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Oxygen isotope exchange kinetics during high-temperature magnesite / dolomite formation experiments

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An experimental study was conducted to investigate the until now less explored kinetics of oxygen isotope exchange during the stepwise formation of magnesite and dolomite from finely ground (10 – 40 μm) $CaCO_3$ reactants (synthetic low-Mg calcite or speleothem aragonite) subject to a Mg-rich brine at temperatures of 150, 180, and 220 °C under distinct alkalinity conditions (50 or 100 mM).

We applied, a novel technique in which the reactive aquaous solution of the experiments was highly depleted in ^{18}O vs. ^{16}O ($\delta^{18}O_{VSMOW}$ = -46 ‰) compared to natural carbonate forming solutions so that $\delta^{18}O$ evolution of the reactive solutions and precipitates could be measured across time-resolved samples throughout the reaction; this proved successful in allowing us to both, trace the oxygen isotope exchange kinetics and to demonstrate that approximate oxygen isotope equilibrium was reached. Analysis of the oxygen isotope exchange as a pseudo-first-order reaction allowed for the pseudo-first-order reaction rate reaction rate constants (k) and half-life times ($t_{1/2}$) to be calculated based on experimental results for the first time. The oxygen isotope exchange was obviously faster at higher temperature with $t_{1/2}$ decreasing from $\sim$ 441 hours at 150°C to only $\sim$ 86 hours at 220°C. Throughout our experiments the initial $CaCO_3$reactant and alkalinity conditions used affected the relative abundance of magnesite:dolomite in the precipitate at any given time; however despite the varied initial experimental conditions and mineralogy across experimental runs at equal temperature the kinetics of oxygen isotope exchange remained the same within the given analytical uncertainties. This leads us to contend that the exchange kinetics of oxygen isotopes between magnesite/dolomite and solution are similar, dominantly controlled by temperature and rather unaffected by the initial $CaCO_3$ reactant used (calcite vs. aragonite) or the alkalinity conditions within the range of our experiment. Moreover, the oxygen isotope fractionation between magnesite - dolomite and the solution at the final stage of the experiments was dependent on neither the relative amounts of magnesite and dolomite nor on the experimental setup. An overall fractionation factor of $10^3 \ln\alpha_{dol/mag-water}$= 2.695(±0.088) * ($10^6/T^2$) + 0.50(±0.28.) was obtained, which is generally consistent with the majority of former experimental and theoretical studies and sits between the suggested oxygen isotope fractionation lines of dolomite-water and magnesite-water.

Further work to separate the dolomite from co-precipitated magnesite using di-Na-EDTA is ongoing so that the oxygen isotope exchange kinetics can be determined and confidently reported for the individual phases as opposed to the mixture.