Influence of grain size, water, and deformation on dolomite reaction rim formation

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ABSTRACT

Solid-solid mineral reaction rates are influenced by the microfabrics of reactant phases and concurrent deformation. To investigate this interplay in carbonate systems, we performed annealing and deformation experiments on polycrystalline and single-crystal calcite and magnesite, forming dolomite (Dol) and magnesio-calcite (Mg-Cal). At a fixed temperature of \( T = 750 \, ^\circ\text{C} \) and confining pressure of \( P = 400 \, \text{MPa} \), samples were either annealed for 29 h, or deformed in triaxial compression or torsion for 18 h using a Paterson-type gas deformation apparatus. At the contact interface of the starting reactants, Dol reaction rims and polycrystalline Mg-Cal layers were formed. The widths of the layers were in the ranges 4–117 and 30–147 \( \mu\text{m} \), respectively, depending on the microstructure of starting materials and experimental conditions. Annealing experiments with polycrystalline reactants in contact with each other resulted in a ~22-fold increase in Dol rim thickness compared to a contact between two single crystals and a larger Mg-Cal layer width by a factor of 5 (cf. Helpa et al. 2014). This suggests that the microstructure of magnesite controls migration of the reaction front. For polycrystalline starting materials, axial stress accelerated Mg-Cal growth rates but not Dol growth rates. Highly strained torsion samples showed Dol formation along grain boundaries in Mg-Cal as well as in the polycrystalline calcite reactant. A reduction of Dol rim thickness between polycrystalline reactants deformed in torsion is possibly caused by concurrent grain coarsening of polycrystalline magnesite. Dol and Mg-Cal growth kinetics between single crystals were unaffected by the addition of ~0.3 wt% water.

The experiments demonstrate that Dol reaction kinetics strongly correlate with magnesite reactant grain sizes, while Mg-Cal growth depends on the calcite reactant grain sizes. The dolomite-forming mineral reaction kinetics are not significantly affected by concurrent deformation. In contrast, deformation enhances Mg-Cal formation, especially at small calcite grain sizes that promote efficient grain boundary diffusion.

Therefore, the fastest reactions forming Dol and Mg-Cal in nature are expected to occur in very fine-grained reactants. Concurrent deformation may drastically enhance reaction kinetics if grain size reduction of the reactants occurs by, for example, cataclasis or dynamic recrystallization.

Keywords: Rim growth, carbonates, diffusion, deformation, water

INTRODUCTION

In nature, metamorphic rocks often exhibit evidence of simultaneous deformation and mineral reactions (e.g., Rubie 1983; Rutter and Brodie 1988; Newman et al. 1999 and references therein). Evidence for the concurrent occurrence of these processes is well documented in natural mylonites (Rubie 1983; Fitz Gerald and Stünitz 1993; Newman et al. 1999; Tsurumi et al. 2003). The results of laboratory experiments addressing syn-deformational reactions suggest a correlation between mineral reactions and deformation in several mineral systems (e.g., de Ronde et al. 2004, 2005; Holyoke and Tullis 2006; de Ronde and Stünitz 2007). In silicate systems, the presence of small amounts of water drastically accelerates deformation and reaction rates (e.g., Post et al. 1996; Hirth et al. 2001; Rutter and Brodie 2004; Gardés et al. 2012; Milke et al. 2013). In contrast, the effect of water on deformation in carbonate systems is minor (de Bresser et al. 2005).

Here, we study the calcite–magnesite (CaCO\(_3\)-MgCO\(_3\)) carbonate system, which produces dolomite [CaMg(CO\(_3\))\(_2\)] following the overall reaction:

\[
\text{CaCO}_3 + \text{MgCO}_3 = \text{CaMg(CO}_3)_2.
\]

The partial reactions at the reactant interfaces are described by Helpa et al. (2014) (their Eqs. 2 and 3). Formation of dolomite is associated with a negative volume change of \(~-12%\) at the calcite interface and a positive volume change of \(~+14\%\) at the contact with magnesite. Between stoichiometric dolomite and pure calcite, a continuous exchange of Ca and Mg produces magnesio-calcite (Ca\(_x\)Mg\(_{1-x}\)CO\(_3\)) and a non-stoichiometric dolomite. Previous experimental studies of this reaction using calcite and magnesite single crystals under isostatic and non-isostatic conditions revealed a diffusion-controlled dolomite reaction rim growth, which was almost unaffected by applied axial stresses up to 38 MPa, but