

## Kinetically controlled lithium isotope fractionation during weathering

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The feedback between CO<sub>2</sub> sources and sinks through chemical weathering is one of the important reasons why Earth has maintained a habitable climate over geological time. Lithium (Li) isotope system has been used as tracers of chemical weathering in various studies including rivers and weathering profiles/soils. However, the Li isotope fractionation mechanism associated with clay formation during weathering is not well understood. Here we performed systematic batch experiments to understand mechanisms and quantify magnitudes of Li isotopic fractionation during its sorption onto a common weathering product – kaolinite.

We performed the experiments in three sets, including 1). Time series sets, where we investigated Li isotope fractionation behaviors as adsorption proceeds with time to make sure experiments reached steady-state; 2). pH-dependent sets, where we varied pH from acidic to alkaline conditions to investigate the pH influence on Li adsorption and isotope fractionation; 3). Concentration-control sets, where we adjusted initial lithium concentrations to reach a wide range of adsorption percentage and degree of isotopic fractionation. We modeled all observed Li isotope data during kaolinite sorption using a Rayleigh distillation model, and obtained an optimal fractionation factor ( $\alpha$ ) of  $\sim 0.992$  between the solid and fluid. Our results are consistent with a recent study focusing on molecular dynamic simulations [1]. In addition, we demonstrated that this kinetic fractionation mechanism can explain previous field observations from worldwide rivers. In contrast to conventionally assumed equilibrium fractionation mechanism, we argue for a kinetically controlled Li isotopic fractionation during weathering. Our results call for reconsidering current quantitative models using Li isotopes to trace the secular evolution of Earth's climate.

[1] Hofmann, Bourg, and DePaolo (2012) Ion desolvation as a mechanism for kinetic isotope fractionation in aqueous systems. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 18689-18694.