

Near-equilibrium reaction kinetics illuminated by laboratory experiments with multiple isotope tracers

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In this session that honors I-ming Chou's contributions to experimental geochemistry, we will highlight some I-ming-like experimental measurements of physiochemical properties of chemical reactions.

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 to near-equilibrium reaction kinetics. Here, we highlight some results and their potential implications.

The measured near-equilibrium dissolution rates for albite, K-feldspar, labradorite, kaolinite, and barite are generally $\sim 10^2$ slower than the far-from-equilibrium rates at similar pH and T. The rates measured with Si isotope ratios are unidirectional dissolution rates, which are unfettered by secondary phase precipitation. The unidirectional rates decreased when the solutions approached equilibrium in experimental systems with low mineral to water ratios, indicating a decrease of mineral surface reactivity. We have also successfully measured rates at solubility equilibrium for quartz, barite[1], and calcite.

Recently, we took a step further and conducted experiments to decipher the coupling of multiple reactions using multiple tracers, i.e., the concurrent labradorite dissolution, calcite precipitation, and clay precipitation and tracked reaction processes using multiple isotope tracers.[2] We doped initial solutions with ^{29}Si , ^{43}Ca , and $\text{Ca}^{13}\text{CO}_3(\text{s})$. Unidirectional rates of labradorite dissolution near equilibrium were approximately two orders of magnitude slower than far-from-equilibrium rates reported in the literature. Calcite growth occurred near equilibrium and the rates were limited by the labradorite dissolution rates. Labradorite was chosen for its role as a major and reactive component in basalt. These experimental results show that using short-term far-from-equilibrium rate constants would lead to an overestimation of feldspar weathering rates at the Earth's surface (e.g., basalt weathering and enhanced rock weathering) and CO_2 mineralization in basalt aquifers.

1. Kang, J., et al., *GCA*, 2022. **317**: p. 180-200.
2. Chen, M., et al., *GCA*, 2025. **390**: p. 181-198.