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Reaction kinetics of dolomite rim growth

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To investigate the reaction kinetics of dolomite ($CaMg[CO_3]_2$) rim growth at elevated pressure and temperature, we performed static annealing experiments using oriented calcite ($CaCO_3$) single crystals in contact with oriented magnesite ($MgCO_3$) single crystals as starting materials. Cylindrical samples of 3-5 mm length and 7 mm diameter were drilled and polished perpendicular to the rhombohedral cleavage planes of natural clear crystals. Experiments were done in a Paterson-type deformation apparatus at 400 MPa confining pressure and temperatures between 750-850 ˚C for annealing duration between 2 and 247 h.

All experiments produced a polycrystalline dolomite reaction rim that expanded with increasing temperature and time. Within the dolomite rim, two distinct textural domains evolved, consisting of (a) elongated palisades (6-41.3 μm) growing perpendicular to the initial calcite/magnesite interface replacing magnesite and (b) granular dolomite (2.6-4.3 μm) growing in contact with calcite. Microprobe analysis shows a nearly stoichiometric Mg/Ca ratio within the palisades and an increasing enrichment of Ca in the granular dolomite towards reactant calcite. Platinum markers deposited on the reactant phases reveal that the interface between granular dolomite and palisades represents the position of the initial calcite/magnesite contact.

At the experimental conditions, also magnesio-calcite formed between the dolomite reaction rim and calcite single crystal. This implies diffusion of MgO across the dolomite growth front into calcite. The magnesio-calcite grains are relatively large (18.5-45.8 μm), partially with straight grain boundaries and equilibrim angles at triple junctions.

Electron backscattered diffraction analysis displays the same crystallographic orientation for granular dolomite, magnesio-calcite and reactant calcite. The crystallographic orientation of dolomite palisades is similar to that of the calcite single crystal in 5 of 7 analysed samples.

The time- and temperature dependence of dolomite layer thickness Δx growing between single crystal reactants follows a parabolic law $\Delta x^2 = kt$, where k is the rate constant and t is the time. Assuming an Arrhenius-type temperature dependence of k yields an activation energy of E= 263±41 kJ/mol and a pre-exponential factor of $k_0 = 10^{-1,5\pm2}$ m^2/s. This value is in good agreement with Ca self-diffusion experiments in natural calcite single crystalls by Fisler & Cygan (1999), who calculated an activation energy of E(Ca)=271±80 kJ/mol.

Dolomite palisades show grain coarsening, with a linear increase of grain size with $\sqrt{t}$, after an incipient stage of fast non-linear growth. Coarsening leads to a successive decrease in grain boundary area fraction, but this does not affect the effective diffusion rate. Consequently, we regard volume diffusion as the rate-controlling process.

Fisler DK, Cygan RT (1999) Diffusion of Ca and Mg in calcite. Am Mineral 84:1392-1399