Direct evidence for isotopic fractionation during congruent dissolution, precipitation and at equilibrium

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This study provides direct experimental evidence of magnesium (Mg) isotope fractionation between an aqueous fluid and magnesite during its congruent dissolution, precipitation, and at equilibrium. Closed-system batch reactor experiments were performed at temperatures from 120 to 200 ºC and at 15 to 30 bars CO_2 pressure. During congruent magnesite dissolution the fluid became enriched in isotopically heavy Mg, with a steady state $\delta^{26}Mg_{fluid}$ composition 0.4 ‰ higher than the dissolving magnesite at 15 bars of CO_2 pressure, and 0.15 ‰ higher at 30 bars of CO_2 pressure. Equilibrium $^{26}Mg/^{24}Mg$ fractionation factors (α_{eqm}) for the were found to be 0.99881 at 150 ºC and 0.99912 at 200 ºC, close to those predicted by density-functional electronic structure models Magnesite precipitation was provoked by increasing the reactor temperature after equilibrium had been attained via dissolution. Kinetic isotope fractionation effects consistent with Rayleigh fractionation were observed immediately after the reactor temperature was increased and rapid magnesite precipitation occurred. However, isotopic exchange continued as the system equilibrated, eradicating the kinetic signal in the precipitated solid. As most natural systems fail to sustain rapid precipitation rates long-term, this observation suggests that kinetic fractionation effects in precipitated minerals will not be preserved in most geological systems.

The results of this study confirm the concept of dynamic equilibrium during water-mineral processes. Dynamic equilibrium also means that minerals and fluids will continue to equilibrate isotopically long after equilibrium is attained. This conclusion likely has significant consequences for the use of mineral isotopic compositions to illuminate chemical weathering processes, water-rock interaction in the crust, and past environmental conditions.

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On the competition between kinetic and equilibrium isotope fractionation during low-T silica precipitation

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Formation of Si-bearing phases due to precipitation or adsorption always favors incorporation of light isotopes (apparent fractionation factor $\Delta_{solid-fluid} < 0$‰), which is usually explained by kinetic isotope fractionation. We challenge this assumption by conducting two sets of laboratory experiments.

First, Si-adsorption experiments (exp. #1) onto suspended gibbsite were performed at different initial monosilicic acid concentrations ($[Si]_{aq}$= 10, 20 and 40 ppm) at pH 7. Adsorption of silicic acid results in an increase of $\delta^{30}Si_{aq}$ values and a chemical steady state is reached after ~ 300 h of experimental runtime. These experiments confirm that $\Delta_{solid-fluid} < 0$‰, but also show that the magnitude of $\Delta_{solid-fluid}$ depends on the initial Si concentration. We show that Si concentrations affect the precipitation rate, but there is no obvious reason why isotope fractionation should depend on precipitation rate in a well-mixed system where no isotope fractionation due to diffusion in the solution should occur.

However, according to DePaolo[1], the fractionation of isotopes between solution and forming solids depends on the ratio of net precipitation rate R_p to the backward reaction rate R_b. When $R_p \approx R_b$, a competition between equilibrium and kinetic fractionation is expected. To test this hypothesis, a second set of experiments (exp. #2) were conducted, where solutions were frozen and thawed within 24 hours up to 130 days and sampled at regular intervals, during which amorphous silica was repeatedly precipitated/adsorbed and redissolved. In this special setup, $R_p \ll R_b$ might be achieved, a condition for isotope fractionation to reflect equilibrium[1]. Several sets of these experiments were performed at pH 4.5 and 7, with solutions initially containing $[Si]_{aq}$ = 45 ppm and $[Al]_{aq}$ = 2.7 or 27 ppm. We suggest precipitation of an Al-O-OH phase and subsequent adsorption of Si and/or coprecipitation of Si and Al. Experiments with high initial Al concentration show changing $\delta^{30}Si_{aq}$ values with experimental runtime. The $\delta^{30}Si_{aq}$ values increased during the first 20 days to up to 2.4‰ and then shows a decline to almost starting values of 0‰ after 130 days. This setup allows that R_p shifts from values $\gg R_b$ to values $R_p \ll R_b$, which results in a change from kinetically- to equilibrium-dominated isotope fractionation.

In the first set of adsorption experiments (exp. #1), where $R_p > R_b$, kinetic isotope fractionation is assumed as Si rarely exchanges with the solution.

To conclude, the withdrawal of Si in natural systems due to precipitation or adsorption is not necessarily dominated by kinetic isotope fractionation. Instead, isotope fractionation might approach $\Delta_{solid-fluid} \geq 0$ if $R_p \ll R_b$, which can then be interpreted as equilibrium isotope fractionation.

[1] DePaolo (2011) *GCA* **75**, 1039-1056