



## Influence of deformation on dolomite rim growth kinetics

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Using a gas-deformation apparatus stacks of oriented calcite ( $\text{CaCO}_3$ ) and magnesite ( $\text{MgCO}_3$ ) single crystals were deformed at  $T = 750^\circ\text{C}$  and  $P = 400$  MPa to examine the influence of stress and strain on magnesio-calcite and dolomite ( $\text{CaMg}[\text{CO}_3]_2$ ) growth kinetics. Triaxial compression and torsion tests performed at constant stresses between 7 and 38 MPa and test durations between 4 and 171 hours resulted in bulk strains of 0.03-0.2 and maximum shear strains of 0.8-5.6, respectively. The reaction rims consist of fine-grained (2-7  $\mu\text{m}$ ) dolomite with palisade-shaped grains growing into magnesite reactants and equiaxed granular dolomite grains next to calcite. In between dolomite and pure calcite, magnesio-calcite grains evolved with an average grain size of 20-40  $\mu\text{m}$ . Grain boundaries tend to be straighter at high bulk strains and equilibrium angles at grain triple junctions are common within the magnesio-calcite layer. Transmission electron microscopy shows almost dislocation free palisades and increasing dislocation density within granular dolomite towards the magnesio-calcite boundary. Within magnesio-calcite grains, dislocations are concentrated at grain boundaries. Variation of time at fixed stress ( $\approx 17$  MPa) yields a parabolic time dependence of dolomite rim width, indicating diffusion-controlled growth, similar to isostatic rim growth behavior. In contrast, the magnesio-calcite layer growth is enhanced compared to isostatic conditions. Triaxial compression at given time shows no significant change of dolomite rim thickness ( $11 \pm 2$   $\mu\text{m}$ ) and width of magnesio-calcite layers ( $33 \pm 5$   $\mu\text{m}$ ) with increasing stress. In torsion experiments, reaction layer thickness and grain size decrease from the center (low stress/strain) to the edge (high strain/stress) of samples. Chemical analysis shows nearly stoichiometric composition of dolomite palisades, but enhanced Ca content within granular grains, indicating local disequilibrium with magnesio-calcite, in particular for twisted samples. The shift from local equilibrium is  $\approx 3$  mol% in triaxial compression and  $\approx 7$  mol% in torsion. Electron backscatter diffraction analysis reveals a crystallographic preferred orientation (CPO) within the reaction layers with [0001] axes parallel to the compression/rotation axis and poles of {2-1-10} and {10-10} prismatic planes parallel to the reaction interface. Compared to isostatic annealing, the CPO is more pronounced and the amount of low-angle grain boundaries is increased. At the imposed experimental conditions, most of the bulk deformation is accommodated by calcite single, which is stronger than magnesite. Application of flow laws for magnesio-calcite and dolomite suggest that the fine-grained reaction products should deform by grain boundary diffusion creep, resulting in lower flow strength than the single crystal reactants. However, microstructural observations indicate that deformation of granular dolomite and magnesio-calcite is at least partially assisted by dislocation creep, which would result in an almost similar strength to calcite. Therefore, flattening of the reaction layers during triaxial compression may be counterbalanced by enhanced reaction rates, resulting in almost constant layer thickness, independent of the applied stress. For simple shear, the reduced reaction kinetics in the high stress/strain region of twisted samples may be related to increased nucleation rates, resulting in a lower grain size and rim thickness.