<td>10071-126†</td>
<td>High-Ti Ilmenite basalt (high K)</td>
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<td>70215</td>
<td>High-Ti Ilmenite basalt</td>
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<td>414ᶠ</td>
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<td>0.04</td>
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<td>74275</td>
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<td><strong>Nonmare Rocks</strong></td>
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<td></td>
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<tr>
<td>12013-170†</td>
<td>Breccia with Granite</td>
<td></td>
<td></td>
<td></td>
<td>-0.01</td>
<td>0.03</td>
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<td>12013-171†</td>
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<td>0.05</td>
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<td>[3]</td>
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<tr>
<td>14301-290†</td>
<td>Regolith Breccia</td>
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<td>-0.13</td>
<td>0.04</td>
<td>12</td>
<td>[3]</td>
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<tr>
<td>14305-330†</td>
<td>Crystalline Matrix Breccia</td>
<td></td>
<td></td>
<td></td>
<td>-0.06</td>
<td>0.04</td>
<td>12</td>
<td>[3]</td>
</tr>
<tr>
<td>60015</td>
<td>Cataclastic anorthosite</td>
<td>174.7</td>
<td>34</td>
<td>83ʰ</td>
<td>-1.16</td>
<td>0.04</td>
<td>12</td>
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</tr>
<tr>
<td>60315-191†</td>
<td>Poikilitic impact melt</td>
<td></td>
<td></td>
<td></td>
<td>-0.06</td>
<td>0.05</td>
<td>12</td>
<td>[3]</td>
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<tr>
<td>62255</td>
<td>Anorthosite with melt</td>
<td>84.1</td>
<td>46</td>
<td>108ⁱ</td>
<td>0.01</td>
<td>0.02</td>
<td>12</td>
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</tr>
<tr>
<td>64435, a</td>
<td>Breccia with glass coat</td>
<td>42.7</td>
<td>173</td>
<td>162ʲ</td>
<td>-2.48</td>
<td>0.03</td>
<td>11</td>
<td>[1]</td>
</tr>
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<td>Sample Code</td>
<td>Description</td>
<td>K&lt;sup&gt;40&lt;/sup&gt;/Ar (Ma)</td>
<td>K/Ar (Ma)</td>
<td>40Ar&lt;sup&gt;37&lt;/sup&gt;/Ar (Ma)</td>
<td>SE (Ma)</td>
<td>Number of Measurements</td>
<td></td>
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<td>------------------------</td>
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<tr>
<td>64435, b</td>
<td>Breccia with glass coat</td>
<td>61.5</td>
<td>129</td>
<td>162&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-2.60</td>
<td>0.01</td>
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<tr>
<td>64435, c</td>
<td>Breccia with glass coat</td>
<td>159.5</td>
<td>159</td>
<td>162&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-2.47</td>
<td>0.03</td>
<td>12 [1]</td>
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<tr>
<td>65015, a</td>
<td>Poikilitic impact melt breccia</td>
<td>68.9</td>
<td>2471</td>
<td>2844&lt;sup&gt;k&lt;/sup&gt;</td>
<td>-0.35</td>
<td>0.02</td>
<td>12 [1]</td>
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<tr>
<td>65015, b</td>
<td>Poikilitic impact melt breccia</td>
<td>40.7</td>
<td>2956</td>
<td>2844&lt;sup&gt;k&lt;/sup&gt;</td>
<td>-0.45</td>
<td>0.03</td>
<td>11 [1]</td>
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<tr>
<td>77215</td>
<td>Cataclastic norite</td>
<td>89.9</td>
<td>945</td>
<td>1054&lt;sup&gt;l&lt;/sup&gt;</td>
<td>-0.12</td>
<td>0.03</td>
<td>10 [1]</td>
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<tr>
<td>MIL 090070</td>
<td>Feldspathic regolith breccia</td>
<td>141.1</td>
<td>223</td>
<td>216&lt;sup&gt;n&lt;/sup&gt;</td>
<td>-0.43</td>
<td>0.04</td>
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<td>MIL 090036</td>
<td>KREEP-bearing feldspathic breccia</td>
<td>101.0</td>
<td>1013</td>
<td>830&lt;sup&gt;m&lt;/sup&gt;</td>
<td>0.23</td>
<td>0.03</td>
<td>17 [1]</td>
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<tr>
<td>NWA 4485</td>
<td>KREEP-rich regolith breccia</td>
<td>6.9</td>
<td>3421</td>
<td>3485&lt;sup&gt;n&lt;/sup&gt;</td>
<td>0.26</td>
<td>0.02</td>
<td>10 [1]</td>
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<tr>
<td>SaU 169-RB</td>
<td>KREEP-rich regolith breccia</td>
<td>3.4</td>
<td>4724</td>
<td>4315&lt;sup&gt;n&lt;/sup&gt;</td>
<td>0.51</td>
<td>0.03</td>
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<tr>
<td>SaU 169-IB</td>
<td>KREEP-rich impact-melt breccia</td>
<td>7.5</td>
<td>4494</td>
<td>3402&lt;sup&gt;n&lt;/sup&gt;</td>
<td>0.25</td>
<td>0.02</td>
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**Pyroclastic Glass**

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<tr>
<th>Sample Code</th>
<th>Description</th>
<th>Ar/Ar (Ma)</th>
<th>Ar/Ar (Ma)</th>
<th>K/Ar (Ma)</th>
<th>SE (Ma)</th>
<th>Number of Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>15426</td>
<td>Green glass clod</td>
<td>113.0</td>
<td>883</td>
<td>821&lt;sup&gt;p&lt;/sup&gt;</td>
<td>2.07</td>
<td>0.03</td>
</tr>
<tr>
<td>74220</td>
<td>Orange glass soil</td>
<td>113.6</td>
<td>671</td>
<td>664&lt;sup&gt;q&lt;/sup&gt;</td>
<td>0.11</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*Standard errors (SE = standard deviation divided by the square root of the total number of measurements)

** Number of measurements

†Data are reported relative to the Bulk Silicate Earth and are converted to values relative to the NIST SRM 3141a via $\delta^{41}\text{K}_{\text{BSE}} = 1.000479 \times \delta^{41}\text{K}_{\text{NIST}} + 0.479230$.

[1]. This study
[2]. Tian et al. (2019)
[3]. Wang and Jacobsen (2016b)
a. Cuttitta et al. (1971)
b. Willis et al. (1971)
c. Rancitelli et al. (1971)
d. Liu et al. (2009)
e. Maxwell et al. (1970)
f. Brunfelt et al. (1974)
g. Rose et al. (1975)
h. Juan et al. (1974)
i. Papike et al. (1997)
j. James et al. (1989)
k. Haskin et al. (1973)
l. Nakamura et al. (1976)
m. Korotev and Zeigler (2014)
n. Calzada-Diaz et al. (2017)
o. Korotev et al. (2009)
p. LSPET (1972)
q. Roedder and Weiblen (1973)
3.3.2. KREEP-bearing lunar meteorites

Four lunar meteorites with KREEP signatures were measured in this study (Antarctic meteorite MIL 090036 [Calzada-Diaz et al., 2017], and hot-desert meteorites SaU 169 [impact-melt lithology], SaU 169 [regolith breccia lithology], and NWA 4485 [Korotev et al., 2009]). Results show that their $\delta^{41}$K values range from +0.23 ± 0.03‰ (2SE; MIL 090036, feldspathic regolith breccia) to +0.51 ± 0.03‰ (2SE; SaU 169-regolith breccia), yielding an average of +0.31 ± 0.27‰ (2SD) (Table 3.2 and Fig. 3.2). The SaU 169-regolith breccia (+0.51 ± 0.03‰, 2SE) deviates substantially from the other three KREEP-rich samples (average of the three is +0.25 ± 0.03‰, 2SD). This average $\delta^{41}$K of KREEP-bearing lunar meteorites is 0.39‰ heavier than the lunar basalts (–0.08 ± 0.09‰; 2SD).

3.3.3. Other lunar nonmare rocks

Contrary to the narrow range defined by mare basalts, lunar nonmare rocks (especially those lacking a KREEP component) span a substantial range (Table 3.2 and Fig. 3.2), from –2.60 ± 0.01‰ (2SE; 64435, b, a highly feldspathic, KREEP-poor IMB from the FHT) to +0.01 ± 0.02‰ (2SE; 62255, anorthosite with impact melt). Cataclastic norite 77215 has an indistinguishable K isotopic composition from that of the lunar basalts (–0.12 ± 0.03‰, 2SE). Wang and Jacobsen (2016b) previously reported five Apollo lunar nonmare rocks whose $\delta^{41}$K values are broadly consistent with lunar basalts. However, none of their samples were from lunar anorthosites. Two lunar anorthosites in this study exhibit heterogeneous $\delta^{41}$K values, with –1.16 ± 0.04‰ for 60015 and +0.01 ± 0.02‰ for 62255. Three replicates of 64435 (–2.48 ± 0.03‰, –2.60 ± 0.01‰, –2.47 ± 0.03‰) and two replicates of 65015 (–0.35 ± 0.02‰, –0.45 ± 0.03‰) broadly overlap with each
other, respectively, when considering the long-term reproducibility of ~ ±0.11‰ during the course of this study. These five subsamples (64435, a, b, and c; 65015, a, b), as well as cataclastic anorthosite 60015, are substantially enriched in $^{39}$K relative to the K isotopic composition of the average lunar basalts.

### 3.3.4 Pyroclastic glasses

We analyzed the K isotopic compositions of two pyroclastic glasses. These include the green glass clod, 15426, and the orange glass soil 74220. These two bulk samples contain not only pyroclastic glass beads but also variable regolith fractions (15426) or moderate to low agglutinate material and lithics (74220) (Meyer, 2011). The K isotopic compositions of 15426 and 74220 are +2.07 ± 0.03‰ and +0.11 ± 0.03‰, respectively. These values are higher than those of lunar rocks and fall into the range of the lunar regolith ($\delta^{41}$K up to ~12‰) that has been analyzed in the past (Barnes et al., 1973; Garner et al., 1975; Church et al., 1976; Humayun and Clayton, 1995b; Wang and Jacobsen, 2016b).
3.4. Discussion

3.4.1 Cosmogenic effects in lunar samples

With no protection from a global magnetic field, the lunar surface is fully exposed to the space environment and is vulnerable to incoming charged particles (e.g., low-energy solar wind, high-energy galactic cosmic rays, and solar energetic particles from coronal mass ejections and solar flares). These charged particles bombard the surface of the Moon and interact with the surface materials, generating secondary neutrons (Reedy et al., 1983). The secondary neutrons further react with surface materials and produce other nuclides (e.g., Hopkins et al., 2019). For example, $^{41}\text{Ca}$ can be produced by the low-energy thermal neutron capture via reaction $^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}$, and the main portion of $^{41}\text{Ca}$ is generated by neutron capture instead of spallation reactions (Nishiizumi et al., 1997). Nishiizumi et al. (1997) made a detailed depth profile of $^{41}\text{Ca}$ in an Apollo deep drill core sample and proposed a maximum $^{41}\text{Ca}$ production of 1 dpm/g at a depth of 150 g/cm$^2$. Radioactive $^{41}\text{Ca}$ decays to the stable nuclide $^{41}\text{K}$ with a half-life of $1.04 \times 10^5$ yr, and thus altering the K isotopic ratio in surface samples with long cosmic ray exposure ages ($>>$ half-life of $^{41}\text{Ca}$). It is important to assess whether the fluxes of thermalized neutrons and the subsequent $^{40}\text{Ca}$ neutron capture reaction might be responsible for any of the observed K isotopic variations. Owing to a lack of information such as the burial depths of each sample in this study, and their localized thermal neutron flux, quantitatively modeling the $^{40}\text{Ca}$ neutron capture effect remains problematic. Here, we qualitatively discuss the possible cosmogenic effects on K isotopic compositions of lunar samples.

The overall cosmogenic $^{41}\text{Ca}$ in the sample is a time-integrated accumulation process and thus correlates with the cosmic ray exposure (CRE) age. Under a constant nuclide production rate, the
longer the sample is exposed to cosmic rays, the more cosmogenic nuclides will be produced. Moreover, a measurable cosmogenic effect on K isotopes is more likely to be found in samples with high Ca content (more $^{40}\text{Ca}$ for the thermal neutron capture reaction) and low K content (minimize the dilution of cosmogenic $^{41}\text{K}$ by indigenous K). Notably, Ca concentrations in the samples of this study, in general, range over less than a factor of two, i.e., they are nearly constant compared to K concentrations. In Fig. 3.3, we plot K isotopic compositions versus Ca/K atomic ratios (Ca contents normalized to K concentrations) times CRE ages (Appendix A). As shown in Fig. 3.3, a lack of correlation between the K isotopic compositions and their corresponding $\frac{\text{Ca}^\ast\text{(CRE ages)}}{\text{K}}$ ratios indicates that cosmogenic $^{41}\text{K}$ did not affect the $\delta^{41}\text{K}$ values of these lunar rocks. When excluding all the “outliers” and focusing on lunar basalts (see Fig. 3.3, right side), despite compositional variations and distinct exposure ages, lunar basalts cluster in a narrow $\delta^{41}\text{K}$ range, obviating concerns about any cosmogenic $^{41}\text{K}$ excess in lunar samples.

We also compare the K isotope data in this study with large-capture-cross-section nuclides measured in the same lunar samples to further examine possible cosmogenic effects. Secondary thermal neutrons produced during cosmic ray bombardment on the lunar surface are preferentially captured by nuclides with large neutron-capture cross sections (e.g., $^{113}\text{Cd}$, $^{149}\text{Sm}$, $^{155}\text{Gd}$, and $^{157}\text{Gd}$). Such nuclides have neutron-capture cross sections $\sim 10^5$ times larger than $^{40}\text{Ca}$ (e.g., 2.540$\times 10^5$ barns for $^{157}\text{Gd}$ [Sands et al., 2001], relative to 0.43 barns for $^{40}\text{Ca}$ thermal neutron capture [Mughabghab et al., 1981]). Therefore, the high sensitivity of these elements to secondary neutron capture makes them ideal for recording cosmogenic effects in lunar samples. Previous studies have shown elevated isotopic ratios of $^{158}\text{Gd}/^{157}\text{Gd}$, $^{150}\text{Sm}/^{149}\text{Sm}$, and $^{114}\text{Cd}/^{113}\text{Cd}$ in lunar materials, including lunar rocks as well as lunar regolith (e.g., [Lugmair and Marti, 1971] for Gd;
We plot K isotopic compositions versus their $^{158}\text{Gd}/^{157}\text{Gd}$ ratios in Fig. 3.4 ($^{158}\text{Gd}/^{157}\text{Gd}$ is chosen here as the proxy for Gd because data are available for most samples measured in this study [Appendix A]). All samples were subjected to neutron bombardment and show subsequent neutron capture effects, yet no corresponding K isotopic variation is observed. To summarize, we find no evidence for any measurable cosmogenic $^{41}\text{K}$ in any of the lunar samples that we studied.
Figure 3.3. Potassium isotopic compositions versus Ca*(CRE ages)/K ratios. The Ca/K atomic ratios are from the compilation in Meyer (2011); whereas the K isotopic compositions are from this study, Wang and Jacobsen (2016b), and Tian et al. (2019). The cosmic ray exposure (CRE) ages from earlier literature sources are compiled in Meyer (2011) and Park et al. (2013) (Appendix A), and the K isotopic compositions are from this study, Wang and Jacobsen (2016b) and Tian et al. (2019). Different symbols stand for different rock types and are shown on the legend. The sub-plot on the right side is an expanded plot for lunar mare basalts (data reported in this study and Wang and Jacobsen [2016b]) and lunar highland breccia in Wang and Jacobsen (2016b). The vertical error bar for each sample represents two standard error (2 SE) values. Note the lack of correlation between the K isotopic compositions and their corresponding Ca*(CRE ages)/K ratios.
3.4.2. Elevated K isotopic compositions of KREEP-bearing lunar meteorites

In the context of the widely-accepted Lunar Magma Ocean (LMO) hypothesis, the KREEP-component (or “urKREEP” as a geochemical reservoir) refers to the late-stage residual melts that were enriched in potassium (K), Rare Earth Elements (REEs), phosphorous (P), and other incompatible elements, which remain in the melt during fractional crystallization (Warren and
Wasson, 1979). Rocks thought to represent urKREEP are absent among the lunar samples, and KREEP-rich samples are rare in the Apollo collection (e.g., KREEP basalt). KREEP-bearing samples, however, such as impact-melt breccia, are common among the samples. Owing to the fact of high K concentrations and the lack of K isotopic data for the KREEP component, we chose four KREEP-bearing brecciated lunar meteorites as its proxy (Korotev et al., 2009 and reference therein; Calzada-Diaz et al., 2017).

The K isotopic compositions of the KREEP-bearing lunar meteorites are distinct from mare basalts, with the KREEP-bearing lunar samples exhibiting elevated $\delta^{41}$K values relative to that of the basalts. Three out of four KREEP-bearing lunar meteorites measured in this study (NWA 4485, SaU 169 IMB, and SaU 169 RB) are from hot deserts. Previous studies have shown that terrestrial K contamination can occur in hot desert meteorites during their residence on Earth (e.g., Crozaz et al., 2003; Tian et al., 2019). All three hot desert meteorites that we analyzed have been affected by terrestrial contamination. They are enriched in Sr and Ba, potentially resulting from fracture-filling precipitates (Korotev et al., 2009; Joy et al., 2011). Further, Korotev et al. (2009) found that NWA 4485 has abnormally high abundances of Br, likely owing to exposure to salty water. There is also evidence that the $\delta^{41}$K values remain unaffected, however. The three hot-desert KREEP-bearing lunar meteorites all display high K concentrations, especially SaU 169 (K$_2$O ~0.5~0.6 wt.%) and NWA 4485 (K$_2$O ~0.5 wt.%), which are the most incompatible-element-rich lunar meteorites (Gnos et al., 2004; Korotev et al., 2009; Lin et al., 2012).
Tian et al. (2019) reported terrestrial K addition and light K isotopic shifts only in hot desert eucrites from Northwest Africa (NWA) that have an order of magnitude lower K (0.03 wt.%) contents. Furthermore, one Antarctic lunar meteorite, MIL 090036, falls in the same range of $\delta^{41}\text{K}$ as the hot desert meteorites (Fig. 3.2). There is no previously reported K isotopic modification for Antarctic meteorites, i.e., they yield the same $\delta^{41}\text{K}$ as falls of meteorites of similar types (Zhao et al., 2019; Tian et al., 2019). For these reasons we infer that terrestrial contamination/alteration is unlikely to affect K isotopes in the KREEP-bearing lunar meteorites. Nevertheless, applying caution, the measured $\delta^{41}\text{K}$ of hot desert samples can be taken as minimum values. Except for lunar soils (Barnes et al., 1973; Garner et al., 1975; Church et al., 1976; Humayun and Clayton, 1995b; Wang and Jacobsen, 2016b), this is the first time that an isotopically heavy reservoir for K relative to the mare basalts has been recognized on the Moon.

A means with which to explain variations in K isotopic compositions of lunar samples is that isotopic heterogeneity originated from the pre-Moon-forming giant impact (i.e., a “memory” effect, Pringle and Moynier, 2017), where the high-energy, high-angular-momentum Giant Impact was proposed to be responsible for the enrichment of heavy K isotopes of the bulk silicate Moon (Wang and Jacobsen, 2016b). In this concept, inheritance of heterogeneous K isotopic compositions from the building blocks of the Moon and incomplete mixing within the lunar interior subsequent to the Moon-forming Giant Impact event led to isotopically distinct K reservoirs within the Moon. (Canup et al., 2015; Hauri et al., 2015; Boyce et al., 2018; Nakajima and Stevenson, 2018; Cano et al., 2020). The weakness of this model is that pervasive isotopic equilibration is likely from the isotopic similarities found in a wide range of elements (Wiechert et al., 2001; Pahlevan and
Therefore, pre-Giant Impact isotopic signatures, if any, were probably completely erased. Hence, we do not consider residual variability remaining from pre-giant-impact materials as a favorable explanation.

An alternative model is that K isotopic fractionation during post-giant-impact processes occurred, perhaps most effectively, during large-scale magma-ocean degassing (Boyce et al., 2015; Barnes et al., 2016; Greenwood et al., 2017; Barnes et al., 2019; Day et al., 2020). Magma ocean degassing is a plausible mechanism for elemental depletions and mass-dependent isotopic fractionations in natural samples (e.g., S, Zn, Ga, and Rb (Paniello et al., 2012; Day and Moynier, 2014; Kato et al., 2015; Pringle and Moynier, 2017; Dhaliwal et al., 2018; Jiang et al., 2019; Sossi et al., 2019; Day et al., 2020)). Degassing as a cause of isotopic fractionation and redistribution has also been advocated for several highly- and moderately-volatile-element isotope systems for the occurrence of distinct isotope reservoirs in the Moon (Boyce et al., 2015; Barnes et al., 2016; Hui et al., 2017; Boyce et al., 2018; Potts et al., 2018; Barnes et al., 2019; Y. Wang et al., 2019).

In the case of the chlorine isotope system, recent studies have revealed two endmembers of Cl reservoirs displaying distinct Cl isotopic signatures. One is the urKREEP reservoir with a high Cl abundance and an elevated $\delta^{37}$Cl, whereas another is the low-Cl and low-$\delta^{37}$Cl mare basalt reservoir (e.g., Boyce et al., 2018; Barnes et al., 2019). Degassing of the metal chloride that occurred throughout the entire LMO stage has been invoked to be the dominant driver for the high-$\delta^{37}$Cl KREEP reservoir on the Moon (Boyce et al., 2015; Boyce et al., 2018). The prolonged thermal history of the Procellarum KREEP Terrane from asymmetrically concentrated heat-
producing elements \( \textit{i.e.,} \) K, Th, U) could potentially extend the duration of degassing \( \textit{e.g.,} \) Wieczorek and Phillips, 2000; Laneuville et al., 2018). We suggest that the high-\( \delta^{41} \)K composition of KREEP-bearing meteorites is also consistent with this interpretation. The heavy K isotope enrichment in the KREEP reservoir can be explained best as a result of extended degassing of K from the LMO as a K-chloride species (Fig. 3.5).

Evidence exists to support a degassed KREEP reservoir that resulted in the observed elevated K isotopic composition. First, K is prone to degassing along with Cl simultaneously in the form of metal chloride (Boyce et al., 2018). Potassium and chlorine are both incompatible elements and are rejected by early crystallized major silicate minerals \( \textit{i.e.,} \) olivine and pyroxene and are enriched in the remaining melt (McCubbin et al., 2015). Sharp et al. (2010) first envisaged a Cl
isotopic fractionation mechanism on the anhydrous Moon in which the $\text{H}/\text{Cl}$ ratio $<< 1$ environment would promote degassing of Cl as metal chlorides, including KCl. Ustunisik et al. (2015) further suggested that even in the high initial hydrogen environment, metal chloride degassing could occur after rapid initial degassing of H-rich vapor.

Thermodynamic models of the chemistry of lunar volcanic gases support K-chloride as being the major gaseous species that carries K (Fegley, 1991; Renggli et al., 2017). Estimates of Cl abundance in urKREEP range from 25 to 170 ppm (Boyce et al., 2018), and to 1100 to 1350 ppm (McCubbin et al., 2015). This is substantially enriched in Cl relative to the mantle ([Cl] $\sim$0.26–0.32 ppm [Boyce et al., 2018] or 0.26–2.9 ppm [McCubbin et al., 2015]). Elevated Cl in urKREEP should consequently yield a higher partial pressure of KCl gas, and thus facilitate degassing of K. Only $\sim$3% degassing of K in the urKREEP reservoir is required to achieve the observed $\sim$0.4‰ $\delta^{41}$K enrichment (using the average of all four lunar meteorites with KREEP signatures of $+0.31\%$) relative to mare source regions via ideal Rayleigh fractionation, $\delta^{41}$K = $\delta^{41}$K$_0$ + [(1000 + $\delta^{41}$K$_0$) * ($F^{-1}$ – 1)], assuming a fractionation factor $\alpha_{\text{KCl}}$ of 0.9868 ($=(74.5/76.5)^{0.5}$) and an initial $\delta^{41}$K$_0$ of the average of mare basalts ($-0.07\%$, see Section 3.4.4). Moreover, if we consider the less heavy K isotopic compositions among MIL 090036, NWA 4485, and SaU 169-IB as a consequence of dilution by non-KREEP components and use the most extreme $\delta^{41}$K value of SaU 169-RB ($+0.51\%$) as the minimum $\delta^{41}$K of the final degassing product, a minimum of $\sim$4.3% degassing of K in the urKREEP layer is required.
There may be some obstacles for such an extended degassing hypothesis to explain the high-$\delta^{41}$K, high-$\delta^{37}$Cl KREEP reservoir. First, it is not clear to what extent a primary anorthosite crust with a poorly constrained permeability might have hampered degassing of the underlying urKREEP melt (Barnes et al., 2016; Dhaliwal et al., 2018). Second, a transient atmosphere, composed of volatiles released from the turbulent early magmatic activity could further suppress, if not totally prohibit, degassing of the LMO (Stern, 1999; Saxena et al., 2017). Barnes et al. (2015) envisioned a scenario to mitigate these possible obstacles where the urKREEP layer or reservoir was exposed owing to one or series of crust-breaching impact events, which could expose urKREEP to a low-pressure environment, facilitating degassing (Fig. 3.5). Nevertheless, the fact that Apollo 11 high-K basalt (Table 3.2) has a typical mare basalt K isotopic composition implies there should be some urKREEP materials at depth remaining un-degassed and retaining the mantle K isotopic signature.

### 3.4.3 Light $\delta^{41}$K among lunar nonmare rocks and its link to the KREEP reservoir

Previously, all lunar samples were found to be isotopically heavy in terms of K relative to CI chondrites (i.e., Ivuna-like carbonaceous chondrite) and the bulk silicate Earth (BSE), with limited variation in $\delta^{41}$K (Wang and Jacobsen, 2016b; Tian et al., 2019). This study shows that the K isotopic compositions of lunar nonmare rocks vary by more than 2‰ and some of them show a significantly lighter K isotopic composition relative to mare basalts (e.g., cataclastic anorthosite 60015 yields a $\delta^{41}$K of $-1.16 \pm 0.04$‰, 2SD and 64435 yield $\delta^{41}$K values ranging from $-2.60$ to $-2.47$‰). This is not entirely surprising since Humayun and Clayton (1995) reported extremely
light K isotope enrichment (−3.9 ± 0.9‰) in the same sample, 60015, which is significantly lighter than all lunar samples in their study (average = +0.50 ± 0.29‰; n=11; precision level at ∼ ± 0.5‰).  

Later lunar-magma-ocean degassing of KCl facilitated by enriched Cl concentrations in urKREEP could drive the separation of the light K-isotope-bearing vapor phase from its isotopically heavy residual melt, making it a favorable mechanism to generate various light K isotopic compositions in the anorthositic crust, as has been shown for Zn (Day et al., 2017). This hypothesis is consistent with the large variability of K isotopes in feldspathic highland rocks because this hypothetical vapor, rich in the lighter isotopes, was heterogeneously distributed on the surface of the Moon (e.g., highlands adjacent to the PKT). Dhaliwal et al. (2018) demonstrated a low Jeans escape flux for Zn, indicating an insignificant loss of Zn through Jeans escape from the Moon. Potassium chloride, presumably the major degassed phase for K, is heavier than Zn and therefore more difficult to lose to space. Moreover, an early ambient transient atmosphere would have further hindered the escape of KCl (Saxena et al., 2017). Therefore, we might expect an extremely inefficient loss of isotopically light K from the solid Moon, and thus a pervasive recondensation of light K back to the surface (Fig. 3.5). The isotopically light K-bearing condensates then went through the turbulent brecciation induced by the meteorite bombardment, and hence substantial δ41K variations were implanted in the megaregolith layer.

Regarding the light K isotope enrichment in nonmare rocks in the context of urKREEP degassing, we propose that the formation of the light K reservoir was a natural consequence of the

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1 Humayun and Clayton (1995) used a different K isotope standard from this study; however, Chen et al. (2019) observed no measurable difference between the two standards, see Section 3.2.2.
transportation of the degassed vapor. Lines of evidence supporting recondensation and redistribution of the isotopically light vapor on the lunar surface come from other moderately volatile elements (e.g., Cu, Zn, and Ga) (Moynier et al., 2006; Kato et al., 2015; Day et al., 2017; Kato and Moynier, 2017). Critical in this assessment is the “rusty rock” 66095, a unique sample with elevated volatile contents (e.g., Colson, 1992; Shearer et al., 2014), where the extremely light Zn and Cu isotopic signatures of 66095 leachate reveal a critical vapor re-condensation history (Day et al., 2017; Day et al., 2019). Gallium isotopic evidence likewise shows light isotope enrichment and overall large variations within ferroan anorthosites (FAN) (Kato and Moynier, 2017). Kato et al. (2015) examined Zn isotopic compositions of a set of FAN samples and found that a positive correlation exists between $\delta^{66}$Zn and 1/[Zn]. They attributed it to the post-crystallization addition of an isotopically light Zn component, which is in agreement with the development of the light K reservoir. These lines of evidence imply that the isotopically light vapor condensates, which have been incorporated into brecciated samples, are ubiquitous for moderately volatile elements that are inclined to degas either through a large-scale LMO or via the localized volcanic fire-fountaining.

If we consider a simple geochemical mixing model, the Apollo sample compositions typically represent either one of three endmembers or mixtures of the three major components, (1) mare basalts, (2) KREEP-rich materials, and (3) feldspathic components (Goles et al., 1971; Korotev et al., 2003; Korotev et al., 2009). The first two constituents (and mixtures dominated by these two) exhibit relatively high initial K abundances (e.g., mare basalts and KREEP-rich mafic impact-melt breccia have average K concentrations of ~500 ppm and ~3000 ppm, respectively (Wieczorek et
al., 2006, online supporting materials Table A3.1-A3.12)). In these reservoirs, K isotopic modification of light vapor condensates would be minor. Conversely, lunar materials dominated by a low-K feldspathic component are more susceptible to inherit K isotopic signatures from the vapor. The Apollo samples were mainly collected at sites that are either located within or bordering the PKT (e.g., Jolliff et al., 2000), and hence may be more vulnerable to light K isotopic addition by vapor phases.

It is noteworthy that high precision K isotope measurements on lunar highland rocks are still limited considering the total geochemical and petrographic complexities of Apollo samples. The currently available data set for highland rocks is not sufficient to establish a detailed survey of the K isotope inventories. Therefore, studies of samples derived from the lunar highlands, especially the feldspathic highlands terrane on the farside where contamination from materials of the PKT is less than in the Apollo zone, are needed. Feldspathic lunar meteorites that have possibly been sampled from the farside FHT are candidate samples for unraveling pristine K isotopic signatures, as well as for testing the light vapor re-condensation model. However, on the other hand, low-K hot-desert lunar meteorites are subject to more severe terrestrial contamination owing to their low bulk-K contents.

### 3.4.4 Estimate of the K isotopic compositions of the lunar mantle and the bulk silicate Moon (BSM)

Although lunar mantle materials could be excavated to the lunar surface through basin-sized impacts (e.g., Yamamoto et al., 2010; Miljković et al., 2015; Li et al., 2019), to date no lunar direct
mantle samples exist among the Apollo and lunar meteorite collection. Therefore, the K isotopic composition of the mantle can be only evaluated by investigation of materials derived from the mantle by partial melting, i.e., volcanic materials such as basalts and pyroclastic glasses.

Pyroclastic glass have been suggested to be the best proxy for lunar mantle compositions, owing to their primitive compositions, because they have not been subjected to fractionation by crystallization processes following their origin by partial melting of deep mantle sources (e.g. Delano, 1986; Shearer and Papke, 1993). For instance, the Mg isotopic composition of the lunar mantle has been estimated from the Apollo 15 picritic green glasses and the Apollo 17 orange glasses (Wiechert and Halliday, 2007). However, the bulk pyroclastic glass 15426 likely fails to probe the K isotopic composition of the lunar mantle owing to contamination by lunar regolith (Meyer, 2011). Pyroclastic glass 74220 is less affected by regolith addition, but may also have a minor regolith content, which can have a high K concentration and which is substantially enriched in heavy K isotopes owing to the interactions between the space environment and the solid Moon (Barnes et al., 1973; Garner et al., 1975; Church et al., 1976; Humayun and Clayton, 1995b; Wang and Jacobsen, 2016b). Therefore, the elevated volcanic glass soil $\delta^{41}$K values ($+2.07 \pm 0.03\%$o, 2SE and $+0.11 \pm 0.03\%$o, 2SE for 15426 and 74220, respectively) are potentially contaminated by the K isotopic signature of the soil and cannot be used as representative of the lunar mantle.

It is also possible to use mare basalts for estimating the K isotopic composition of the lunar mantle. Mare basalts result from partial melting of mantle source regions (e.g., Neal and Taylor, 1992). Day and Walker (2015) suggested a partial melting degree between 5% and 11% based on highly
siderophile element abundance constraints. Potassium is a monovalent, highly incompatible, lithophile element. Therefore, potassium tends to be quantitatively removed from source rocks into melts during partial melting with no measurable isotopic fractionation effect. Previous studies have shown that the K isotopic fractionation during igneous processes is not resolvable either in Earth rocks and 4-Vesta rocks (Wang and Jacobsen, 2016a; Chen et al., 2019; Tuller-Ross et al., 2019; Tian et al., 2019). Moreover, there appears to be no correlation between Mg# (100×Mg/(Mg+Fe) in atomic ratios) and corresponding $\delta^{41}$K values in mare basalts (Fig. 3.6). The lack of isotopic fractionation during igneous processes makes mare basalts useful recorders of the K isotopic composition of their mantle sources.
Figure 3.6. Potassium isotopic compositions versus bulk Mg numbers (Mg# = 100*Mg/(Mg+Fe) in atomic ratios) in lunar mare basalts. Horizontal dashed line and the shaded area represent the average of lunar mare basalts ± 2SD. The K isotopic compositions are compiled from this study, Wang and Jacobsen (2016b) and Tian et al. (2019). The vertical error bar for each sample represents two standard error (2 SE) values. The Mg and Fe contents are from a compilation of Meyer (2011). Note the overall $^{41}$K enrichment in lunar mare basalts relative to BSE ($-0.48\%$) and the lack of difference in $\delta^{41}$K regardless of their Mg numbers in mare basalts.

Different types are distinguished by compositional criteria; first and foremost, Ti content serves as a discriminating criterion in their classification (see Section 2.1). Judging by remote sensing observations (Clementine UV-VIS, LROC WAC UV/VIS), low-Ti basalts predominate the exposed mare basalts relative to high-Ti basalts (Giguere et al., 2000; Sato et al., 2017). An isotopic dichotomy between low-Ti and high-Ti basalts has been observed in many isotopic systems, reflecting mantle source heterogeneities (e.g., O, Li, Mg, Ti, and Fe, Spicuzza et al., 2007; Liu et al., 2010; Sedaghatpour et al., 2013; Wang et al., 2015; Day et al., 2016; Millet et al., 2016); whereas some stable isotope systems show isotopic similarities among different mare basalt types (e.g., Cr and Zn, (Paniello et al., 2012; Dauphas et al., 2014 and references therein; Bonnand et al., 2016).
The K isotopic compositions of both low-Ti and high-Ti basalts display consistency at the level of analytical uncertainty (–0.08 ± 0.08‰, 2SD and –0.09 ± 0.11‰, 2SD, respectively, Fig. 3.2) despite petrological, mineralogical, and geochemical differences.

In order to further subdivide mare basalt types, Al and K contents are commonly used as secondary and tertiary criteria (Neal and Taylor, 1992). With respect to these criteria, there is no distinguishable K isotopic compositional difference between low-Al/high-K (10017) and other low-Al/low-K basalts. The overall K isotopic consistency further indicates that the lunar mantle is an isotopically homogeneous reservoir for K. To summarize, lunar mare basalts provide the best constraint on the K isotopic composition of the lunar mantle. Combining this study with previously reported data (Wang and Jacobsen, 2016b; Tian et al., 2019), the K isotopic compositions of all lunar basalts yield an overall average δ41K value of –0.07 ± 0.09‰ (2SD). We propose this value (–0.07 ± 0.09‰, 2SD, n=10) as the current best estimate for the K isotopic composition of the lunar mantle.

The newly-inferred 41K-enriched reservoir (i.e., urKREEP) and complementary 39K-enriched endmember (i.e., variably enriched anorthositic crust) on the Moon suggests a planetary-scale differentiation, which introduced the heterogeneous distribution of K isotopes (see Section 4.2 and 4.3), in addition to the primary K isotope fractionation during the Giant Impact event (Wang and Jacobsen, 2016b; Nie and Dauphas, 2019; X. Wang et al., 2019). Such re-distribution of K isotopes was possibly triggered by the degassing of the last vestige of the lunar magma ocean, which implanted the extremely light K isotope signature onto the lunar surface, meanwhile enriching the
KREEP reservoir in heavy K isotopes (Fig. 3.5). Nevertheless, the K isotopic composition of the bulk silicate Moon **should not** be modified during the redistribution processes (see Section 3.4.3). The K content of the high-δ⁴¹K urKREEP is higher than that of the summed major ³⁹K-reservoirs (e.g., highlands that are subjected to light vapor contaminations from the degassing of the urKREEP). Yet the K isotopic compositions of the ³⁹K-enriched reservoirs are more extreme (down to ~−2.60‰, see Table 3.2). Taken together, we propose that the bulk silicate Moon K isotopic composition is best represented by that of the lunar mantle of −0.07 ± 0.09‰ (2SD, n=10), being consistent with the previously reported ~0.4‰ K isotopic difference between the bulk silicate Earth and the bulk silicate Moon (Wang and Jacobsen, 2016b).
3.5. Conclusions

In order to better constrain the K isotope distribution among major reservoirs within the Moon, and to provide the best estimate to date for the K isotopic composition of the bulk silicate Moon for inter-planetary comparison, we analyzed nineteen samples, including both Apollo samples and lunar meteorites. A range of lithologies were analyzed in this study including low- and high-Ti (both low- and high-K) mare basalts, pyroclastic glasses, and nonmare rocks (KREEP-bearing and feldspathic lunar meteorites, Mg-suite norite, anorthosites, and Apollo 16 impact melt breccia). Potential cosmogenic effects on lunar samples were also examined and found to be negligible. Lack of correlations between the K isotopic compositions and both their corresponding $\frac{Ca^*(CRE\ ages)}{K}$ ratios and $^{158}\text{Gd}/^{157}\text{Gd}$ ratios (representative of nuclides with large neutron-capture cross sections) obviate concerns regarding cosmogenic $^{41}\text{K}$ excess in samples measured in this study.

All lunar basalts analyzed in this study define a narrow $\delta^{41}\text{K}$ range, varying from $-0.15 \pm 0.04\%$ to $-0.04 \pm 0.04\%$, with an average of $-0.08 \pm 0.09\%$ (2SD). The new mare-basalt data agree with the previous reported data from (Wang and Jacobsen, 2016b). On the basis of homogeneous K isotopic compositions among different types of mare basalts as well as lack of correlations between $\delta^{41}\text{K}$ and their corresponding Mg#, we infer that no K isotopic fractionation occurred as a result of igneous processes, and that the K isotopic composition of an isotopically homogeneous mantle reservoir is well represented by the average of mare basalts of $-0.07 \pm 0.09\%$ (2SD, n=10, this study and [Wang and Jacobsen, 2016b; Tian et al., 2019]).
Contrary to the restrained mare basalt $\delta^{41}\text{K}$ range, the nonmare rocks vary substantially by more than 2‰, and some of them show a significantly light K isotopic composition. The KREEP-bearing lunar meteorites exhibit elevated $\delta^{41}\text{K}$ values ($\pm 0.31 \pm 0.27\%\text{oo}$, 2SD) relative to that of the basalts, and we infer that these represent an isotopically heavy reservoir on the Moon, separately from lunar soils, which are also isotopically heavy. We propose that heterogeneous reservoirs with distinct K isotope signatures preserved pre-, and syn-Giant Impact are improbable. Extended degassing of K from the late-stage LMO liquid as the K chloride species is our preferred interpretation to address the heavy K isotope enrichment in the (or a portion of the) urKREEP reservoir. The complementary isotopically light K-bearing vapor phases, condensed back onto the lunar surface, were remixed with crustal materials through turbulent impact-breccia formation, and hence were mingled with different lunar lithologies (particularly visible in K-poor anorthosites). The re-condensation and the brecciation processes both initiate the sample heterogeneities to a large extent in terms of the K isotope distribution, which reconcile the substantial variations observed in lunar nonmare rocks.
Acknowledgments

This work was primarily supported by the McDonnell Center for the Space Sciences. Z.T. acknowledges a fellowship from the McDonnell International Academy, Washington University. Editorial handling by Julie Prytulak and reviews from Jessica Barnes and two anonymous reviewers are gratefully acknowledged. We thank CAPTEM, ANSMET, the Meteorite Working Group, Dr. Ryan Zeigler, and Dr. Kevin Righter at NASA’s Johnson Space Center for curation and allocation of Apollo lunar samples and Antarctic meteorites. US Antarctic meteorite samples are recovered by the Antarctic Search for Meteorites (ANSMET) program, which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Acquisition and Curation Office at NASA Johnson Space Center.
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Chapter 4:
Potassium isotope composition of Mars reveals a mechanism of planetary volatile retention

Abstract

The abundances of water and highly to moderately volatile elements in planets are considered critical to mantle convection, surface evolution processes, and habitability. From the first fly-by space probes to the more recent ‘Perseverance’ and ‘Tianwen-1’ missions, ‘follow the water’, and more broadly ‘volatiles’, has been one of the key themes of martian exploration. Ratios of volatile relative to refractory elements (e.g., K/Th, Rb/Sr) are consistent with a higher volatile content for Mars than for Earth, despite the contrasting present-day surface conditions of those bodies. This study presents K isotope data from a spectrum of martian lithologies as a new isotopic tracer for comparing the inventories of highly and moderately volatile elements and compounds of planetary bodies. Here, we show that meteorites from Mars have systematically heavier K isotopic compositions than the bulk silicate Earth (BSE), implying a greater loss of K from Mars than from Earth. The average ‘bulk silicate’ $\delta^{41}$K values of Earth, Moon, Mars, and the asteroid 4-Vesta, correlate with surface gravity, the Mn/Na “volatility” ratio, and most notably, bulk planet H$_2$O abundance. These relationships indicate that planetary volatile abundances result from variable volatile loss during accretionary growth, where larger mass bodies preferentially retain volatile elements over lower mass objects. There is likely a threshold on the size requirements of rocky (exo)planets to retain enough H$_2$O to enable habitability and plate tectonics, with mass exceeding that of Mars.
Significance Statement

Using spacecraft data and elemental abundances derived from martian meteorites, earlier studies set a paradigm of a volatile- and water-rich Mars relative to Earth. Nevertheless, inherent difficulty in determining the volatile budget of bulk silicate Mars (BSM) makes it challenging to directly compare the extents of volatile depletions among differentiated bodies in the Solar System. This study provides an alternative for evaluating the nature of volatiles on Mars using potassium (K) isotopes. The new K isotopic composition of BSM and the strong correlation between $\delta^{41}\text{K}$ and planet mass reveals that the sizes of planetary bodies fundamentally control their ability to retain volatiles. This could further shed light on habitability of planets and assist with constraining unknown parent body sizes.
4.1. Introduction

Examining the presence, distribution, and abundance of volatile elements and compounds, including water, on Mars has been a central theme of space exploration for the past 50 years. The majority of all past, ongoing, and future Mars missions involve the direct or indirect study of volatile element inventories, including the recent “Perseverance” and “Tianwen-1” missions (Williford et al., 2018; Jolliff et al., 2019). Direct study of volatiles in martian meteorites, along with remote sensing efforts, have significantly broadened understanding of the volatile inventory of Mars, and spurred the development of competing bulk chemistry models for Mars. These models can broadly be divided into three groups: (1) those based on cosmochemical implications of elemental ratios (Dreibus and Wänke, 1987; Wänke and Dreibus, 1988; Wänke and Dreibus, 1994), (2) those attempting to reproduce the martian O isotope composition by mixing different proportions of chondritic materials (Lodders and Fegley, 1997; Sanloup et al., 1999) and equating these to volatile abundances, and (3) those combining spacecraft data and meteorite chemistry to estimate the composition of bulk silicate Mars (Yoshizaki and McDonough, 2020). These models all adopted the ratios of volatile element K to the refractory elements U and Th as a proxy of volatile depletion because these elements are all highly incompatible and lithophile during igneous processes, i.e., such ratios are not strongly affected by partial melting followed by melt fractionation that lead to the formation of basaltic rocks and their derivatives that constitute the present-day martian crust. Furthermore, the concentrations of K, Th, and U of this martian crust can be measured remotely from orbit using gamma-ray spectrometry (GRS). All previous models for the composition of bulk silicate Mars, as well as GRS data of exposed martian surface materials
have shown that Mars has elevated K/Th as well as higher contents of a greater suite of moderately volatile elements relative to Earth (Fig. 4.1), together implying a volatile-rich early Mars (G. Jeffrey Taylor et al., 2006; G. Jeffrey Taylor et al., 2006; Yoshizaki and McDonough, 2020). A caveat with these models is the inherent difficulty in determining the K/Th of bulk silicate Mars from surface data, as well as the marked inconsistency between meteorite analyses and GRS data of martian surface regions (G. Jeffrey Taylor et al., 2006).

![Figure 4.1](image_url)

**Figure 4.1.** Potassium to thorium ratios versus the corresponding K concentrations of martian meteorites (basaltic, olivine-phyric, and lherzolitic shergottites, and other categories), the martian surface detected by the Mars Odyssey Gamma Ray Spectrometer, and terrestrial Mid Ocean Ridge Basalts (MORB) and Ocean Island Basalts (OIB). To avoid potential terrestrial contamination effects, only meteorite falls and Antarctic finds are plotted. Data are from compilations for martian meteorites (Lodders, 1998; Shirai and Ebihara, 2004; Anand et al., 2008; Lin et al., 2008; Sarbadhikari et al., 2009; Agee et al., 2013; Day et al., 2018; Udry and Day, 2018), Mars Odyssey GRS data from (Boynton et al., 2004), MORB (Gale et al., 2013), and for OIB from GEOROC (http://www2.mpch-mainz.mpg.de/~geo/Databases/Databases.html). The bulk silicate Earth has a K abundance of 240 ppm and a K/Th of 2900 (McDonough and Sun, 1995). Note the systematically high K/Th for martian surface materials measured by GRS compared with martian meteorites. Terrestrial rocks, especially MORB, exhibit a wide K/Th range overlapping with martian meteorite samples.
An alternative means of examining the volatile history of Mars is by measuring the isotopic ratios of moderately volatile elements (MVE) in martian meteorites. Of the MVEs, which are defined as having 50% equilibrium condensation temperatures (50% \( T_c \)) of less than 1335 K at a total pressure of 10\(^{-4}\) bar for a Solar System gas composition (Lodders, 2003), K is one of the most abundant (50% \( T_c \) = 1006 K (Lodders, 2003)). The isotopic ratios of K in igneous rocks from planetary bodies are insensitive to igneous processes (e.g., melting and fractional crystallization (Tuller-Ross et al., 2019b)) and secondary effects such as impact-induced vaporization (Jiang et al., 2019) and eruptive degassing (Ni et al., 2019), and thus are a strong proxy for volatile depletion in planetary interiors. Here, the K isotope compositions of twenty martian meteorites are reported. These meteorites have previously been established to originate from Mars on the basis of triple-oxygen isotope systematics, trapped noble gas inventories, and the generally young crystallization ages (<1.34 Ga for the SNC) (Stolper and McSween, 1979; McSween and Stolper, 1980; Bogard and Johnson, 1983; McSween, 2002). The twenty examined meteorites cover a range of rock types (basaltic, olivine-phyric, lherzolitic, and picritic shergottites, nakhlites [clinopyroxene-rich cumulates], a chassignite [cumulate dunite], and a basaltic crustal breccia [Northwest Africa 7034], Appendix B, Table B1) and geochemical signatures (incompatible element-enriched, -intermediate, and -depleted shergottites). With the exception of the basaltic breccia NWA 7034, only observed meteorite falls and Antarctic meteorite finds were considered in order to avoid uncertainties related to terrestrial contamination and alteration, which commonly affect hot desert finds (Tian et al., 2019).
4.2. Potassium Isotopic Composition of Bulk Silicate Mars

Potassium isotopic compositions of martian samples, reported as $\delta^{41}$K = $\left( \left( \frac{^{41}K/^{39}K}_{\text{sample}} / \left( ^{41}K/^{39}K \right)_{\text{standard}} \right) - 1 \right) \times 1000$, range from -0.59‰ to -0.08‰ (Fig. 4.2a). Where different subfragments of meteorite samples could be analyzed (Table S1), all but two samples yielded analytically indistinguishable K isotopic compositions (Appendix B). The $\delta^{41}$K values of the two aliquots of Nakhla (a witnessed fall) differ by 0.34‰. This feature likely reflects post-crystallization aqueous modifications on Mars, as previously suggested for nakhlites (Magna et al., 2015a). The lower K/Al and K/Nb as well as elevated Ba/La in the isotopically light Nakhla aliquot suggest that the K isotopic composition of this aliquot stems from alteration of primary igneous minerals. Potassium isotope fractionation during aqueous alteration on the martian surface is not yet understood. Nonetheless, terrestrial analogs show that regardless of weathering environment and secondary minerals formed, the weathered product is an isotopically light endmember in the global K cycle (Li et al., 2019; Chen et al., 2020). These results hint at an enrichment of K and other volatiles in the martian crust, and that the K cycle on Mars is likely to be complex at the surface.

Excluding the isotopically light Nakhla aliquot and the hot desert meteorite NWA 7034, martian meteorites measured in this study and (Tian et al., 2019; Ku and Jacobsen, 2020) define a mean $\delta^{41}$K of -0.28 ± 0.18‰ (2 standard deviations, n = 30). Potassium tends to be quantitively removed into the melt fraction during partial melting of mantle rocks owing to its incompatibility in the residual mantle mineralogy; accordingly, the K isotopic composition of the melt is expected to be
unfractionated with respect to its mantle source (Tuller-Ross et al., 2019b). No correlation is found between bulk Mg[#100 × Mg/(Mg + Fe) in atomic ratios], and their corresponding δ⁴¹K. Moreover, there is no resolvable difference between the mean values of shergottites (including their petrological subgroups), nakhlites, Chassigny, and NWA 7034, indicating only a limited K isotopic fractionation in Mars. We hence use this value as a direct proxy for the K isotopic composition of bulk silicate Mars. This newly determined δ⁴¹K value indicates that bulk silicate Mars is ~ 0.2‰ heavier than bulk silicate Earth [-0.43 ± 0.17‰] (Tuller-Ross et al., 2019a), but isotopically lighter than the bulk silicate Moon and asteroid 4-Vesta (the probable parent body of howardite, eucrite, and diogenite meteorites) by ~ 0.2‰ [-0.07 ± 0.09‰] (Tian et al., 2020), and ~ 0.65‰ [+0.36 ± 0.16‰] (Tian et al., 2019), respectively. These differences are significant on the basis of summed Gaussian distributions of δ⁴¹K values (Fig. 4.2B) and statistically significant as determined by a two-sample Student’s t-test (P-t-test << 0.001 between any two group means).
Figure 4.2. (a) Potassium isotopic compositions of martian meteorites. Data are compiled from this study and (Tian et al., 2019; Ku and Jacobsen, 2020). Dashed line and light grey bar represent the $\delta^{41}\text{K}_{\text{NIST}}$ of bulk silicate Earth (BSE, $-0.43 \pm 0.17\%$) defined by (Tuller-Ross et al., 2019a); darker grey bar represents the BSE value ($-0.48 \pm 0.03\%$) defined by (Wang and Jacobsen, 2016a). No significant differences are observed among mean values of each martian lithology. Samples with different subsamples from different sources analyzed in this study and compiled from the literature are labelled (e.g., Shergotty, Zagami, Nakhla, Tissint, EETA 79001A, and MIL 03346). Color scheme for shergottites: green denotes depleted, orange intermediate, and red enriched shergottites. (b) Histogram and “Summed Gaussian” plot of the K isotopic compositions of Mars, the Earth, Moon, and the asteroid 4-Vesta. Bins for the histogram are in 0.05‰ increments. (c) Potassium isotopic compositions of the four parent bodies. Shaded areas and dashed lines denote the $\delta^{41}\text{K}_{\text{NIST}}$ of the bulk silicate planets. The Earth is represented by a set of MORB, oceanic basalts, and back-arc basin basalts, which provide an estimate for bulk silicate Earth (Tuller-Ross et al., 2019a). The K isotopic composition of the average Upper Continental Crust (UCC) is also presented (Huang et al., 2019). Lunar mare basalts are plotted as representative of the bulk silicate Moon to eliminate the effects of secondary K isotope distributions on the Moon (Wang and Jacobsen, 2016b; Tian et al., 2020). The $\delta^{41}\text{K}_{\text{NIST}}$ of the asteroid 4-Vesta is represented by a group of eucrites and howardites reported in (Tian et al., 2019). Data for Mars are compiled from (Tian et al., 2019; Ku and Jacobsen, 2020) and this study. Only meteorite falls and Antarctic finds are considered in calculating the K isotopic compositions of bulk silicate values for planets.
4.3. Nebular Processes in Shaping the K Isotope Systematics of Planetary Bodies

A key issue relating to the differences in K isotope compositions among various planetary bodies is whether these reflect mass-dependent variations in “nebular” processes, or mass-independent variations among different nucleosynthetic sources, or planetary-scale volatile depletion processes. Nucleosynthetic variations of K are considered unlikely, as known nucleosynthetic isotope anomalies to date are limited to elements having 50% $T_c$ above 1400 K (Vollstaedt et al., 2020), except for the highly volatile noble gases. Moreover, evidence against nucleosynthetic variability as the cause of K isotope variations is found when considering $\delta^{41}$K versus the mass-independent $\mu^{48}$Ca (Schiller et al., 2018). Variable $\mu^{48}$Ca among inner Solar System bodies has been attributed to a rapid change in the composition of disk materials associated with early mass accretion to the proto-Sun, rather than spatial variations in nucleosynthetic components (Kruijer et al., 2020). Crucial to this assessment is that the $\mu^{48}$Ca values of the Earth and Moon are indistinguishable (Appendix B, Fig. B1). The decoupling of $\mu^{48}$Ca and $\delta^{41}$K of the Earth and Moon along with the slight negative correlation between $\mu^{48}$Ca and $\delta^{41}$K in the inner disk bodies suggest that neither nucleosynthetic anomalies nor $^{41}$K production from $^{41}$Ca decay can be the main cause of K isotope variations.

Another potential cause of K isotopic fractionation is nebular-scale partial evaporation or incomplete condensation of volatiles in planetary feedstocks before planet formation (Humayun
and Clayton, 1995). In this scenario, variations in $\delta^{41}$K would occur because of different extents of volatile depletion in precursor materials (Humayun and Clayton, 1995). The different accretionary time scales for planetary bodies may have enabled initial admixing of early-accreted volatile depleted components with later-stage volatile-rich materials, especially in larger planetary bodies. It is, however, difficult to reconcile the isotope effect generated during gas-dust interactions (condensation and evaporation) with the tight correlation observed between $\delta^{41}$K and parent body sizes (Fig. 4.3A and Appendix B, Fig. B2). This is because $\delta^{41}$K heterogeneity in building blocks would be anticipated to produce $\delta^{41}$K variations among bulk planets that contradict the observation, i.e., the distribution of volatile-rich planetary building blocks in the outer Solar System and “drier” feedstocks in the inner Solar System would be expected to have led to more scattered K isotopic compositions that might correlate with the heliocentric distance of planetary bodies. Additional evidence precluding a nebular volatile depletion is the decoupling of K/U and K/Th from K isotopic compositions. Different accretion timescales for planetary bodies may have enabled initial admixing of volatile depleted components with later-accreted volatile rich feedstocks, especially to large parent bodies such as the Earth. If nebular volatile depletion and accretion durations were the only contributing factors accounting for K isotope variations among bulk planets, then K/U and K/Th should also scale with planetary body size. However, intermediate mass objects in the Solar System, such as Mercury (K/U of ~ 12,800) (Peplowski et al., 2011) and Mars (K/U of ~ 15,000) (Lodders and Fegley, 1998), have K/Th and K/U values broadly similar to, or slightly higher than those of larger mass objects such as Earth (K/U of ~ 13,800) (Arevalo et al., 2009) and Venus (K/U of ~ 10,000) (Lodders and Fegley, 1998) based on surface
measurements. Taken together, it is unlikely that the K isotope variations in the inner Solar System are a consequence of nebular processes, but rather reflect loss of volatile elements primarily during the formation and accretion of the planets.

Figure 4.3 (a). Average $\delta^{41}$K of Mars, Earth, Moon and Vesta versus their corresponding surface gravity. Potassium isotope data are compiled from (Wang and Jacobsen, 2016b; Tuller-Ross et al., 2019a; Tian et al., 2019; Ku and Jacobsen, 2020; Tian et al., 2020) and this study. (b). Average $\delta^{41}$K of enstatite chondrites and the four differentiated terrestrial planetary bodies versus their Mn/Na. The K isotope data are compiled from (Wang and Jacobsen, 2016b; Tuller-Ross et al., 2019a; Tian et al., 2019; Ku and Jacobsen, 2020; Tian et al., 2020; Zhao et al., 2020). The bulk Earth Mn/Na is from (Siebert et al., 2018), and takes into account the metal-silicate partitioning behavior of Mn during core formation in Earth. The Mn/Na data of enstatite chondrite, Mars, Moon, and 4-Vesta are from (O’Neill and Palme, 2008). Error bars on data points represent two standard deviations (2SD) on the full dataset.
The goodness of the linear regression fit is shown as $R^2$. The black solid lines represent the 95% confidence error envelopes (shaded area). (c). Average $\delta^{11}$K of four parent bodies versus their corresponding water content estimates. The water contents are from (McCubbin and Barnes, 2019). Note a negative correlation between water contents and their corresponding $\delta^{11}$K among four planetary bodies.
4.4. Volatile Loss During Accretionary Growth of Planetary Bodies

Day and Moynier (Day and Moynier, 2014) suggested that the volatile element inventories of planetary bodies in the Solar System are related to physical characteristics, including surface gravity, although the relationship was not well defined. A striking feature of the new average δ⁴¹K data for bulk silicate Mars is that it lies on a negatively correlated trend (R² = 0.995) with the three other known bulk silicate planetary compositions in the inner Solar System as a function of surface gravity and other related parameters (Fig. 4.3A and Appendix B, Fig. B2). The mean δ⁴¹K values for the respective parent bodies in the inner Solar System also correlate (R² = 0.870) well with their Mn/Na (Fig. 4.3B), an independent chemical index for late-stage volatilization during accretionary growth (O’Neill and Palme, 2008; Siebert et al., 2018; Sossi et al., 2018), as stronger loss of Na relative to Mn was favored under increasingly oxidizing conditions relative to the solar nebula (O’Neill and Palme, 2008). Additionally, Rb behaves geochemically similar to K while being somewhat more volatile both under solar nebular conditions and during planetary evaporation (Lodders, 2003; Sossi et al., 2019). Although the currently available data are limited for stable Rb isotope systematics (Pringle and Moynier, 2017), the mean δ⁸⁷Rb of Earth, the Moon, and 4-Vesta also negatively correlate with surface gravity (Appendix B, Fig. B3). Most importantly, the negative correlation between planetary sizes and stable isotopic compositions also applies to the highly volatile element H (Fig. 4.3C), where bulk planet water contents correlate with their K isotopic compositions (McCubbin and Barnes, 2019). This suggests that the same
underlying cause is responsible for the depletion of K and water among planetary bodies, which is consistent with a recent study showing that enstatite meteorites contain sufficient quantities of H to account for Earth’s water content, obviating the need for a late delivery of water through carbonaceous chondrites or comets (Piani et al., 2020). These relationships confirm that smaller differentiated planetary bodies, with lower gravity, underwent greater volatile depletion and stronger K isotope fractionation than larger bodies relative to their precursor materials. More importantly, the relationships suggest that K depletion resulted from planetary processes affecting the bodies themselves, rather than from nebular processes acting on their precursors.

Vapor loss during accretion of small, low-gravity bodies, and concomitant chemical fractionation has been proposed as an important contributor to the elemental and isotopic budgets of planetary bodies (Lodders, 1994; Hin et al., 2017; Dhaliwal et al., 2018; Young et al., 2019). Variability among volatile-depleted accreting materials could have led to variations in the K isotope compositions of the planetary bodies relative to the initial $\delta^{41}\text{K}$ of the Solar System. A “sum” effect (i.e., integrated over an object’s accretionary growth) of fractionation owing to vapor loss from planetary bodies, has been proposed to account for Mg isotopic fractionation among planetary bodies on the basis of simulations of collisional accretion and a vapor-melt fractionation model derived from thermodynamic properties (Fig. 4.4a) (Hin et al., 2017). In this model, the Mg isotopic composition of the Earth requires such large vapor mass losses that it demands the Earth accreted from relatively volatile-rich planetary feedstocks once it grew larger than approximately Mars-size to account for the abundances of moderately volatile elements such K and Na. Such a model may account for the similarity of the K isotopic compositions of Earth and enstatite
chondrites (presumably building blocks of the Earth). Nonetheless, it is unlikely to cause the tight correlation between bulk planetary δ⁴¹K and their current masses from integration over all accretionary collisions as observed in Fig. 4.3A. We hypothesize that such correlation instead implies that the ultimate K inventory of a bulk planet is dominated by the final accreted mass, regardless of its accretion and differentiation history, unlike more refractory elements such as Li and Mg that require more extreme temperatures for significant vaporization and are hence less likely to be dominated by a late-stage vaporization event (Fig. 4.4B) (Rodovská et al., 2016; Hin et al., 2017). This hypothesis is further supported by the fact that the Moon exhibits heavier δ⁴¹K than that of the Earth. The Moon is considered to have formed later in the Solar System’s history by a single-stage giant collision between a Mars-sized body and the proto-Earth that homogenized the stable isotopes of refractory elements (Lock et al., 2018). That the Moon does not exhibit the same K isotope composition as the Earth is a major impediment to a time-integrated volatile depletion mechanism for K, indicating that the volatile depletion of planetary feedstocks alone cannot explain the variations between δ⁴¹K and surface gravity.
Figure 4.4. Schematic diagram of mechanisms of volatile loss during accretionary growth that can potentially generate the K isotope compositions observed in different parent bodies. Two scenarios are shown here: (a) Time-integrated effect of vapor loss and isotope fractionation over a planetary body’s growth history. Two mechanisms are involved in vapor loss during accretion: impact-induced vaporization and vapor losses above impact-generated magma ponds (Hin et al., 2017). (b) Chemical fractionations dominated by a late-stage evaporation event. Large bodies are able to retain volatiles more efficiently once they reached sufficient sizes (“critical size”). In contrast, the gravity of small bodies is insufficient to prevent volatile losses, which results in preferential loss of vapor relatively enriched in light K isotopes, leaving the residual portion enriched in heavy K isotopes. Such K isotopic fractionation effects are shown in Appendix B, Fig. B4, with different equilibrium fractionation factors under different temperatures. The new K isotope data presented here are in line with the conclusion that the ultimate K (and possibly MVEs with similar volatility) budget of rocky planetary bodies in our Solar System is dominated by vapor loss at a late stage in their accretion.
4.5. A “Dry” Versus “Wet” Mars

The K isotopic compositions among inner Solar System planetary bodies and their strong dependence on planetary sizes are consistent with isotopic fractionation during depletion of MVE from these bodies. Small, differentiated bodies such as 4-Vesta and the Moon, irrespective of their formation processes, had insufficient gravity to prevent volatile losses, leading to the preferential escape of isotopically light K and resultant heavy silicate portions (Fig. 4.4A). In contrast, Earth, and by analogy Venus, reached sufficient size to retain volatiles that accreted to them more efficiently once they exceeded a certain size (Fig. 4.4B). The gas giants (e.g., Jupiter and Saturn) fall at the end of the spectrum, quantitatively retaining all volatile elements and compounds as evidenced by their atmospheric compositions resembling that of the Sun. An intriguing question arises regarding the mass threshold required to retain K (and other elements and compounds with similar volatility), partially or fully, in rocky planets. Previous numerical models placed the threshold at approximately the size of Mars, above which vapor loss ceased (Hin et al., 2017). Our new K isotope data are consistent with planets larger than Mars enabling enhanced retention of volatiles and having highly variable K/Th and K/U. As such, variability in elemental ratios may demonstrate the variability in the volatile abundances of planetary feedstocks, and later crustal differentiation processes.

The new K isotope results for Mars, in the broader context of planetary volatile depletion, are seemingly at odds with the long-standing paradigm based on K/Th and K/U that Mars is volatile-rich. The new K isotope constraint indicates that the volatile abundances of Mars were primarily
set during accretionary growth. The K to refractory element ratios, however, were likely modified from the original ratios acquired during accretion (Appendix B). Supporting evidence comes from GRS surveys (G. Jeffrey Taylor et al., 2006) of the martian surface, which consistently point to a volatile-rich crustal environment relative to igneous martian meteorites. Mars likely underwent an early stage differentiation followed by long-term isolation of mantle reservoirs, as indicated by the greater variance in time-integrated Rb/Sr and Sm/Nd of martian meteorites compared with terrestrial igneous rocks (Kleine et al., 2009; Day et al., 2018). The apparent high K/Th and K/U of Mars are therefore a consequence of sampling of a highly-differentiated volatile-rich surface environment, a conclusion that is also consistent with heterogeneous volatile reservoirs previously reported for Mars from the D/H of martian meteorites (Barnes et al., 2020). This differs from Earth, where some of the volatile elements are subducted and recycled into the mantle via active plate tectonic processes. On the basis of K isotopes, the volatile budget of bulk Mars is low and the likelihood for the habitability of Mars is limited, as it lies roughly at the threshold where a rocky planet is large enough to retain significant budgets of life-sustaining volatiles. The strong correlation between K isotopes and planetary gravity could therefore provide key insights into constraining parent body sizes (e.g., angrite and ureilite parent bodies) and for determining the ‘Goldilocks’ zone for habitability of exoplanets on the basis of their masses, in addition to distance from their host star.
4.6. Materials and Methods

As the current sample collection contains no martian meteorites directly excavated from the mantle, the K isotopic composition of bulk silicate Mars can only be inferred from the partial melting products of their mantle source regions. To a first order, martian lithologies can be divided into shergottites (basaltic, lherzolitic, olivine-phyric, and picritic on the basis of their mineralogy and texture; or depleted, intermediate, and enriched on the basis of incompatible trace elements contents); nakhlites (clinopyroxenites), chassignites (dunites), an orthopyroxenite (ALH 84001), a basaltic regolith breccia (NWA 7034/7533 and other pairings), and the >2 Ga augite basalts (NWA 7635/8159). Widespread shock metamorphism is recognized in most martian meteorites to various degrees (e.g., plagioclase is commonly transformed into maskelynite in basaltic shergottites; in more extreme shock events, high-pressure polymorphs can be present as well, including ringwoodite and silicate perovskite). The depleted and enriched shergottites likely crystallized at different oxygen fugacity, with enriched shergottites crystallizing under more oxidized conditions (along with high La/Yb, high initial $^{87}$Sr/$^{86}$Sr, and negative $\varepsilon^{143}$Nd), depleted shergottites under more reduced conditions (along with low La/Yb, low initial $^{87}$Sr/$^{86}$Sr, and positive $\varepsilon^{143}$Nd), and intermediate shergottites being a mixture of enriched and depleted endmembers. This suggests the existence of either heterogeneous martian mantle reservoirs (Barnes et al., 2020), or an ancient martian crustal component and a primitive depleted mantle source (McSween, 2015). The nakhlite-chassignite suite exhibits both the same crystallization and ejection ages, and is thought to have a comagmatic origin (McCubbin et al., 2013). Twenty martian
meteorites (twenty-three subsamples) were investigated in this study, covering a wide range of geochemical and petrologic types. Most samples from the suite have previously been analyzed for stable Li, Mg, Ca, and V isotope compositions (Magna et al., 2015a; Magna et al., 2015b; Magna et al., 2017; Nielsen et al., 2020). High-precision data from previous studies were also included (Tian et al., 2019; Ku and Jacobsen, 2020).

The high-precision K isotope analytical procedure used here was adopted from (Chen et al., 2019). About 10 – 150 mg of homogeneously pulverized samples were dissolved in a concentrated HF-HNO₃ mixture (~ 3:1 v/v) either in Teflon beakers or Parr high-pressure digestion vessels. The samples were refluxed with 6 M HCl after being completely dried down on a hot plate. The fully dissolved samples were then desiccated and re-dissolved in 0.7 M HNO₃. Ultrapure water (Milli-Q, 18.2 MΩ•cm), and double-distilled HCl and HNO₃ were used in sample dissolution and ion-exchange chromatography to reduce blank levels. The samples were centrifuged before loading onto columns for chemical purifications.

A three-step procedure was deployed to separate K from other matrix elements, including one “big column” (ID = 1.5 cm, BIO-RAD Econo-Pac, resin volume of 19 mL in water medium) and two repeated “small column” steps (ID = 0.5 cm, BIO-RAD Glass Econo-Column, resin volume of 2.4 mL in 4N HCl). BIO-RAD AG50-X8 (100-200 mesh) cation-exchange resin was pre-cleaned and conditioned in 0.7 M and 0.5 M HNO₃ for the “big” and “small” columns, respectively. Detailed protocols can be found in Table 1 of (Chen et al., 2019). All elemental concentration measurements, including major and trace elements, were performed using a Thermo Scientific
iCAP Q quadrupole ICP-MS, with a typical uncertainty of 5% (2 RSD). A K recovery rate of ~100% is required to avoid artificial isotope fractionations during ion-exchange chromatography. Hence, fractions collected before and after K-collecting volumes were monitored to ensure > 99% K yields for all samples measured in the course of this study. Furthermore, the proportion of matrix elements was constrained to within 2% of the total K inventories to eliminate drift introduced by matrix effects during measurements (Chen et al., 2019). The total-procedure blank was 0.26 ± 0.15 µg, with a distinct K isotopic composition of −1.31 ± 0.05‰ (Chen et al., 2019). In all cases, contamination introduced by blanks was negligible.

Potassium isotope analyses were performed with a Neptune Plus MC-ICP-MS (Thermo Scientific). To enhance the instrumental sensitivity while minimizing the generation of hydrides and oxides, an APEX Omega desolvating nebulizer (Elemental Scientific) was used as the sample introduction system. The measurements were conducted on the low-mass “shoulder” of the peak in the instrument’s high-resolution mode (m/Dm > 10,000) to resolve the peaks of $^{40}\text{Ar}^1\text{H}^+$ and $^{41}\text{K}^+$. A conventional standard-sample-standard bracketing technique was used, and concentrations between samples and standards were matched to within 3% to avoid concentration effects on K isotope measurements. NIST SRM 3141a was used as the K standard solution. All results are expressed in the delta notation, where:

$$d^{41}\text{K} (‰) = \left(\frac{[^{41}\text{K}/^{39}\text{K}]_{\text{sample}}}{[^{41}\text{K}/^{39}\text{K}]_{\text{NIST SRM 3141a}} - 1}\right) \times 1000 \quad (4.1)$$
Each sample was measured approximately ten times in a ~ 300 ppb solution. The internal (i.e., within-run) reproducibility is reported as two standard errors (2SE, typically ~ 0.05‰) along with the weighted mean value for each sample. The long-term reproducibility (~ 0.11‰, two standard deviations, 2SD) of the technique has been evaluated via routinely measuring the same geo-reference material over ~ 20 months in different analytical sessions (Chen et al., 2019). The same geo-reference material, BHVO-2, was also measured here (along with the martian samples) in each analytical session to monitor instrumental drift among different sessions and to undertake inter-laboratory comparisons (Appendix B, Table B1). Within analytical uncertainties, the K isotopic values for BHVO-2 reported here are indistinguishable from those found in other studies (Wang and Jacobsen, 2016a; Chen et al., 2019; Tian et al., 2019).
Acknowledgments

Reviews by Dr. Alan Brandon and two anonymous referees, and editorial handling by Dr. Mark Thiemens are gratefully acknowledged. This work was primarily supported by the McDonnell Center for the Space Sciences. Z.T. acknowledges a fellowship from the McDonnell International Academy, Washington University. K.W. acknowledges support from NASA (Emerging Worlds Program grant number #80NSSC21K0379). K.M., T.M., and E.E.S. are grateful to the Helmholtz Association through the research alliance HA 203 “Planetary Evolution and Life”. T.M. contributed through the Strategic Research Plan of the Czech Geological Survey (DKRVO/ČGS 2018-2022). J.M.D.D. is supported by NASA Emerging Worlds (80NSSC19K0932). Work by K.L. is in part supported by NSF AST 1517541 and the McDonnell Center for the Space Sciences. We thank the Antarctic Search for Meteorites (ANSMET), the Meteorite Working Group, Dr. Kevin Righter at NASA’s Johnson Space Center, Dr. Glenn MacPherson at Smithsonian National Museum of Natural History, Dr. Philipp Heck at The Field Museum of Natural History, Dr. Laurence Garvie at the Center for Meteorite Studies, Arizona State University, and National Institute of Polar Research (NIPR), Japan for providing meteorite samples. US Antarctic meteorite samples are recovered by ANSMET program, which has been funded by NSF and NASA, and characterized and curated by the Department of Mineral Sciences of the Smithsonian Institution and Astromaterials Acquisition and Curation Office at NASA Johnson Space Center.
References


Piani L., Marrocchi Y., Rigaudier T., Vacher L. G., Thomassin D. and Marty B. (2020) Earth’s water may have been inherited from material similar to enstatite chondrite meteorites. *Science (80-. ).* **369**, 1110–1113.


## Appendix A: For Chapter 3

### Supplementary Table S1. Potassium isotopic compositions versus Ca*(CRE ages)/K and \(^{158}\text{Gd}/^{157}\text{Gd}\) in lunar samples.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Type</th>
<th>CaO/ wt%</th>
<th>Ca/ ppm</th>
<th>K2O/ wt%</th>
<th>K/ppm</th>
<th>Ca/K</th>
<th>CRE age</th>
<th>error</th>
<th>Isotope system</th>
<th>Ca*CRE/K</th>
<th>(^{158}\text{Gd}/^{157}\text{Gd})</th>
<th>error</th>
<th>deltaK*</th>
<th>2SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Ti Basalt</td>
<td>12018 Low-Ti olivine basalt</td>
<td>8.54</td>
<td>61000</td>
<td>0.04</td>
<td>332</td>
<td>179</td>
<td>195</td>
<td>16</td>
<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>34942</td>
<td>1.58928</td>
<td>0.00038</td>
<td>-0.117</td>
<td>0.035</td>
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<td>Low Ti Basalt</td>
<td>12063 Low-Ti Ilmenite basalt</td>
<td>10.18</td>
<td>74929</td>
<td>0.061</td>
<td>506</td>
<td>144</td>
<td>95</td>
<td>5</td>
<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>13711</td>
<td>1.58786</td>
<td>0.00016</td>
<td>-0.043</td>
<td>0.044</td>
</tr>
<tr>
<td>Low Ti Basalt</td>
<td>12065 Low-Ti Pigeonite basalt</td>
<td>12.6</td>
<td>90000</td>
<td>0.072</td>
<td>597</td>
<td>147</td>
<td>200</td>
<td>(^{21}\text{Ne}/^{38}\text{Ar})</td>
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<td>-0.049</td>
<td>0.034</td>
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<tr>
<td>Low Ti Basalt</td>
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<tr>
<td>High Ti Basalt</td>
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<td>10.9</td>
<td>77857</td>
<td>0.3</td>
<td>2489</td>
<td>30</td>
<td>480</td>
<td>25</td>
<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>14637</td>
<td>1.59668</td>
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<td>-0.15</td>
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<td>10017* High-Ti Ilmenite basalt (high K)</td>
<td>10.9</td>
<td>77857</td>
<td>0.3</td>
<td>2489</td>
<td>30</td>
<td>480</td>
<td>25</td>
<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
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<td>78000</td>
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<td>126</td>
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<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>23096</td>
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<td>0.026</td>
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<tr>
<td>High Ti Basalt</td>
<td>74275 High-Ti Ilmenite basalt</td>
<td>10.26</td>
<td>73286</td>
<td>0.09</td>
<td>747</td>
<td>96</td>
<td>32.2</td>
<td>1.4</td>
<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>3081</td>
<td>-0.085</td>
<td>0.022</td>
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<tr>
<td>Non Mare</td>
<td>14301* Regolith Breccia</td>
<td>10.1</td>
<td>72143</td>
<td>0.64</td>
<td>5311</td>
<td>13</td>
<td>102</td>
<td>30</td>
<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>1351</td>
<td>-0.129</td>
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<td>Non Mare</td>
<td>14305* Crystalline Matrix Breccia</td>
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<td>70929</td>
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<td>5311</td>
<td>13</td>
<td>27.6</td>
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<td>Non Mare</td>
<td>60015 Cataclasitic anorthosite</td>
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<td>0.01</td>
<td>83</td>
<td>1590</td>
<td>1.9</td>
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<td>(^{81}\text{Kr}/^{83}\text{Kr})</td>
<td>3022</td>
<td>-1.16</td>
<td>0.04</td>
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<tr>
<td>Non Mare</td>
<td>60315* Poikilitic impact melt</td>
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<td>74357</td>
<td>0.35</td>
<td>2904</td>
<td>25</td>
<td>4.5</td>
<td>0.1</td>
<td>(^{37}\text{Ar})</td>
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<td>-0.059</td>
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<tr>
<td>Non Mare</td>
<td>62255 Anorthosite with melt</td>
<td>19.1</td>
<td>136429</td>
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<td>(^{38}\text{Ar})</td>
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<td>0.01</td>
<td>0.02</td>
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[180]
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<th>Y</th>
<th>Age (My)</th>
<th>Ar/Ar (Ma)</th>
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<td>108571</td>
<td>0.02</td>
<td>0.7</td>
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<tr>
<td>64435</td>
<td>Breccia with glass coat</td>
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<td>108571</td>
<td>0.02</td>
<td>0.7</td>
</tr>
<tr>
<td>64435</td>
<td>Breccia with glass coat</td>
<td>15.2</td>
<td>108571</td>
<td>0.02</td>
<td>0.7</td>
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<td>65015</td>
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<td>85929</td>
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<tr>
<td>65015</td>
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<td>85929</td>
<td>0.32</td>
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<tr>
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<td>Feldspathic regolith breccia</td>
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<td>121429</td>
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<tr>
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<td>Cataclastic norite</td>
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<td>64000</td>
<td>0.14</td>
<td>27.2</td>
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<td>MIL 090036</td>
<td>KREEP-bearing feldspathic breccia</td>
<td>15.5</td>
<td>110714</td>
<td>0.1</td>
<td>10</td>
</tr>
</tbody>
</table>

*Literature data for K isotopic compositions are from (Wang and Jacobsen, 2016; Tian et al., 2019); **The Ca/K atomic ratios are from the compilation in the Lunar Compendium (Meyer, 2011); The cosmic ray exposure (CRE) ages from earlier literatures are compiled in (Meyer, 2011) and (Park et al., 2013). The $^{158}\text{Gd}/^{157}\text{Gd}$ ratios for lunar samples and terrestrial materials are reported in (Lugmair and Marti, 1971).

Reference


Appendix B: For Chapter 4

Potassium isotopic variations within martian meteorites

Two Nakhla subsamples obtained from different sources yield resolvable K isotope variations that are outside analytical uncertainties (Δ = 0.34‰ relative to a typical within-run reproducibility of ±0.05‰ and a long-term reproducibility of ±0.11‰). It has been well-demonstrated that nakhlite meteorites underwent aqueous modification, likely during crystallization and emplacement on Mars (Bunch and Reid, 1975). To demonstrate potential chemical weathering, elemental ratios with elements exhibiting different mobilities during weathering were plotted for all nakhlites (Fig. S5). Potassium is mobile relative to the immobile elements Al and Nb. Thus, aqueous alteration would modify K/Al and K/Nb as dissolution and subsequent removal of K would enrich the weathered products in Al and Nb. The coupled light K isotopic composition and low K/Al and K/Nb indicate the occurrence of aqueous alteration in the isotopically light Nakhla subsample. Hence, this sample is excluded from the calculation of the mean bulk silicate Mars δ⁴¹K. Furthermore, despite Nakhla being a meteorite fall, elevated Ba/La (enrichment in Ba, an index of terrestrial alteration) was observed in the same sub-sample, suggesting possible contamination by terrestrial material or modification on the martian surface.

Another sample that exhibits significant isotopic heterogeneity is Zagami, which shows a δ⁴¹K range from −0.33 ± 0.04‰ (Ku and Jacobsen, 2020) to −0.08 ± 0.03‰ (this study). The −0.33 ± 0.04‰ (Ku and Jacobsen, 2020) value is consistent with the average δ⁴¹K of martian meteorites defined in this study (−0.28 ± 0.18‰, 2SD, n = 30). A suite of progressively evolved magmatic compositions has been reported in Zagami along with spatial variations in textures and mineralogy (McCoy et al., 1992; McCoy et al., 1999). Zagami crystallized from a “dry” magma that might have undergone near-surface degassing (McCoy et al., 1999), which could account for the variations in δ⁴¹K seen among the different fragments. Moreover, smaller sample aliquots are more likely to sample isotopic heterogeneities. Such a “size effect” was shown previously in that the largest aliquot of Juvinas, a main group basaltic eucrite, has the closest δ⁴¹K to the eucrite average, whereas the other two smaller aliquots deviate from the average significantly (Tian et al., 2019). Potassium isotopic compositions of Zagami reported in (Ku and Jacobsen, 2020) are from larger amounts of crushed powders and hence could be more homogeneous than Zagami measured in this study in terms of δ⁴¹K.

Northwest Africa (NWA) 7034 may also contain nonindigenous K, as it is a hot desert find. A previous study demonstrated pervasive terrestrial contamination by K in Northwest Africa eucrite finds (Tian et al., 2019), with the post-addition materials being isotopically light relative to the bulk silicate Earth. Nevertheless, these eucrites have an order of magnitude lower K contents than NWA 7034. Additionally, incompatible-element-rich, KREEPy lunar meteorites found in hot deserts, which have K contents similar to that of NWA 7034 (K₂O ~ 0.5 wt.%), have been shown to be insensitive to terrestrial modification (Tian et al., 2020). Therefore, NWA
Sample NWA 7034 is of high significance because it establishes a direct link between meteoritic compositions with orbital and lander compositional data collected for the martian surface (Agee et al., 2013).

**Potassium isotopic composition of bulk silicate Earth, Moon, and 4-Vesta**

With the increased application of high-precision K isotope analysis techniques over the past five years, numerous terrestrial samples (e.g., geological reference materials, magmatic rocks, sedimentary rocks, and loess) have been analyzed. This provides a better understanding of the K isotope distribution on the Earth’s surface and its interior, thus constraining the $\delta^{41}\text{K}$ value of the bulk silicate Earth (BSE) and facilitating comparisons with other planets. Despite the absence of direct measurements of mantle xenoliths, mantle-derived oceanic basalts can be used to represent the mantle and bulk silicate Earth. (Wang and Jacobsen, 2016a) defined BSE $\delta^{41}\text{K}$ of $-0.479 \pm 0.027\%$ based on three basalts derived from different geological settings. Later, a global survey on oceanic basalts was conducted by (Tuller-Ross et al., 2019), covering a geologically, geographically, and geochemically wider range. This study suggested a homogeneous upper mantle reservoir in terms of K isotopes and modified the BSE $\delta^{41}\text{K}$ to $-0.43 \pm 0.17\%$, which is considered the best available estimate for BSE to date. The mantle and oceanic crust comprise $\sim$70% of the total Earth’s K budget. The remaining $\sim$30% of K is contained in the other major K reservoir, the continental crust. A recent systematic survey (Huang et al., 2019) of upper crustal materials revealed isotopically heterogeneous K within the upper continental crust (UCC), yet with a weighted average resembling the bulk silicate Earth value ($-0.44 \pm 0.05\%$). The K isotopic compositions of both middle and lower continental crust remain unclear. Nevertheless, it is likely they are similar to that of the UCC owing to the overall agreement between the UCC and BSE (Huang et al., 2019).

The K isotope composition of the lunar mantle and bulk silicate Moon was estimated by (Tian et al., 2020) on the basis of ten mare basalts that sampled different lunar mantle reservoirs. Non-mare lithologies in general span a substantially wider $\delta^{41}\text{K}$ range compared to the “narrow” mare basalt average in terms of K isotope composition. In particular, some feldspathic non-mare rocks show extreme light $\delta^{41}\text{K}$ values (down to $-2\%$) whereas KREEPy lunar meteorites are all isotopically heavier than the mare basalt average. Such isotope fractionation and re-distribution in the lunar interior can also be seen in the other moderately volatile isotope systems (e.g., Cl, Zn, and Ga (Kato et al., 2015; Barnes et al., 2016; Kato and Moynier, 2017)). Merely averaging all lunar samples would lead to a biased “bulk silicate Moon” value, as it fails to take K contents among different lithologies into consideration. The K elemental and isotopic mass balance in the lunar interior is beyond the scope of this paper. Nevertheless, (Tian et al., 2020) suggested that secondary K re-distribution should not modify the overall $\delta^{41}\text{K}$ of the bulk silicate Moon, as the lunar gravitational field along with an early, transient atmosphere prohibited the escape of KCl (the major vapor speciation for K during urKREEP degassing). Redistribution of K may, however, cause isotopic heterogeneities among various lunar lithologies.
The estimate of the K isotopic composition of bulk silicate Vesta was established by averaging eleven noncumulative eucrites and howardites (Tian et al., 2019). Basaltic eucrites, which are the partial melting products of their corresponding mantle source region, serve as a proxy for the K isotopic composition of the Vestan mantle. Howardites are mechanical mixtures of eucrites and diogenites. The K isotope composition of howardites is dominated by that of the eucritic component owing to its relatively high-K content and is unaffected by impact gardening on the Vestan surface. Diogenites, another major lithology in the Vestan crust, are intrusive orthopyroxenites and harzburgites. The unconstrained K isotopic composition of diogenites currently represents an obstacle to refining the $\delta^{41}$K of bulk silicate 4-Vesta. Here, a simplified mass balance model is performed to evaluate the importance of diogenites for K in the interior of Vesta. We adopt a thickness of 18 to 22 km for a noncumulative eucrite upper crust layer, 13 to 19 km for a diogenite-predominated lower crust layer with thin layers of cumulate eucrite and dunite (1–2 km and 300–500 m, respectively), 119 to 130 km for an ultramafic mantle layer whose thickness varies along with the thickness of the Vestan crust, and 110 km for a metallic core (Mandler and Elkins-Tanton, 2013). Two near-end-member scenarios are considered here neglecting cumulate eucrite and dunite layers: (A) 20 km noncumulative eucrite + 10 km diogenite + 130 km harzburgitic mantle and (B) 24 km noncumulative eucrite + 17 km diogenite + 119 km harzburgitic mantle (from top to bottom). We assigned ~ 400 ppm K for noncumulative eucrites and ~ 20 ppm K for both diogenites and ultramafic mantle (Prettyman et al., 2015); the diogenites contained 1.9% and 2.6% of the bulk Vesta K budget in scenarios A and B, respectively. Assuming the average $\delta^{41}$K of diogenites is within 1‰ of that the eucrite average, the change in isotope composition introduced by diogenites does not exceed ±0.03‰, which is indistinguishable within analytical uncertainty. Hence, the orthopyroxene-rich (low-K) diogenite makes it of minor importance in the overall elemental and isotopic K budget for Vesta.

**K/Th and [K] estimate of bulk silicate Mars**

The K/Th of Mars is estimated either through bulk rock chemical analysis of the current martian meteorite collection or via a gamma-ray spectrometer (GRS) survey (Halliday et al., 1995 and references therein). Potassium and Th (or U) concentrations generally correlate during igneous processes as they are both highly incompatible lithophile elements. The small mineral-melt partitioning coefficients in major mantle minerals (e.g., olivine, orthopyroxene, clinopyroxene, and garnet (Hauri et al., 1994; Borg and Draper, 2003)) lead to the quantitative removal of K and Th during partial melting, while retaining a constant K/Th. The most recent estimate of the bulk composition of Mars utilized a martian surface K/Th value of 5300 ± 220 measured by GRS on Mars Odyssey (G.J. Taylor et al., 2006; G Jeffrey Taylor et al., 2006), yielding a bulk [K] of 360 ppm (Yoshizaki and McDonough, 2020).

Nevertheless, the involvement of minor phases, for which the mineral-melt partitioning coefficients for K and Th differ, could cause K/Th fractionation relative to the source region (Halliday et al., 1995; Jones, 1995). McLennan (2003) (McLennan, 2003) found that variation in K/Th (as well as K/U and K/La) correlates with the degree of LREE-depletion (e.g., La/Sm, see Figure 6 therein). Thus, it has been proposed that this variability results from mixing of depleted mantle reservoir and an enriched crustal component. For a ~50-km thick martian
crust and with 5000 ppm K, more than 50% of K resides in the crust, indicating a less volatile-enriched composition of Mars. Besides, previous work has shown a statistically significant decrease of K and Th concentrations (and potential K/Th variations) with decreasing apparent surface ages (Hahn et al., 2007). Whether such a correlation in different surface types reflects crustal evolution or merely indicates sampling from distinct mantle reservoirs remains unsettled. Lastly, aqueous alteration on the martian surface could potentially influence K/Th as indicated by both an acidic leaching experiment on the basaltic shergottite Zagami (Dreibus et al., 2008) and in-situ analysis on surface sedimentary rocks with the Curiosity Rover (Mangold et al., 2015; Le Deit et al., 2016). This is evidenced by the fact that the K/Th detected by GRS, which probed the upper few centimeters of the martian surface, is systematically higher than that of martian meteorites. To summarize, both the K and Th contents, thus the K/Th, of the exposed martian surface as measured by GRS and martian meteorites are subject to change via the aforementioned mechanisms and are not necessarily representative of the bulk planet volatile budget.
Figure B1. The average $\delta^{41}$K of the four differentiated terrestrial planetary bodies versus their corresponding mass-independent $\mu^{48}$Ca. Potassium isotope data are compiled from (Wang and Jacobsen, 2016b; Tuller-Ross et al., 2019; Tian et al., 2019; Ku and Jacobsen, 2020; Tian et al., 2020) and this study; Ca isotope data are from (Schiller et al., 2018). Note a slight negative correlation between $\delta^{41}$K and $\mu^{48}$Ca in Earth, Mars, and asteroid 4-Vesta (shown as a grey arrow), as well as the identical $\mu^{48}$Ca values of Earth and the Moon.
Figure B2. The average K isotope compositions of four differentiated terrestrial planetary bodies (The Earth, Mars, Moon, and asteroid 4-Vesta, from the right bottom to the left top in each sub-plot) versus their corresponding radius, mass, and escape velocity in log scale. Potassium isotope data are compiled from (Wang and Jacobsen, 2016b; Tuller-Ross et al., 2019; Tian et al., 2019; Ku and Jacobsen, 2020; Tian et al., 2020) and this study. The black dashed line stands for the linear regression fitting, whereas the black solid lines represent the 95% confidence error envelopes. The error bars are 2SD. The goodness of fit of the linear regression is shown as $R^2$. Note the tight negative correlations observed for all parameters.
Figure B3. The average Rb isotopic compositions of three differentiated terrestrial planetary bodies (The Earth, Moon, and asteroid 4-Vesta, from the bottom right to the top left in each subplot) versus their corresponding radius, mass, surface gravity, and escape velocity in log scale. The Rb isotope data are from (Pringle and Moynier, 2017). The black dashed line represents the linear regression, whereas the black solid lines represent the 90% confidence error envelopes. Error bars are 2SD. The Rb isotopic composition of 4-Vesta is poorly constrained, with only two samples being measured (Juvinas and Stannern). In Juvinas, secondary volatile loss has modified its K (and potentially Rb) isotope composition(Tian et al., 2019); hence, the Rb isotope composition of 4-Vesta is represented by Stannern. As with K, negative correlations are observed in $\delta^{87}$Rb vs. all four parameters in log scale. The $\delta^{87}$Rb of bulk silicate Mars is predicted to fall on the regression line between Earth and Moon.
Figure B4 Potassium to Th ratio on a logarithmic scale versus K isotopic compositions of enstatite chondrite and four differentiated bodies. The K/U values are compilations from (Taylor, 1982; Lodders and Fegley, 1998; Kitts and Lodders, 1998; Arevalo et al., 2009; Barra et al., 2012), whereas the $\delta^{41}$K values are from (Wang and Jacobsen, 2016b; Tuller-Ross et al., 2019; Tian et al., 2019; Ku and Jacobsen, 2020; Tian et al., 2020; Zhao et al., 2020) and this study. Error bars are 2SD. The colored straight lines represent Rayleigh fractionation curves for different fractionation factors (0.9996, 0.9997, 0.9998, and 0.9999). The equilibrium fractionation factors between vapor and melt (using K-feldspar as approximation) are from the ab initio calculation by (Li et al., 2019), where 0.9996, 0.9997, 0.9998, and 0.9999 correspond to 1000K, 1250K, 1500K, and 2000K, respectively. The grey curves indicate hypothetical mixing lines between a late-accreted EC-component and an extremely volatile-depleted proto-Earth with different compositions.
Figure B5. Potassium isotope compositions versus (a) K abundances; (b) chondrite-normalized La/Sm values (Barrat et al., 2012); (c) bulk Mg numbers; Mg$^\# = 100\times$Mg/(Mg + Fe) in atomic ratios; (d-f) K/Al, K/Nb, and Ba/La, respectively, for nakhlites. Major and trace elemental abundances as well as K isotopic compositions for plots are from this study (See Supplementary Table 1 and 2 for details). Color scheme for shergottites (enriched, intermediate, and depleted; basaltic, olivine-phyric, lherzolitic, and picritic), nakhlites, chassignite, and basaltic breccia is the same as in Figure 2.
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[192]
*Standard errors (SE = standard deviation divided by the square root of the total number of measurements)
** Number of measurements
¶(Ku and Jacobsen, 2020)
†(Tian et al., 2019)
Table B2. Selected major and trace elemental abundances (ppm) whole rock analysis for martian meteorites by iCAP Q quadrupole ICP-MS (typical analytical error ~ 5% 2RSD, with In 5ppb internal standard).

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‡ ISO ref. value
References


Publication List