Si isotope fractionation factors for polymerization and for fast attachment onto Si-Al surfaces

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The rate at which Si-bearing solids are being formed from dissolved silica governs the associated Si stable isotope fractionation. This we show in a series of Si isotope fractionation experiments, where we accelerate the exchange rates by means of cyclic freezing and thawing that lead to repeated changes from super- to undersaturated conditions. We conducted several experiments under acidic and neutral pH (pH 4.5, 5 and 7), with solutions initially containing $[Si]_{aq}$ = 1.6 mmol/l and with additions of 0.1 mmol/l and 1 mmol/l of dissolved Al, and in the absence of Al. We observe a decrease in Si concentration and a formation of an Si containing solid in all experiments. No Si isotope fractionation occurs during formation of almost pure Si solids in experiments with no or low addition of Al. This absence of Si isotope fractionation suggests that the fractionation factor $\Delta_{\text{solid-solution}}$ associated with polymerization of silicic acid and the formation of pure Si containing solids is 0‰. In contrast experiments with high Al concentrations show during the first 20 days attachment of Si onto solids that is 2.4 ‰ lighter than Si in the solution and then reverts to almost starting values of 0‰ after 130 days. We suggest that in the initial phase the formation of an Al-O-OH phase and subsequent adsorption of Si and/or coprecipitation of Si and Al occurs. In this phase the fractionation regime is dominated by unidirectional kinetic isotope fractionation. With ongoing runtime these solids re-dissolve. When steady-state is attained the $^{30}Si/^{28}Si$ ratio of the solid is almost identical to the solution ($\Delta_{\text{solid-solution}} \approx 0$).

For the interpretation of Si stable isotopes in weathering or ocean environments or in the geologic record these results imply that the enrichment of light Si isotopes is caused exclusively by an unidirectional kinetic isotope effect during fast precipitation of solids, aided by co-precipitation with Al- or other carrier phases. In contrast during slow precipitation under equilibrium conditions, no Si isotope fractionation is expected and Si isotopes will retain the signature of the Si source.