

Rates, mechanisms and microstructures of transport-controlled reaction front propagation

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Fluid-mediated mineral reactions are governing the redistribution of elements and isotopes in the geosphere. Incomplete elemental redistribution is preserved in the rock record in the form of geochemical reaction fronts. Key features of such systems are reaction induced creation/destruction of porosity increasing/decreasing permeability and further focussing of fluid into/away from the zone of reaction; hence this results in a positive or negative feedback between reaction, fluid ingress and further reaction. To the same end, sluggish element mobility can lead to variations in fluid chemistry within the propagating reaction front controlling the stable mineral assemblage and its chemical/isotopic composition. Recent studies provided conclusive evidence for the presence of transport-controlled reaction fronts in mineral reactions such as the replacement of calcite single crystals by Mg-carbonates (Jonas et al. 2015; 2017). Here, we present a follow-up investigation providing detailed chemical and microstructural data as well as a model for the kinetically controlled evolution of the reaction rim.

The replacement reactions of single calcite cubes (2 mm) were carried out experimentally in batch reactor vessel at 200 °C using a 1 M MgCl₂ fluid and a water-to-rock-ratio of 10 for run durations of 2-30 days. Solid reaction products have been characterized using an FEG-SEM including EBSD and chemical variations have been measured using an electron microprobe.

Experimental results reveal the time-dependent formation of a layered, multiphase reaction rim by dissolution-precipitation forming Mg-carbonate phases of different composition and variable porosity. The initial reaction rim is formed of small, rhombic almost pure magnesite crystals which become more Ca-rich as the reaction progresses. Subsequently, a sharp interface marks the change to the precipitation of high magnesium calcite (HMC) instead of magnesite, albeit the HMC precipitates with a constant X_{Mg} of 0.4. With increasing run durations, the reaction does not progress but grains in the existing reaction rim exhibit grain coarsening and elimination of (interconnected) porosity. This grain growth is accompanied by a chemical adjustment starting from the former magnesite-HMC interface initiating two new reaction fronts adjusting the magnesite composition, i.e., replacing Ca by Mg and the recrystallization of HMC by a VHMC phase with X_{Mg} of 0.5 representing a dolomite stoichiometry. EBSD analysis reveal that the recrystallization of the inner part of the reaction rim is accompanied by the formation of subgrain boundaries and rotation of c-axis during grain coarsening.

This study highlights the importance to quantitatively understand the link between reaction progress, fluid composition, fluid transport and the evolution of fluid pathways to describe and model reaction front propagation in reactive transport models.

Jonas L, Müller T, Dohmen R, Baumgartner L, Putlitz B (2015): Transport-controlled hydrothermal replacement of calcite by Mg-carbonates. - *Geol* 43, 779-782, doi: <https://doi.org/10.1130/G36934.1>

Jonas L, Müller T, Dohmen R, Immenhauser A, Putlitz B (2017): Hydrothermal replacement of biogenic and abiogenic aragonite by Mg-carbonates: Relation between textural control on effective element fluxes and resulting carbonate phase. - *Geochim Cosmochim Acta* 196, 289-306, doi: <https://doi.org/10.1016/j.gca.2016.09.034>