

Geochemical kinetics: A net reaction rate vs. forward and backward reaction rates

HUIMING BAO¹² AND XIAOBIN CAO¹²

¹ Department of Geology & Geophysics, Louisiana State University, Baton Rouge, LA 70803, U.S.A.

² School of Earth & Space Sciences, Peking University, Beijing 100871, China

A net rate (r) is a commonly used parameter in studying geochemical kinetic processes including mineral precipitation/dissolution and mineral-water exchange that are fundamental to rock-water interactions. However, a net rate reflects the degree of disequilibrium of a set of processes and is often of limited power in deducing the reaction mechanisms that underlie the observed phenomenon. For example, it is at zero when a reaction is at equilibrium or steady state, but the chemical reaction continues with the forward and backward reaction rates are equal. Only the forward and backward rate constants (k) are the intrinsic parameters for a defined elementary reaction step. They are directly linked to the reaction mechanism at molecular level and are only affected by temperature. Therefore, a truly reductionist's approach to geochemical kinetic study must use the intrinsic forward and backward rate constants, rather than a changing net reaction rate or net reaction rate constant.

However, determining a forward or backward rate constant is not a trivial task because these two rates are always going together in opposite directions during a reaction. In fact, most of geochemical kinetic studies lack forward or backward rate constant, because it would require the knowledge of the transition state of that reaction path. There are established experimental methods for obtaining forward or backward rate constant for a reaction of interest. Here we present a new approach in which a chemical system at equilibrium is perturbed by a natural-abundance stable isotope disequilibrium. By measuring the temporal trajectory of a three-isotope system, e.g., $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$, $\delta^{25}\text{Mg}$ - $\delta^{26}\text{Mg}$, or $\delta^{29}\text{Si}$ - $\delta^{30}\text{Si}$ space, we can sensitively and accurately determine the forward or backward rate constant with the concentrations of chemical species involved remaining unchanged at all time. In a two-reservoir equilibrium oxygen isotope exchange case, we can determine the apparent kinetic isotope effect associated with the exchange mechanisms. Real-world example of mineral-water exchange or dissolution/precipitation cases will be analysed to illustrate the utility of the three-isotope method on geochemical kinetic study.