

Equilibrium isotope fractionation between water adsorbed on mesoporous materials and water vapor with implications for the hydrologic cycle

YING LIN^{1*}, JUSKE HORITA^{1*}, OSAMU ABE²

¹Department of Geosciences, Texas Tech University,
Lubbock, TX, USA 79409-1053 (*correspondence:
ying.lin@ttu.edu, juske.horita@ttu.edu)

²Department of Earth and Environmental Sciences, Nagoya
University, Nagoya, Aichi, Japan 464-8601

Soil water dynamics within a thick vadose (unsaturated) zone is a key component in the hydrologic cycle, especially in arid regions. In applying the Craig-Gordon evaporation model to obtain isotopic compositions of soil water and the evaporation flux in land-surface models (LSMs), it has been assumed that the equilibrium isotope fractionation factor between soil water and vapor ($\alpha_{\text{adsorbed L-V}}$) is identical to that of bulk water and vapor ($\alpha_{\text{L-V}}$). The adsorption isotope effect (AIE) is due to the intermolecular forces between the adsorptive and the surface adsorbate and also lateral interactions. There exist abundant spectroscopic studies showing a shift in intramolecular OH stretching frequency upon adsorption and that the tetrahedral H-bond structure of water is distorted. Thus we carried out experiments to test whether $\alpha_{\text{adsorbed L-V}}$ is identical to $\alpha_{\text{L-V}}$. In Lin and Horita [1], a mesoporous silica (15 nm) was used as a soil analog. In this study, we carried out more experiments on silica (6 nm) and alumina (5.8 nm). Our results demonstrated that $\alpha_{\text{adsorbed L-V}}$, both for oxygen and hydrogen, are smaller than $\alpha_{\text{L-V}}$ and decrease with decreasing p/p_0 . The trends can be explained by the increasing hydrophilic interaction between the water molecules and the pore surfaces, and thus greater distortion in the tetrahedral H-bond structure of the water molecules, at lower water content. Decreased adsorption potential upon heavy isotope substitution may also play a role. The isotopic profiles of these three materials differ due to the differences in the pore volumes and the pore surface areas. Our results from triple oxygen isotope analyses demonstrated that the isotope effect observed is mass-dependent in nature. Empirical formula relating $\alpha_{\text{adsorbed L-V}}$ to the proportions of filled pores (f) are developed for potential application to LSMs.

[1] Lin and Horita (2016) *Geochim. Cosmochim. Acta* **184**, 257-271.