



Calcite-water oxygen isotopic fractionation revisited

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The dependence of calcite-water oxygen isotopic fractionation on formation temperature is still being discussed especially due to the demand of increasing accuracy of paleotemperature calculations. Although experimentally determined equations have been available and verified by theoretical calculations (considered as representative of isotopic equilibrium), many natural formations do not seem to follow these relationships. In order to test if existing fractionation-temperature relationships can be used for natural deposits, we have studied calcite formations precipitated in various environments: travertines precipitating from hot and warm waters in open-air or quasi-closed environments, as well as cave deposits formed in closed systems. Measuring precipitation temperatures along with oxygen isotope compositions of waters and calcites yielded environment-specific fractionation-temperature equations.

Modelling oxygen diffusion through calcite crystal lattice revealed that under realistic precipitation rate conditions in the low-temperature regime the oxygen isotopic fractionations between dissolved inorganic carbon (DIC) species and H₂O will be „frozen” in the precipitating carbonate and the system would rather follow the CO₃(²⁻)–HCO₃(⁻)–H₂O fractionation than the calcite-H₂O relationship. Additionally, pH, CO₃(²⁻)-preference during precipitation and growth rate can further modify the actual fractionation-temperature relationship. Finally, on the base of new data and the above considerations, the use of different calcite-water oxygen isotopic fractionation relationships and application strategies to obtain the most reliable information are evaluated in this paper.