

LOSS AND ISOTOPIC FRACTIONATION OF ALKALI ELEMENTS DURING DIFFUSION-LIMITED EVAPORATION FROM MOLTEN SILICATE

Z. J. Zhang¹, N. X. Nie^{1,2}, R. A. Mendybaev¹, Ming-Chang Liu³, J. Y. Hu¹, T. Hopp¹, E. E. Alp⁴, B. Lavina⁴, E. S. Bullock², K. D. McKeegan³, N. Dauphas¹, ¹Department of the Geophysical Science, The University of Chicago, Chicago, IL 60637, USA (zhez@uchicago.edu); ²Earth & Planets Laboratory, Carnegie Institution for Science, Washington, DC 20015, USA; ³Department of Earth, Planetary and Space Sciences, UCLA, Los Angeles, CA 90095, USA; ⁴Advanced Photon Source, Argonne National Laboratory, IL 60439, USA

Introduction: Moderately volatile elements (MVEs) are variably depleted in planetary bodies relative to the solar composition, reflecting the imprints of nebular and post-nebular processes [1]. Among MVEs, alkali elements are valuable tracers of the depletion histories of MVEs in different planetary bodies (asteroids and planets) and some of their constituents (e.g., chondrules) due to their similar geochemical behaviors but their tendency to be chemically and isotopically fractionated by evaporation/condensation processes. Recent improvement in K and Rb isotopic analysis have enabled us to resolve their small isotopic differences in meteorites, which provides better insight into their depletion history (i.e., the saturation degree during evaporation [2]). Laboratory experiments have been proven as robust tools for quantitatively understanding MVEs' depletion history and their isotopic fractionation mechanisms. Previous studies have investigated the chemical fractionation of alkali elements under different conditions [3,4], and kinetic isotopic fractionation for K [5]. However, the results are not consistent and there is no data available for Rb isotopes. Here we report results of vacuum evaporation experiments of Na, K and Rb, and also their associated K and Rb isotopic fractionation.

Experimental: In the present work, we have conducted vacuum evaporation experiments at the University of Chicago using a synthetic MORB-like basaltic melt under 1200 and 1400 °C for different heating durations to investigate their evaporation kinetics and isotopic fractionations. The chemical compositions of evaporation residues were measured both by MC-ICPMS at the University of Chicago and by EPMA at the Earth and Planets Laboratory, Carnegie Institution for Science. The Rb isotopic compositions of the evaporation residues were measured by MC-ICPMS at the University of Chicago, and the K isotopic compositions were measured by secondary ion mass spectrometer (SIMS) at UCLA. To better constrain the oxygen fugacity during evaporation, we measured the $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio in the silicate residues with Mössbauer spectroscopy.

Results and Discussions: The results show that Na, K, and Rb were lost under the experimental conditions. For both the 1200 and 1400 °C runs, volatility decreases following the order of Na, Rb, and K. The evaporation residues for 1200 °C runs are characterized by flat chemical and isotopic profiles. However, zoning profiles were observed in the 1400 °C run products, where the K and Rb contents have decreased from center to the rim and the heavier K isotope became more enriched near the surface compared with center. This observation suggests that the transport of K and Rb within the molten droplet was limited by diffusion at 1400 °C, and the evaporation at 1200 °C was not diffusion-limited. The measured Rb and K isotopic compositions of bulk residues follow a Rayleigh distillation law, and the fractionation factors are consistent with kinetic theory as given by square root of their inverse mass ratio. The measured $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio in residues determined by Mössbauer spectroscopy translates to an $f\text{O}_2$ of $\text{IW}+6.2$ to $+7.2$. However, such high $f\text{O}_2$ would result in a high escape flux of O_2 and a rapid reduction of Fe^{3+} to Fe^{2+} , which is not observed in the experiments. Most likely, the Fe reduction is limited by slow diffusion of Fe^{2+} and Fe^{3+} , and the actual $f\text{O}_2$ during the evaporation is controlled by oxygen released from the dissociated alkalis. Taking into account the diffusion effect, and using the calculated $f\text{O}_2$ and evaporation trajectory from experiments, we are able to constrain the evaporation kinetics and predict the evaporation and activity coefficients for alkalis in silicate melts.

Applying these new insights from laboratory experiments, we further investigated the origin of MVEs depletion history for asteroid 4-Vesta. 4-Vesta (as sampled by HED meteorites) is characterized by highly fractionated K/Rb ratio (~6x higher than CI), large depletion in K and Rb abundances but enrichment in their heavy isotopes (compared with Earth [6,7]). We calculated the K/Rb ratio, $\delta^{41}\text{K}$, and $\delta^{87}\text{Rb}$ values of the residues after evaporating 94% of K under different temperatures in both vacuum and a 98.8% saturated medium. The modeling results show that the chemical and isotopic signature of K and Rb in Vesta can be well reproduced with evaporation of chondrule-size objects (0.01-0.1 cm) at moderate temperatures (~1050 °C) in a 98.8% saturated medium. Currently, we are testing possible effects of melt composition on chemical and isotopic fractionation of MVEs in experiments using different melt compositions.

References: [1] Davis A. M. (2006) In: Meteorites and the Early Solar System II: 295-307. [2] Nie N. X and Dauphas N. (2019) The Astrophysical Journal Letters 844.2: L48. [3] Shimaoka et al. (1994) Proc. NIPR symp. Antarct. Meteorites 7: 164-177. [4] Sossi P. A. et al. (2018) Geochimica et Cosmochimica Acta 260: 204-231. [5] Richter et al. (2011) Meteoritics & Planetary Science 46: 1152-1178 [6] Pringle E. A. and Moynier. F. (2017) Earth and Planetary Science Letter 473: 62-70. [7] Tian Z. et al. (2019) Geochimica et Cosmochimica Acta 266: 611-632