

The rates of ^{13}C isotope evolution in calcite at fluid-mineral *bulk chemical* equilibrium

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The stable isotopic composition of minerals can evolve towards fluid-mineral *isotopic* equilibrium even when the system is at *bulk chemical* equilibrium. To quantify this process we have monitored the temporal evolution of the ^{13}C composition of calcite and its coexisting fluid phase at fluid-mineral *bulk chemical* equilibrium in both biotic and abiotic systems.

Calcite was precipitated in the presence and absence of *Synechococcus* sp. cyanobacteria in batch reactors. The presence of cyanobacteria promoted calcium carbonate formation and altered significantly the carbon isotopic composition of dissolved inorganic carbon due to the preferential incorporation of ^{12}C into the biomass. The carbon isotope composition of the calcite evolved continuously towards mineral-fluid *isotopic* equilibrium after calcite precipitation was complete at geometric surface area normalized rates ranging from 1.75×10^{-14} to 1.71×10^{-13} mol $^{13}\text{C}/\text{m}^2/\text{s}$. Parallel experiments were run in abiotic closed system reactors isolated from the atmosphere, where either natural or synthetic calcite was placed in contact with isotopically distinct carbonate-bearing aqueous fluids for up to one year. *Bulk chemical* equilibrium was verified to have been attained within 5 days, yet the carbon isotopic composition of both the calcite and the fluid continued to evolve towards equilibrium throughout each experiment at surface area normalized rates consistent with those of the biotic experiments. Measured rates suggest that the carbon isotopic composition of calcite ($\delta^{13}\text{C}_{\text{calcite}}$) might noticeably change if the calcite was continuously in isotopic disequilibrium with its co-existing fluid. Further mass balance calculations suggest that the $\delta^{13}\text{C}_{\text{DIC}}$ compositions of fluids in carbonate-rich rocks would commonly be buffered by the $\delta^{13}\text{C}_{\text{calcite}}$ of the co-existing solid. Nevertheless, significant $\delta^{13}\text{C}_{\text{calcite}}$ variations could occur after calcite precipitation when the fluid remains out of *isotopic* equilibrium with this mineral, for example through the presence of local carbon sources such as decomposition of organic material.