

## REAPPRAISAL OF K AND Rb ISOTOPE FRACTIONATION IN LUNAR SOILS AND THE ORIGIN OF THE LUNAR EXOSPHERE

T. Hopp<sup>1</sup>, N. X. Nie<sup>1,2</sup>, and N. Dauphas<sup>1</sup>, <sup>1</sup>Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, IL, USA. <sup>2</sup>Geophysical Laboratory, Carnegie Institution for Science, Washington, DC, USA. (hopp@uchicago.edu)

**Introduction:** One of the major scientific discoveries of the Apollo missions was the detection of a tenuous exosphere of He and Ar around the Moon [1]. Later, ground-based observations discovered that besides the relatively large amount of (light) noble gases in the lunar atmosphere [2], minor amounts of atomic sodium (Na) and potassium (K) are also present [3].

Based on previous studies, the most likely sources of K (and other alkali elements) in the lunar exosphere are: 1) Photon-stimulated/electron-stimulated desorption and charged particle sputtering [4], and 2) Meteoroid impacts and volatilization of elements in the target lunar soil [5]. On the other hand, the possible sinks of atoms in the atmosphere are gravitational escape ( $v_{\text{escape}} \sim 2.4$  km/s), re-implantation and/or loss to space of ions in the solar wind electric field, and condensation and reaction with the lunar soils [6]. While these possible processes involved in the conservation of the lunar atmosphere are identified, the uncertainty on the actual contribution of the individual processes is large.

Recently, the successful ‘The Lunar and Dust Environment Explorer’ (LADEE) mission, and improvements in the ground-based spectral analysis of alkali elements in the lunar exosphere led to renewed interest and insights into the origin of the lunar atmosphere [e.g., 6,7]. These observations reveal a dawn-dusk and north-south asymmetry of the K intensity in the exosphere as well as contribution of meteoroid impacts, and an influence of the underlying soil composition, i.e. proximity to the KREEP terrane [6,7].

The lunar soils collected during the Apollo program allow direct investigation of the reservoir that contributes atoms to the lunar exosphere. Following the sample return of the Apollo missions, detection of heavy K isotope compositions in lunar soils provided the first direct evidence for alkali element loss from the lunar surface [8-10]. In theory, such isotope fractionation signatures have the potential to distinguish between different processes of K loss to the lunar atmosphere. However, the K isotopic composition alone do not allow to decipher loss by volatilization or by gravitational escape. In contrast, coupled rubidium (Rb) and K isotope measurements of lunar soils can provide tighter constraints on the sources and sinks in the lunar atmosphere [8] because Rb is geochemically similar to K but behaves differently during sputtering and gravitational escape due to its higher mass.

Recent advances in mass spectrometry led to a several orders of magnitude better precision on isotope analysis and a renewed interest in K and Rb isotope geochemistry [11-14]. In light of prospective sample return missions from airless asteroids (e.g., OSIRIS-REx [15]) and missions investigating the exosphere of other terrestrial planets (e.g., Mercury, BepiColombo [16]), we revisit the K and Rb isotope fractionation mechanisms during the formation of the lunar exosphere. In detail, we will build a theoretical framework to understand the K and Rb isotope systematics of the individual sources and sinks of K and Rb atoms in the lunar atmosphere. This will ultimately allow us to decipher the contributions of these processes to the lunar exosphere in prospect of upcoming high precision K and Rb isotope analysis of lunar soils.

**Methods:** In the first step, we evaluate possible isotope fractionation induced by the individual sources and sinks of K and Rb in the lunar atmosphere. We start from a simplified model where we limit the sources of K and Rb to photon-stimulated desorption and impact volatilization. Of these, it can be assumed that only volatilization induces significant isotope fractionation, which can be calculated using the Hertz-Knudsen equation [17] and Rayleigh-distillation. In case of the sinks, both gravitational escape and re-condensation onto the surface can potentially fractionate K and Rb isotopes. Isotope fractionation during gravitational escape is strongly dependent on the temperature and the mass of the atoms [18]. In a simplified case of solely atomic species, the velocity distribution of atoms in lunar exosphere can be represented by a Maxwellian distribution function [18]. Based on this distribution the fraction of atoms of a specific mass with velocities higher than the lunar escape velocity (at a fixed T) can be calculated [18]. Modeling the fraction of <sup>39</sup>K, <sup>41</sup>K, <sup>85</sup>Rb, and <sup>87</sup>Rb lost to space allows to calculate the isotope fractionation induced by this process.

In the next steps, the simplified calculations will be implemented into a more complex box model in which these processes interact to produce possible K and Rb isotope signatures in lunar soils for different scenarios of the origin of the lunar exosphere.

**Results and Discussion:** The K isotopic compositions of lunar soils are heavier compared to the bulk moon [10,11]. In contrast, the available Rb isotope data of lunar soils does not resolve any isotope frac-

tionation. Figure 1 compares the dataset of combined K and Rb isotopic compositions in lunar soils (orange circles) from [8] with modeled isotope fractionation of K and Rb during impact evaporation and gravitational escape.

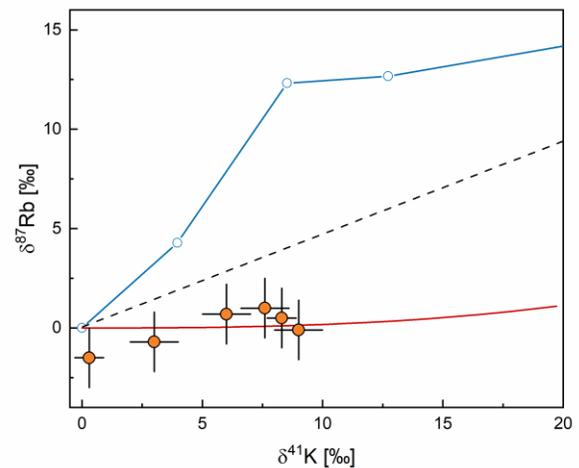
Isotope fractionation during evaporation induced by meteoroid impacts would lead to correlated heavier K and Rb isotopic compositions in lunar soils. However, the magnitude of isotope fractionation depends on the volatility and evaporation kinetics of both elements. We calculated two scenarios of isotope fractionation during evaporation. In the first, we assume that Rb is evaporated more efficiently than K based on experiments of [19] (blue line in Fig. 1). In this case, lunar soils are expected to have similarly heavy K and Rb isotopic compositions. In the second scenario, the volatility and evaporation kinetics of K and Rb are similar (dashed line in Fig. 1). The magnitude of isotope fractionation is controlled by the mass difference of the elements, and the K isotope fractionation in lunar soils is  $\sim 2x$  larger than for Rb. The large uncertainties on the available Rb isotope data for lunar soils do not allow to exclude correlated K and Rb isotope fractionation due to such evaporation with similar volatilities (Fig. 1).

Gravitational escape (red line in Fig. 1) leads to heavier isotopic compositions of K remaining in the exosphere as a function of the temperature. In contrast, the higher mass of Rb suppresses gravitational loss. Therefore, the Rb remaining in the exosphere is not significantly fractionated. In general, this result fits to the isotopic compositions of the lunar soils, i.e., fractionated K, but unfractionated Rb isotopes (Fig. 1). However, to imprint this gravitational escape signatures of K and Rb into the lunar soils, both elements have to be re-implanted to the surface without inducing additional isotope fractionation.

**Outlook:** We will implement calculations of K and Rb isotope fractionation for the possible processes related to the origin of the lunar exosphere into a box model to quantitatively evaluate different scenarios of the origin of K and other alkali elements in the lunar exosphere. In light of future missions to terrestrial bodies with detectable exospheres, e.g., BepiColombo mission to Mercury, such a theoretical framework for the lunar atmosphere will be critical for understanding the mechanisms of exosphere formation in general.

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**Figure 1.** Possible scenarios of K and Rb isotope fractionation induced by processes involved in the establishment of the lunar exosphere. The magnitude of isotope fractionation is given in  $\delta$ -notation as permil deviation from the natural isotopic composition. Gravitational escape alone (red solid line) leads, depending on the temperature evolution, to large isotope fractionation for K, but no significant isotope fractionation for Rb. In contrast, impact volatilization of K and Rb produces correlated isotope fractionation signatures dependent on the volatility and evaporation kinetics (blue solid line for  $K < Rb$  in volatility [19], while black dashed line for  $K = Rb$  [20]). The orange points are literature values of K and Rb isotopic compositions from [8].