

The utility of three-isotope method

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The equilibrium isotope fractionation factor α is a fundamental parameter in stable isotope geochemistry. Although equilibrium α can be determined by theoretical calculation or by measurement of natural samples, direct laboratory experiments are ultimately required to verify those results. The attainment of a true exchange equilibrium in experiments is often difficult, but three methods have been devised and used to ensure that an equilibrium α has been obtained in an isotope exchange experiment. These are the two-directional method, partial-exchange method, and three-isotope method. Of these, the three-isotope method is thought to be the most rigorous. However, over the years some researchers have cautioned on the limitations of this method, but the foundation of the three-isotope method has not been properly examined and the method is still widely used in calibrating equilibrium α for both traditional and non-traditional isotope systems today. Here, using water-water oxygen exchange as a model system, we conduct an isotopologues-specific kinetic analysis of the exchange processes and explore the underlying assumptions and validity of the three-isotope method. We demonstrate that without knowing the detailed exchange kinetics a priori the three-isotope method cannot lead to a reliable equilibrium α . For a two-component system, α determined by this method may be equilibrium α , kinetic isotope effect (*KIE*), apparent *KIE* (*AKIE*), or steady-state α , which can all bear different values. When multiple components exist during the exchange, the evolving trajectory can be complex and hard to predict. Instead of being a tool for equilibrium α determination, three-isotope method should be used as a tool for studying exchange kinetics as well as important fundamental parameters such as *KIE* or *AKIE*, which provides useful information about diffusion, dissolution, precipitation, and surface reaction processes.