

# **Silicate dissolution reaction mechanisms and rates as foundational science for carbon sequestration**

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Quantitative predictions of the efficiency, scalability, safety, and permanence of CO<sub>2</sub> sequestration in subsurface and surface environments require a new level of understanding of geochemical reaction kinetics. Silicate dissolution reaction mechanisms and rates have been the subjects of geochemical kinetic studies for over half a century, but recent advances in non-traditional stable isotope analytical techniques allow us to use the isotope tracer method and evaluate the reaction mechanisms and rates at conditions not attainable before. Specifically, we can now measure unidirectional rates at ambient temperature, near-neutral pH, and close to equilibrium conditions (Gruber et al., 2013; Zhu et al, 2016).

Our study of albite dissolution (Zhu et al., 2020) shows, at 50 oC and near-neutral pH, albite dissolution is irreversible, and the reverse reaction of albite precipitation is negligible. Although the irreversibility is well known, the wide use of the rate law in geochemical modeling, so-called transition-state-theory rate law and derived from the principle of detailed balance, inadvertently modeled silicate dissolution as reversible reactions near-equilibrium conditions. This practice should discontinue.

We also tested the hypothesis of reaction mechanism switch from far-from-equilibrium to near-equilibrium conditions (Burch et al., 1993) for kaolinite (Gong et al., 2019) and albite (Zhu et al., 2021). The Burch hypothesis stipulates that at far from equilibrium, dissolution proceeds with etch pit opening but step retreat is the dominant mechanism near equilibrium. In our studies, we conducted a series of experiments with different levels of departure from equilibrium. We found that the unidirectional rates for kaolinite and albite dissolution did not vary more than two standard deviations from the average in these low-temperature and near-neutral pH conditions. These results suggest that the mechanism switch hypothesis, speculated from hydrothermal temperature and alkaline pH conditions, was not operating in low-temperature, near-neutral pH systems, a condition that resembles CO<sub>2</sub> sequestration in aquifers and soils.

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