An explanation of why isotopic fractionation varies with precipitation rate and temperature

Isotopic fractionation is the separation of two isotopes of a given element during some process. In the Earth Sciences, one process commonly of interest is precipitation of a mineral from an aqueous solution. For at least the stable isotopes of oxygen and carbon, the extent of fractionation depends on rate of precipitation and on temperature (much more so for O than C). This document attempts to explain why.

**General explanation:**

- **Heavier isotope**, or radical group containing heavier isotope of one of its constituent atoms.
- **Lighter isotope**, or radical group containing lighter isotope of one of its constituent atoms.

**Three specific cases:**

- **Lower temperature; slower precipitation**
  - With faster precipitation, most ions haven’t time to leave, and fewer have time to leave, so proportions in solid approach same as in solution (which is lessened fractionation). We consider this to be non-equilibrium fractionation.

- **Higher temperature**
  - Growth buries almost all ions but only a few. Most ions present at any one time drift away before being buried. Thus the ratio of heavier to lighter ions is greater in the solid than in the solution - and that is fractionation. (However, the much greater abundance of heavy in the solution makes it the dominant constituent of the solid.)

- **Faster precipitation**
  - We use this varying extent of fractionation of O to calculate the temperature at which precipitation of the mineral took place, and thus we have a “paleothermometer” (if we are confident that we know the δ18O of the water from which the mineral precipitated).

For each of the two isotopes, the curve above is the distribution of the probability (on the vertical axis) of survival for different lengths of time (on the horizontal axis). The distributions are assumed here to be normal (i.e., symmetrical around coincident mean, median, and mode).

This concept of survival times of atoms or radical groups on the mineral surface lets us then consider the different diagrams at right as explanations of why fractionation varies with precipitation rate and temperature.