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Deuterium excess in the Rayleigh model

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The deuterium excess is a useful quantity for measuring nonequilibrium effects of isotopic fractionation, and can therefore provide information about the meteorological conditions in evaporation regions (e.g., relative humidity over the ocean or the fraction of plant transpiration over land). In addition to nonequilibrium fractionation, there are two other effects that can change the deuterium excess during phase transitions. The first is the dependence of the equilibrium fractionation factors on temperature, the second is the nonlinearity of the delta scale, on which the deuterium excess is defined. We tested the impact of these three effects (nonequilibrium, temperature and delta scale) in a simple Rayleigh condensation model simulating the isotopic composition of an air parcel during a moist adiabatic ascent. The delta scale effect is important especially for depleted air parcels where it can change the sign of the deuterium excess in the remaining vapour from negative to positive. In this case the deuterium excess to a large extent reflects an artefact of its own definition, which overwrites both the nonequilibrium and the temperature effect. This problem can be solved by an alternative definition for the deuterium excess that is not based on the delta scale.