The theory of kinetic isotope effect of interstitial diffusion in solids

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Diffusion is a universal phenomenon in minerals. Light and heavy isotopes have different diffusion rates, which will lead to the diffusion isotope effect (DIE) of solid. With the development of high space resolution mass spectrometer (HRMS), the study of isotope fractionation in minerals becomes a research hotspot recently. Although isotope data along profiles in minerals are rapidly accumulating, there are still many pending questions. How long the heating history is? What's the diffusion speed difference for different isotope systems? Therefore, the quantum-mechanics-based theoretical framework and basic diffusion parameters in these processes are urgently needed now.

Previous studies thought that the isotope effect in solid-state diffusion processes was evaluated using the product of the correlation coefficient *f* (denoting the degree of deviate from a random walk for the diffusion process) and the coupling coefficient *K* (representing the degree to which the motion of an atom is coupled to that of other nearby atoms during a diffusive jump). We show that the previous treatments are improper due to some approximations used in them. There are other factors can affect isotope fractionations besides *f* and *K*. We provide a unified equation for solid-state interstitial diffusion by one elemenary jump step based on the microscopic expression of diffusion coefficient. The harmonic vibrational frequency of mineral in the unified equation was calculated using first-principles method based on the density functional theory. Moreover another equation is also provied to caluculate the isotope effect for interstitial diffusion over a mineral grain. We figure out the diffusion pathways using the climbing images nudged elastic band method. Take He diffusion in periclase and olivine for example, we calculate the magnitude of isotope effect ($^{4}He/^{3}He$) in diffusion processes, and also can theoretically estimate the migrate distance of He at a certain temperature and pressure condition.