POTASSIUM ISOTOPE CONSTRAINTS ON NEAR-SURFACE FRACTIONATION EFFECTS OF BULK LUNAR SOILS AND APOLLO 15 DEEP DRILL CORE, Z. Tian\textsuperscript{1*}, M. Neuman\textsuperscript{1}, P. Koefoed\textsuperscript{1}, and K. Wang (王昆)\textsuperscript{1} Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130, USA (t.zhen@wustl.edu, wangkun@wustl.edu); \*Current address: Albemarle Corporation, 348 Holiday Inn Rd, Kings Mountain, NC 28086, USA.

Introduction: Lunar soil is the fine-grained fragmental layer of debris on the lunar surface caused by its exposure to high-energy particles (e.g., solar winds, cosmic rays, secondary neutrons) and meteoroid bombardment. Significant heavy isotope enrichment in various highly and moderately volatile element isotope systems has been recognized in lunar soils since the 1970s (e.g., O, S, Se, Si, Cl, K, Fe, Cu, Zn, Cd, [1-16]). As shown in Fig. 1, these isotopic fractionations observed in volatile elements are typically correlated with the ferromagnetic resonance (FMR) maturity index (L/FeO). On the contrary, mass-dependent isotopic fractionation in refractory element (e.g., Mg, Ca) is limited [17,18], indicating that element volatility plays an important role in controlling the observed isotopic compositions of lunar soils.

![Fig 1. Selected stable isotopic compositions in lunar soil vs. maturities (L/FeO) [1-16].](image)

Potassium is a moderately volatile element (50% condensation temperature=1006 K [19]). Previous studies [12-14] have shown substantial heavy K isotope enrichment in lunar soils compared to lunar basalts and terrestrial igneous rocks (up to ~10‰). Nevertheless, early attempts at K stable isotope measurements had relatively low resolution owing to analytical challenges. This study aims to provide a systematic investigation of the K isotopic compositions of bulk lunar soils, and more importantly, samples from the Apollo 15 deep drill core with depth and other information. Numerical modelling will be developed on the basis of high-precision K isotope data from this study to quantitatively constrain the near-surface volatile depletion and isotope fractionation processes. The results will be reported in the conference.

Samples and Methods: Thirteen bulk lunar soils from Apollo 12, 15, 16, and 17, two pyroclastic (green and orange) glasses, as well as twenty interval samples from the Apollo 15 deep drill core 15004 to 15006 (from the surface to 100.4 cm) were analyzed in this study. The USGS rock standard (BHVO-2) was also analyzed in each analytical session for quality control.

The analytical procedure was adapted from [20]. About 10 to 80 mg samples were dissolved in concentrated HF-HNO\textsubscript{3} on a hot plate. The fully dissolved samples were passed through AG50W-X8 100-200 mesh cation-exchange chromatography columns twice to purify K. A recovery rate > 99% was maintained to ensure no isotopic fractionation during ion-exchange chromatography. The total-procedure K blank was negligible for all samples in this study.

A high-precision K isotope analysis method using a Thermo Scientific Neptune Plus MC-ICPMS and an Elemental Scientific APEX omega desolvating nebulizer was applied here [20]. Sample-standard bracketing protocol was used, and K isotopic compositions are reported in the delta notation (δ\textsuperscript{41}K) relative to the K standard NIST SRM 3141a. The within-run reproducibility is the two standard error (2SE) of ~10 analyses in one analytical session for each sample and is evaluated as ~0.05‰. The long-term reproducibility is evaluated by the two standard deviation (2SD) of the geo-reference material BHVO-2 in different analytical sessions over ~20 months and is ~0.11‰ [20].

Results and Discussion: The K isotopic compositions from both this study and the literature are shown in Fig. 2 (bulk lunar soils and pyroclastic glasses) and Fig. 3 (interval samples from the Apollo 15 deep drill core). Nearly all lunar soils are enriched in heavy K isotopes compared to the K isotopic composition of the bulk silicate Moon (BSM) defined by mare basalts (~0.07 ± 0.09‰) [21]. While mare basalts show a restricted range of K isotopic variation from ~0.15 ± 0.04‰ to ~0.04 ± 0.04‰ [21], bulk lunar soils vary considerably from 0.00‰ (61220, immature trench soil) to +11.77‰ δ\textsuperscript{41}K (15041, surface trench soil). The orange glass soil 74220 resembles the δ\textsuperscript{41}K of the BSM, whereas the green glass 15426 is enriched in heavy K isotopes. Four bulk lunar soil samples were measured both by this and previous studies [12-14]. For three
samples (12033, 12070, and 15041), the new values agree with the literature values within analytical uncertainties, despite the different analytical methods used (MC-ICPMS vs. TIMS and SIMS). The only exception is 15426 and this small discrepancy is likely attributed to sample heterogeneity. Potassium isotopic compositions of the interval samples from the Apollo 15 deep drill core all drift towards heavier $\delta^{41}$K relative to the BSM, and generally decrease with increasing depth. The variation in K isotopic compositions versus depth broadly mirrors the maturity variation [22].

Fig. 2. $K$ isotopic compositions of bulk lunar soils and pyroclastic glasses vs. maturities (I/FeO).

Compared to the literature data (gray symbols in Fig. 2), this study unambiguously shows that soil maturity is the dominant controlling factor for K isotopic fractionation on the lunar surface (Figs. 2 and 3). Such a positive correlation with lunar soil maturity is not unique to K, as [1] observed that the S, Si, and O isotopic compositions also positively correlate with soil maturity. They further suggested that such a correlation strongly supports thermal volatilization by micrometeorite impacts as being responsible for the volatile loss and heavy isotope enrichment in lunar soils. The extreme K isotopic fractionation could also be attributed to kinetic fractionation during micrometeorite bombardment, which would cause lunar soils to preferentially lose light K isotopes relative to the mare basalts. Alternatively, these enrichments in heavy K isotopes ($^{41}$K) could be attributed to the cosmic-ray effect, where $^{40}$Ca can be produced via the low-energy neutron capture reaction: $^{40}$Ca($n, \gamma$)$^{41}$Ca. The short-lived radionuclide $^{41}$Ca (half-life: $1.04 \times 10^5$ yr) subsequently decays to $^{41}$K. Cosmicogenic live $^{41}$Ca has been measured in this core and other lunar soil samples [23]; however, no correlation between $^{41}$Ca and $\delta^{41}$K is observed here, which indicates the amount of cosmogenic $^{41}$K is negligible compared to the indigenous K in lunar soils.

Fig. 3. $K$ isotopic compositions of samples from Apollo 15 deep drill core vs. maturities (I/FeO) [22] and depth from the surface. Note that the K isotope and maturity analyses were not conducted on the same sample or at the same exact depth.

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