

Theoretical Constraints on the Mass Dependence of Isotope Diffusion in Minerals

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An important mechanism of stable isotope fractionation in high temperature geochemistry is due to mass-dependent differences in the diffusion rates of isotopes. At high temperatures the vibrational frequency of a diffusing atom is inversely proportional to the square root of its mass, causing heavier isotopes to diffuse more slowly. However, in general the mass dependence of isotope diffusion is weaker than a square root dependence. The isotope effect in minerals is diminished in two ways, by: (1) coupling to the motion of other lattice atoms when a jumping atom is at the saddle point, and (2) correlation in the direction of successive atomic jumps. An expression for the diffusivity ratio of two isotopes in a crystal that incorporates these effects is [1]: $D_1/D_2 = f\Delta K(\sqrt{m_2/m_1} - 1) + 1$, where f is the correlation coefficient and ΔK reflects the degree of coupling with other atoms during a jump. In metals, halides and oxides, ΔK has been found experimentally to have values of $\sim 0.5-1$. The correlation coefficient, on the other hand, can take a wide range of values between 0 and 1, depending on the diffusion mechanism and the relative frequencies of the various jumps involved in diffusion. The correlation coefficient can be calculated based on several different kinds of experimental data or on atomistic simulation data. This has been done in some cases for relatively simple minerals and synthetic crystals, and the isotope effect on diffusivity estimated from the correlation coefficients is in good agreement with direct experimental measurements, where they are available.

Exact calculations on the correlation coefficient are very difficult for complex minerals with low symmetry and multiple cation and interstitial sites. However, some general inferences regarding the isotope effect can be drawn from calculations on simpler minerals. 1) The isotope effect is maximized for cations that diffuse very slowly relative to the major solvent cation, or for cations that diffuse very rapidly by a simple interstitial mechanism. 2) The isotope effect can be strongly dependent on temperature, for cation impurities that diffuse by a vacancy mechanism, and may increase significantly with temperature for rapidly diffusing cations.

[1] LeClaire, A.D. (1966) *Phil. Mag.* **14**, 1271-1284