

Effect of Ca on magnesite growth – a fundamental approach towards solving the dolomite problem

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The dearth of modern dolomite precipitation – despite aqueous supersaturation in marine depositional environments – together with the challenge of precipitating dolomite in the laboratory at temperatures less than 100 °C feed the argument that the understanding of dolomite precipitation kinetics is the key to solving the dolomite problem. Carbonate mineral reaction kinetics are limited by the rate of exchange of water molecules in their respective metal aquo ion [1]. However, calcite growth inhibition in the presence of aqueous Mg^{2+} demonstrates the influence of Mg entrapment on calcite precipitation kinetics. In this study we attack this question from the opposite direction by investigating the influence of Ca^{2+} on magnesite growth kinetics.

Macroscopic and microscopic experiments on magnesite growth kinetics at 100°C and pH 8 were conducted in the presence of aqueous Ca concentrations from 0 to 1 mmol/L. Experiments were performed using hydrothermal mixed-flow reactors (HMFR) and hydrothermal atomic force microscopy (HAFM). HAFM measurements of obtuse step velocities showed a bimodal concentration dependence of rates on aqueous Ca. Experiments at a magnesite saturation state $\Omega = 100$ and Ca^{2+} concentrations above 0.1 mmol/L lead to decreased obtuse step propagation rates while concentrations of ~ 0.01 mmol/L promoted obtuse step advancement. In contrast, HMFR experiments with 0.01 mmol/L Ca^{2+} showed a strong inhibition of magnesite growth while forming a magnesite with up to 6 mol% Ca under steady state conditions.

These results indicate that Ca slows magnesite growth primarily by its incorporation into acute step sites suggesting a strong crystallographic control on carbonate growth rate inhibition by trace elements.

[1] Pokrovsky & Schott (2002) *Environ. Sci. Technol.*, **36**, 426-432