Modelling hydrothermal replacement of calcite

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The process of dolomitization is considered to take place by the replacement of a precursor limestone. So far, most experimental studies on rates of hydrothermal dolomitization are based on experiments with powdered carbonate material. In previous stages of this project we conducted experiments using single calcite crystals reacting with a Mg-rich fluid to study the microstructure of the replacement product, its chemical composition with high spatial resolution and the reaction progress with time. In this contribution, we present a kinteic model that reproduces the evolution of the replacement reaction and the necessary element fluxes controlling the overall rate of the replacement.

Experiments for different run durations at 200 °C and ~16 bar revealed that calcite is replaced by a porous, double-layered reaction rim of magnesite and dolomite. The reaction takes place by a dissolution-precipitation mechanism, but compositional gradients are found for Mg and Ca perpendicular to the reaction front. With increasing distance from the crystal surface, the amount of Mg incorporated into the respective layers decreases countered by an increase in Ca. Inductively coupled plasma spectrometry revealed that the Ca/Mg ratio in the fluid increases following a square-root-of-time relation indicating that the diffusive transport of the aqueous species in the pore fluid is the rate-limiting step controlling the replacement.

To test this hypothesis we developed kinetic model in which mass balance is applied and local equilibrium is assumed at each interface between the different layers, the original calcite and the fluid reservoir. We further assume a quasi-steady state flux of the aqueous species in the fluid, which allows to analytically solve the set of governing equations. The porosity and its evolution within the reaction rim could not be quantified experimentally and was optimized in the model to reproduce the progress of the reaction and the replacement product's chemical composition as a function of time. Our results highlight the fact that the quantitative description of reaction rates is crucial to predict the rates and spatial patterns of carbonate replacement processes in natural systems.