

THEORY OF KINETIC ISOTOPE FRACTIONATION DURING EVAPORATION

S. Inada¹, T. Hama², and S. Tachibana¹, ¹Department of Earth and Planetary Science, The University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan, inada@eps.s.u-tokyo.ac.jp, ²Komaba Institute of Science, The University of Tokyo, 3-8-1 Komaba, Tokyo 153-8902, Japan.

Introduction: Kinetic isotope fractionation during evaporation causes the heavy-isotope enrichment in the residual condensed phase. This phenomenon has been used, for example, to investigate transient heating events which caused evaporation of igneous calcium-aluminum-rich inclusions (CAIs) in the early Solar System [1]. The magnitudes of the fractionation can be quantified as the kinetic isotope fractionation factor α . According to the conventional equilibrium-based evaporation rate theory (the Hertz-Knudsen equation), α is given by the square root of the inverse mass ratios of the isotopic evaporating species, $(m'/m)^{1/2}$ [2]. The validity of this prediction was suggested from the experiments on evaporation of Fe from metallic solid iron [3]. On the other hand, α for evaporation of Mg and Si from forsterite and CAI-like melts are found to be significantly closer to unity than $(m'/m)^{1/2}$ of the thermodynamically stable gas-phase species (Mg and SiO) [4-7]. This discrepancy has been attributed to kinetic effects, including (i) production of molecules heavier than the equilibrium species [4,7] and/or (ii) unknown molecular-level dynamics under non-equilibrium conditions [5,6], although both have remained unproven. In this study, we investigated the latter possibility in the framework of the non-equilibrium evaporation rate theory established by Inada et al. [8], aiming to clarify whether and in what conditions α can deviate from $(m'/m)^{1/2}$ of evaporating species.

Methods: By applying the transition state theory [9], the non-equilibrium evaporation kinetics can be statistically evaluated instead of describing the detailed microscopic evaporation dynamics [8]. Here, we formulated the kinetic isotope fractionation factor α through this approach. To simplify the problem, we focused on evaporation in a single-component system consisting of structureless rigid particles like atoms. In our formulation, the high-temperature limit of α is given by the isotopic ratio of the vibrational frequencies at the transition state along the reaction coordinate. To evaluate α based on this formulation, we considered a simplified one-dimensional harmonic model including many-body motions of the condensed phase. Then, we numerically calculated α , focusing on its dependence on the curvature of the potential energy surface at the transition state along the reaction coordinate.

Results and Discussion: The results of the calculations indicated that α is equal to $(m'/m)^{1/2}$ as predicted by the conventional theory for barrierless evaporation with the flat transition state. On the other hand, when there exists a potential energy barrier along the reaction coordinate of evaporation, α becomes closer to unity than $(m'/m)^{1/2}$ (Fig. 1). As an application of the theory, we discussed evaporation of metallic Fe, which can be directly compared to the present single-component hard-sphere model. Using the previous experimental data, we found that both the evaporation rates [10] and the associated isotopic fractionation [3] that were independently measured indicate that there is no potential energy barrier for this evaporation. It is expected that this relationship between α and the potential energy surface can be qualitatively extended to multicomponent systems. Thus, the deviation of α from $(m'/m)^{1/2}$ for silicate compounds might imply the presence of a potential energy barrier for their evaporation. For further investigations, the remaining hypothesis should be separately tested through the experimental speciation of evaporation products under non-equilibrium conditions.

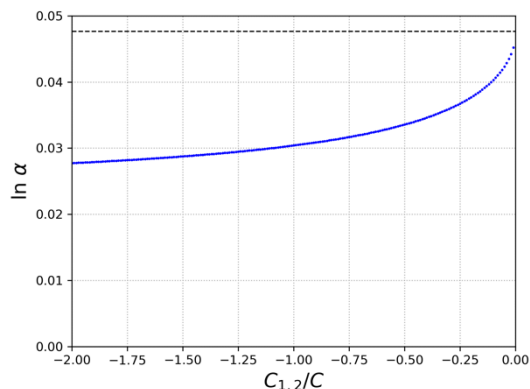


Fig. 1. α calculated with our model (blue dotted line) plotted against the force constant of the dissociating bond correlating with the curvature of the potential energy surface at the transition state. The black dashed line shows $(m'/m)^{1/2}$. Both are calculated for $m'/m = 1.1$.

References: [1] Grossman L. et al. (2000) *Geochimica and Cosmochimica Acta* 64:2879–2894. [2] Davis A. M. and Richter F. M. (2014) *Treatise on Geochemistry 2nd Edition*, 335–360. [3] Tachibana S. et al. (2007) *Meteoritics & Planetary Science* 37:A138. [4] Wang J. et al. (1999) *Geochimica and Cosmochimica Acta* 63:953–966. [5] Yamada M. et al. (2006) *Planetary and Space Science* 54:1096–1106. [6] Richter F. M. et al. (2007) *Geochimica and Cosmochimica Acta* 71:5544–5574. [7] Mendybaev R. A. et al. (2021) *Geochimica and Cosmochimica Acta* 292:557–576. [8] Inada S. et al. (2024) *The Journal of Chemical Physics* 16:154710. [9] Eyring H. (1935) *Chemical Reviews* 17:65–77. [10] Tachibana S. et al. (2011) *The Astrophysical Journal* 736:16.