

An experimental study of kinetic oxygen isotope fractionation during CaCO₃ polymorphism

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In order to examine the effect of polymorphic transition on oxygen isotope fractionation between calcite and water, aragonite-calcite mixture of different proportions were precipitated sequentially by controlling transition time from 5, 30, 60, 300 to 1440 minutes, and CaCO₃ minerals and water were obtained at different time intervals during the polymorphic transition from aragonite to calcite. The initial aragonite was prepared by the one- and two-step approaches, respectively, with different states of disequilibrium or equilibrium oxygen isotope fractionation with water. Relative content of calcite in aragonite-calcite mixtures was estimated by the XRD technique. For the one-step experiments at 50°C, oxygen isotope fractionations between calcium carbonate and water almost have constant $10^3 \ln \alpha$ values of 23.89 to 24.03‰ with changing the transition time from 5 to 1440 min and thus the percentage of transformed calcite from 0 to 100%. This implies that the rates of oxygen isotope exchange among DIC species are much faster than the rates of polymorphic transition in aqueous solution.

For the two-step experiments, nevertheless, the oxygen isotope fractionations between CaCO₃ and H₂O progressively increase with time as the polymorphic transition from aragonite to calcite proceeds, and finally approach the fractionation values for the pure calcite. With increasing the transition time from 5 to 1440 min, they change from 21.77‰ at 100% aragonite to 23.51‰ at 100% calcite at 50°C, and from 18.84‰ at 100% aragonite to 20.36‰ at 100% calcite at 70°C. There is a linearly increased relationship of $10^3 \ln \alpha_{\text{CaCO}_3\text{-H}_2\text{O}}$ to the calcite content, indicating that the kinetics of oxygen isotope exchange among DIC species parallels the kinetics of polymorphic transition in aqueous solution. The all one- and two-step approach experiments demonstrate that the degree of oxygen isotope reequilibration between secondary calcite and water heavily depends on the equilibrium state of initial aragonite and thus the reaction mechanism involved during the precipitation of initial calcium carbonates. The observed difference may thus be caused by the difference in kinetic rate between oxygen isotope exchange among the DIC species and the aragonite-calcite polymorphic transition in aqueous solution.