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## Isotopic fractionation of water during evaporation

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### Abstract

[1] Variations in the isotopic content ( $^{18}\text{O}/^{16}\text{O}$  and D/H ratios) of water in the natural environment provide a valuable tracer of the present-day global hydrologic cycle and a record of the climate over at least 400,000 years that is preserved in glacial ice. The interpretation of observed isotopic ratios in water vapor, rain, snow, and ice depends on our understanding of the processes (mainly phase changes) that produce isotopic fractionation. Whereas equilibrium isotopic fractionation is well understood, kinetic effects, or diffusion-controlled fractionation, has a limited experimental foundation. Kinetic effects are significant during evaporation into unsaturated air and during

condensation to form ice from vapor. Kinetic effects are also thought to control the deuterium excess ( $d = \delta D - 8\delta^{18}O$ ) of precipitation. We describe experiments to observe kinetic effects associated with evaporation. Analysis of our own and previous experiments shows that surface cooling of the liquid is a crucial variable affecting fractionation from evaporating water that has not been properly considered before. Including the effects of evaporative surface cooling reconciles observed D/H fractionation with kinetic theory and removes the need to invoke an unusual size for the HDO molecule. Thus the isotopic molecular diffusivity ratios are  $D(H_2^{18}O)/D(H_2^{16}O) = 0.9691$  and  $D(HD^{16}O)/D(H_2^{16}O) = 0.9839$ . Implications of this work for representation of kinetic fractionation in global circulation models and cloud physics models are briefly discussed.

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