Silicon isotopic reequilibration during amorphous silica precipitation and implications for Critical Zone processes

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The isotopic fractionations associated with chemical reactivity in terrestrial environments are often quantified using Rayleigh distillation models. However, this irreversible kinetic treatment fails to capture the contribution of multiple transient reactive pathways often observed in the Critical Zone, where the balance between primary mineral dissolution and secondary mineral precipitation govern the chemical and isotopic evolution of fluid interacting with bedrock. As a result, discrepancies have been observed between laboratory and field generated fractionation factors (α). In this study, we use both laboratory experiments and reactive transport modeling to demonstrate variability in the silicon isotope fractionation factor during secondary amorphous silica precipitation that can be attributed to isotopic reequilibration resulting from continued exchange between the amorphous silica and surrounding fluid as the system approaches equilibrium.

A series of free drift amorphous silica batch precipitation experiments were conducted at ambient temperatures in closed reactors over a period of 18 days. The reactors contained high-purity silica powders suspended in an initially oversaturated silica solution at a starting pH of 7.35. The initial fluid phase Si ($\delta^{30/28}$Si) isotope ratio was -1.69 ± 0.05‰, within error of the solid phase value of -1.72 ± 0.05‰. During the first 5 days of the experiment, Si concentrations decreased through time in the fluid phase due to precipitation, and the corresponding fluid isotope ratios showed kinetic enrichment to a maximum value of +0.89 ± 0.05‰, followed by a subsequent re-equilibration back to values approaching the solid phase, reaching -1.36 ± 0.06‰ by day 18. This behavior was accurately reproduced by a transient model using coupled TST rate expressions for the two isotopes of Si. These results suggest that the α observed in natural settings where flow is dynamic should be dependent on fluid transit times, reflecting a balance between fast and slow flowpaths. Hence, transient α values are anticipated and should be considered in quantifying contributions of secondary amorphous silica precipitation to overall silicate weathering rates in the Critical Zone.