

Variability in the mass dependence of equilibrium isotope fractionation in crystals

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First-principles calculations of $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ fractionation in silicate, carbonate, oxide, sulfate and phosphate minerals will be presented. In light elements (especially oxygen and sulfur), slight variations in the mass dependence of isotope fractionation in equilibrium processes lead to subtle "mass-independent" fractionation signatures that are of emerging interest as potential tracers of provenance, temperature, and reaction histories in the hydrological cycle, chemical sediments and other environments. Measurements are now capable of resolving variations that are so small that disentangling equilibrium signatures from disequilibrium (or even highly diluted nucleosynthetic heterogeneity) is sometimes difficult, and theory may be useful for resolving ambiguities. So far, theoretical calculations of the mass dependence of equilibrium stable isotope fractionation have mostly been limited to models of molecules and molecular clusters. In the present study we explore a broader range of crystalline materials, including structures representing the major mineral groups (ortho-, ino-, sheet, and framework silicates, carbonates, phosphates, sulfates, oxides and hydroxides). In agreement with previous studies, we find that equilibrium $\Delta^{17}\text{O}$ offsets for mineral- $\text{H}_2\text{O}(\text{v})$ or mineral-mineral pairs generally become smaller as temperatures increase, relative to the 0.5305 high-temperature mass fractionation exponent or the commonly used 0.528 exponent. We also find that, for a variety of minerals and temperatures, there is a consistent (if rough) relationship between the equilibrium $^{18}\text{O}/^{16}\text{O}$ fractionation factor and $\Delta^{17}\text{O}$ offset relative to water vapor, suggesting that it may be possible to crudely estimate equilibrium $\Delta^{17}\text{O}$ vs. T behavior using experimental and empirical $^{18}\text{O}/^{16}\text{O}$ calibrations. Large $\Delta^{17}\text{O}$ offsets and unusual mass law exponents observed in some recent studies of high-temperature rocks and mineral separates are not easily explained on the basis of harmonic or quasi-harmonic equilibrium isotope fractionation theory.