# Inter-diffusion of Mg/Ca in synthetic polycrystalline carbonates at elevated temperature and pressure

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The transport rates of $MgCO_3$ from dolomite into calcite were measured within synthetic dry dolomite-calcite polycrystalline aggregate at 1.6 GPa and isothermally at 800, 850, and 900 ℃ over different run durations. Aragonite in the starting dolomite-aragonite aggregate was first transformed rapidly to calcite, which, then, reacted with dolomite to form Mg-calcite progressively rich in Mg at slower rates.

The average contents of Mg in calcites determined by XRD increase with run time, which can be described empirically by the first-order rate law. The temperature dependence of the overall transport rate of $MgCO_3$ from dolomite into calcite can be estimated by the kinetic parameters (E = 231 kJ and Ao = 22.7 hr^{-1}). The extrapolation using the Arrhenius equation to the prograde metamorphic conditions reveals that the formation of Mg-calcite saturated with Mg from dolomite-calcite aggregate in the absence of metamorphic fluid may not completed at temperatures below medium-grade metamorphism (< 350 ℃ and < 10 my; Fig. 1). The extrapolation of the rate to the conditions during exhumation of UHPM rocks, at which the P-T path entered calcite stability field from dolomite-aragonite field, indicates that the reaction of dolomite with calcite can be completed in a geologically short period (< 1 my).
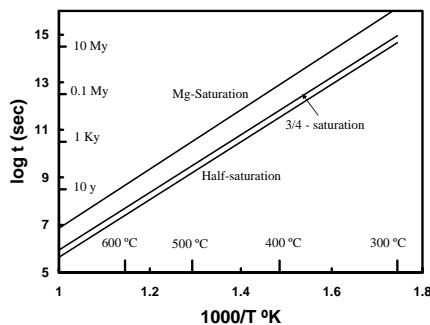
Figure 1. T-t exposures for reacting calcite with dolomite to form Mg-calcite in poly-crystalline aggregate with grain size similar to those (around 10 µm) in experiments.

The SEM-EDS analysis of individual calcite grains shows that the Mg contents in calcite grains progressively decease with increasing the distance from dolomite-calcite grain boundary, suggesting a diffusion control of the reaction. The Mg/Ca inter-diffusion coefficient at 850 ℃ calculated using the diffusion equation is around 3 x 10-16 m^2/sec. The calculated closure temperatures for Mg/Ca inter-diffusion as a function of cooling rate and grain size in calcite reveal that the Ca/Mg resetting in calcite in dry polycrystalline carbonate aggregate may not occur at temperatures below 600 ℃ at geological cooling rate (> 100 ℃/my), unless other processes were involved.

Reference

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Pressure dependence of viscosity of hydrous rhyolitic melts

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Knowledge of viscosity of silicate melts is critical to the understanding of igneous processes. Numerous viscosity measurements have been carried out on the natural and synthetic silicate melts under ambient pressure, but only a few investigations have examined the pressure dependence of viscosity of silicate melts. "Hydrous species reaction viscometer" (Zhang *et al*., 2003) based on the concentrations of two hydrous species in the melts after a known cooling history is applied to investigate pressure dependence of viscosity of hydrous rhyolitic melts at near glass-transition temperatures.

The samples used here are natural obsidian glass with about 0.85 wt% water and hydrated natural obsidian glasses with higher water contens (2 wt% and 4 wt%). The experiments were conducted in piston cylinder apparatus at 1, 2 and 3 GPa. A prerequisite for viscosity inference with this "viscometer" is to know the temperature dependence of the equilibrium constant *K* of the interconversion reaction at a given pressure. Hence, pressure dependence of the speciation of dissolved water in these samples was investigated. Comparing with speciation model at ambient pressure (Ihinger *et al*., 1999), equilibrium constant changes with pressure nonlinearly, decreasing from 0.1 MPa to 1 GPa and then increasing from 1 GPa to 3 GPa.

Cooling rates varied from ~ 100 K/s to 0.1 K/s in the cooling-rate experiments. Viscosity (in Pa·s) at the apparent equilibrium temperature of the hydrous species reaction (i.e., glass transition temperature) is obtained as $10^{11.45}/q$ where *q* is cooling rate in K/s. So the total range of viscosity inferred from this method in this study is 3 orders of magnitude. Preliminary results show that viscosity of hydrous rhyolitic melts increases by about 1.4 log unit from 0.1 MPa to 3 GPa. The behavior of viscosity as a function of pressure for hydrous rhyolitic melts with water content of 0.8 wt% or more at low temperature range is similar to that of depolymerized melts.

References

Ihinger P.D., Zhang Y. and Stolper E.M. (1999) *Geochim. Cosmochim. Acta* **63**, 3567-3578.

Zhang Y., Xu Z. and Liu Y. (2003) *Am. Mineral.* **88**, 1741-1752.