

Experimental constraints on potassium isotope fractionation between potassium solutions and clay minerals

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Potassium (K) is primarily hosted in silicates, in particular clays, stable K isotopes ($^{41}\text{K}/^{39}\text{K}$ or $\delta^{41}\text{K}$) are therefore promising tracers for silicate weathering. One of the novel discoveries resulting from recent advance in high-precision stable K isotope analysis is that the $\delta^{41}\text{K}$ value of seawater is $\sim 0.6\%$ higher than that of the bulk silicate Earth. This difference has important bearing on the global K cycle and the intimately linked global carbon cycle, but its exact cause remains unknown. Formation of secondary clays during continental weathering is considered to increase $\delta^{41}\text{K}$ values of river waters, but existing data seem to suggest that the riverine input is unlikely to fully explain the $\sim 0.6\%$ difference. Other processes such as authigenic clay formation and cation-exchange with clay minerals in the ocean are postulated to have played important roles. Testing these hypotheses and unambiguous interpretation of field $\delta^{41}\text{K}$ data require detailed knowledge on K isotope fractionation between solutions and clay minerals.

We conducted controlled experiments to constrain K isotope fractionation between aqueous K and representative clay minerals, including kaolinite, smectites (montmorillonite and nontronite), and illite. Three types of experimental techniques were used for each clay at circumneutral pH and room temperature. Products including solutions, K extracted from clays, and residues were analyzed. The first technique is the conventional exchange experiment where parallel reactors with identical quantities of K solution and clay were sampled at different reaction time over a period of ~ 1 month. The second technique involved repeated reaction of the same KCl solution with several batches of fresh clay, with each cycle removing $\sim 50\%$ K from the solution. This method amplifies the effect of K isotope fractionation, so small fractionation could be more precisely constrained. In the third type of experiments, clay minerals, pre-equilibrated in K solution, were reacted with ^{40}K -enriched tracer solutions at near chemical equilibrium. This allows for quantification of K isotope exchange kinetics, and it also elucidates whether there is continued aqueous K exchange with non-expandable interlayers in illite at chemical equilibrium. We will highlight implications and significance of our results during this conference.