Saturation State and Temperature Controls on Magnesite Nucleation and Growth Mechanisms

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This study was motivated by several reasons including:
1) to assess the potential of magnesite precipitation for the mineralogic storage of CO_2, and
2) to illuminate the relative contribution of nucleation versus growth in contributing to mineral growth rates.

The mechanisms and rates of magnesite precipitation were characterized in this study through a series of hydrothermal atomic force microscopy (HAFM) experiments.

Experiments were run at temperatures up to 120 °C and the experimental system was pressurized to prevent reactive solution degassing. The experimental system consisted of magnesite crystals, as a substrate, and a solution composed of NaCl, HCl, $MgCl_2$, $NaHCO_3$, NaOH and deionized water.

Various experiments were performed by varying 1) the saturation state of the solution with respect to magnesite and 2) the Mg^{2+}/CO_3^{2-} ratio of the solution.

Random two dimensional nucleation was observed only at saturation states Ω greater than about 150 (with $\Omega = Q/K$; Q = aqueous ion activity product, K = equilibrium constant for the magnesite hydrolysis reaction), which clearly demonstrates a huge energetical barrier for nucleation of magnesite.

At lower degrees of supersaturation, magnesite grows exclusively by defect assisted step generation mechanisms. In most cases, dislocations were detected to be the source of steps. At $\Omega < 70$ and temperatures < 80 °C active step generation mechanisms became so slow that magnesite growth exclusively took place at pre-existing steps. It cannot be excluded, however, that the step generation could proceed at these conditions, but at a rate too slow to observe.

The observed decrease in step generation activity at low temperatures might be a consequence of the magnesite growth anisotropy (c.f., Jordan et al., 2001, for dissolution anisotropy).

Further experiments were performed to assess the effect of varying fluid Mg^{2+}/CO_3^{2-} ratios. Magnesite growth rates at a constant saturation index slow with increasing fluid CO_3^{2-} activity. This observation is consistent with the surface complexation model proposed by Pokrovsky et al. (1999) for magnesite dissolution.

Microscopic rates determined by the AFM data will be compared with macroscopic rates as obtained by mixed flow reactors. The comparison will provide information on the growth kinetics as the system approaches equilibrium and therefore will help illuminate the processes that limit or make possible magnesite formation in natural environments.

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