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

ERIC H. OELKERS*, CHRISTOPHER R. PEARCE, GIUSEPPE D. SALDI and JACQUES SCHOTT

1 Géosciences Environnement Toulouse, GET/ CNRS UMR 5563, 14 Avenue Edouard Belin, 31400 Toulouse, France, oelkers@get.obs-mip.fr (* presenting author)
2 Department of Environment, Earth and Ecosystems, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK.
3 Earth Sciences Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

This study provides direct experimental evidence of magnesium (Mg) isotopic 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 CO2 pressure. During congruent magnesite dissolution the fluid became enriched in isotopically heavy Mg, with a steady state 26Mg/24Mg fractionation factor of 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 isotopic 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 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.

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

M. OELZE1*, F. VON BLANCKENBURG1, D. HÖLLEN2, M. DIETZEL2, J. BOUCHEZ1

1 GFZ German Centre for Geosciences, Potsdam, Germany, oelze@gfz-potsdam.de (* presenting author)
2 Institute of Applied Geosciences, Graz University of Technology, Austria

Formation of Si-bearing phases due to precipitation or adsorption always favors incorporation of light isotopes (apparent fractionation factor Δsolid-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 δ30Si values and a chemical steady state is reached after ~ 300 h of experimental runtime. These experiments confirm that δ30Si values >> R b to values Rp << R b, which results in an increase of δ30Si values of 0‰ after 130 days. This setup allows that Rp shifts from values Rp ≈ Rp during low-T silica precipitation. In this special setup, Rp shifts from Rp ≈ Rp during low-T silica precipitation to 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, Rp << 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 formation of Si-bearing phases due to precipitation or adsorption.

If R b, the fractionation of isotopes between solution and forming solids depends on the ratio of net precipitation rate R p and the backward reaction rate R b. When R p << 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, Rp << 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 formation of Si-bearing phases due to precipitation or adsorption.

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 Δsolid-fluid ≥ 0 if R p << R b, which can then be interpreted as equilibrium isotope fractionation.