

Rate constants of isotopic changes in DIC assed for clumped and stable isotopes in instantaneously precipitated strontium carbonate

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Carbonate minerals typically reflect the stable and clumped isotope composition of the parent solution. Variations in e.g., temperature, pH or salinity lead to changes in DIC composition and to temporary deviations from expected equilibrium values. The reaction rate constant, at which the new equilibrium of stable and clumped isotopes is reached, is uncertain for temperatures above 38°C.

In this study the DIC evolution in 0.1 molar NaHCO₃ solutions at pH=8 and various temperatures (40°C-90°C) was examined. A quantitative and instantaneous precipitation of the DIC was achieved by adding SrCl₂ and NaOH solution. For all temperatures C,O and clumped isotopes values of the strontium carbonate were measured. As δ^{13} C was constant, δ^{18} O and Δ_{47} could be simply fitted with an Arrhenius plot. The resulting rate constants indicate that the extrapolation of the model by Uchikawa and Zeebe (2012) can be used to describe the changes in oxygen isotope values at least up to 70°C. The Δ_{47} values show good agreement with the model up to a temperature of 55°C. Our experiments suggest that the isotopic equilibration of DIC in a solution with pH<10 is rapid (at 70°C: 4.5 min, at 90°C: 36 s for 99% equilibrium) and that even in the case of short-term temporal changes an equilibrated DIC composition is very likely for solutions in the diagenetic temperature range. In general, clumped isotopes show a very similar behaviour to oxygen isotopes in the investigated temperature range.