

Near-equilibrium reaction kinetics illuminated by isotope tracers and implications for geochemical modeling

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In this session that honors Sue Brantley's wide-ranging contributions to geochemical kinetics, I thank Sue for her support of the isotope tracer workshop that we held at the 2021 Goldschmidt Conference. This presentation will highlight her contributions to near-equilibrium kinetics.

Most geochemical reactions occur at near chemical equilibrium because of the immensity of geological time, but the study of these reactions has been extremely challenging because secondary phases precipitate and the overall reaction rates are unmeasurably low near equilibrium. In the past ten years, we have applied non-traditional stable isotope tracers using the isotope-doping method (which was invented by chemists in the 1920-30s) to long-standing geochemical problems. Here, we highlight the significant results and their potential implications.

We measured unidirectional dissolution rates at truly near-equilibrium for albite, K-feldspar, and kaolinite, which are unfettered by secondary phase precipitation because they are constrained by isotope ratios. These rates are $\sim 10^2$ slower than the far-from-equilibrium rates at similar pH and T. The results illuminate that the "Burch type" rate law addresses an "etch pit opening" transition still far from equilibrium and is theoretically and mathematically unsound. Unidirectional dissolution rates decrease continuously toward equilibrium and its magnitude depends on solid-fluid ratios. Silicate weathering is irreversible and should be modeled as such with a unidirectional dissolution rate coupled with secondary phase precipitation.

Fast-reacting minerals like barite are probably at solubility equilibrium with waters in most geological systems at most times. Without isotope doping, it is not possible to determine the rates at chemical equilibrium even though we know it is there. We successfully measured rates at solubility equilibrium for quartz and barite. For barite, the unidirectional attachment and detachment fluxes inform us about the rate dependence on ionic ratios, reaction mechanisms, and Ba and S isotope equilibrium fractionation factors at chemical equilibrium (see McKailey Sabaj's poster). More importantly, long-term isotope doping experiments allowed us to profile barite with NanoSIMS and Atomic Probe Tomography, which showed 100s nm penetration within two years of reaction. The results have profound implications for the fidelity of paleo-proxies and the interpretation of isotope and trace element data.