

Rapid isotopic fractionation among minerals and fluids during dissolution, precipitation, and at equilibrium

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We have performed a suite of batch reactor experiments reacting single mineral powders with initial aqueous fluids of a variety of pH conditions, temperatures from 25 to 200°C, and highly undersaturated to supersaturated with respect to the present mineral phase. In all experiments mineral precipitation or dissolution drove the fluid towards bulk chemical equilibrium conditions with respect to the mineral phase; in many experiments the fluid remained in bulk chemical equilibrium with the mineral phase over the excess of several months.

Studied minerals include calcite, dolomite, magnesite, hydromagnesite, quartz, amorphous Si, and chert. In nearly all cases, the isotopic composition, including the isotopes of C, O, Mg, Ca, and Si, of the fluid and the coexisting mineral phases evolved rapidly and substantially during stoichiometric dissolution and at equilibrium. For example, the $\delta^{44}\text{Ca}$ of calcite decreased by 17‰ during its congruent dissolution and at equilibrium over 9 days. The evolution of isotopic compositions is observed to continue for at least a year at near to equilibrium conditions. Precipitation from initially highly undersaturated fluids yielded Rayleigh isotope fractionation effects. However, isotopic exchange is observed to continue after the system equilibrated, eradicating this Rayleigh signal.

The observation that the isotopic compositions of minerals and coexisting fluid evolve rapidly and significantly during their ambient temperature interaction 1) supports the theoretical hypothesis that mineral-fluid equilibrium is dynamic, 2) complicates the application of isotopic tracers to deduce fluid flow paths, and 3) suggests that the preservation of paleo-environmental isotopic signatures in minerals requires some sort of combination of the isolation of fluid-mineral system from external chemical input and/or the existence of a yet to be defined calcite dissolution/precipitation inhibitor.