

A Unified Theory of Stable Isotope Fractionation Driven by Temperature Gradients

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If a homogeneous system is under temperature gradient for enough time, both its chemical and isotopic compositions will be significantly changed between the hot and the cold ends. The knowledge of how isotopes to be fractionated in thermal diffusion processes is important for explaining the existing isotope data in various systems. Recently, a few studies have investigated stable isotope fractionations in high-T silicate melts under thermal gradients. However, there are still large disagreements about the theoretical treatments and isotope fractionation mechanisms for these systems.

Huang et al.(2010) found that the extent of isotope fractionation would be linearly depended on the temperature gradient. Richter et al. (2011) used the molten andesite to show that Mg isotope fractionations against temperature didn't look like a straight line. Huang et al. (2011) provided more data to show a linear distribution despite increase or decrease of the local slopes. Dominguez et al.(2011) related the transition-state theory (TST) to the thermal diffusion process. They approximated the energy barrier difference between heavy and light isotope species to the difference of their zero-point vibrational

energies. Other kinetic energies which are commonly nontrivial at high temperatures were ignored in their study. They also ignored all the kinetic energy differences of activated complexes at the transition state. Lacks et al. (2012) questioned the work of Dominguez et al. (2011). They proposed a new model based on Chapman-Enskog theory and used a specially designed classical molecular dynamics (MD) method to treat temperature gradients. However, the Chapman-Enskog theory was originally set up for treating ideal gas collision. It can be only reasonable under extremely high temperatures.

Here we provide a unified theory of isotope fractionation driven by thermal diffusion. This theoretical model doesn't include many simplifications for high-T conditions as previous models employed and can treat systems at any temperature conditions. It therefore has great potential to be used in almost all situations involving thermal gradients. We also tested our theory by using high-T silicate melt systems as an example. Our results can explain those arguing points related to isotope fractionations of silicate melts under temperature gradients.