Geophysical Research Abstracts
Vol. 12, EGU2010-7712, 2010
EGU General Assembly 2010

pH-dependence of calcite growth kinetics at constant solution calcium to carbonate activity ratio and supersaturation: an in situ Atomic Force Microscopy study

Encarnación Ruiz-Agudo (1), Christine V. Putnis (1), Carlos Manuel Rodriguez-Navarro (2), and Andrew Putnis (1)

(1) University of Münster, Institut für Mineralogie, Münster, Germany (eruiz_01@uni-muenster.de), (2) University of Granada, Department of Mineralogy and Petrology, Granada, Spain

Calcite-solution reactions (growth, dissolution and replacement) are critical in a range of both engineering and natural processes. Classical crystal growth theory relates calcite growth rates to the degree of supersaturation. The solution composition may also affect the growth rate of carbonate minerals, via the Ca^{2+} to CO_3^{2-} concentration ratio (Nehrke et al., 2007; Perdikouri et al., 2009), ionic strength (Zuddas and Mucci, 1998) or the presence of organic matter (Hoch et al., 2000). Most calcite growth studies so far have been performed at a constant pH of ca. 8 or 10, or changing the pH together with the degree of supersaturation with respect to calcite and/or the a_{Ca2+} to a_{CO32-} ratio in solution, which hinders an evaluation of the pH effect on calcite growth kinetics. In this work, *in situ* Atomic Force Microscopy (AFM) was employed to study the growth of calcite at a constant supersaturation (Ω = 6.46) and solution stoichiometry (Ca^{2+}/CO_3^{2-} = 1) in the pH range 7.5 to 12. How pH may influence calcite growth is relevant to improve our understanding of the effects on carbonate-solution reactions when variations in atmospheric CO_2result in changes in the pH of the oceans and surface waters. We observed that the calcite growth rate decreases with increasing pH in the studied range. The results can be successfully explained by the mechanistic model for calcite growth based on surface complexation proposed by Nilsson and Sternbeck (1999) and by solute hydration. At pH below 8.5, growth occurs mainly by $CaCO_3^0$ incorporation at $>CaHCO_3^0$ surface sites. $CaCO_3^0$ should be more easily incorporated than free Ca^{2+} ions, as water exchange usually is faster if water molecules in the ion hydration shells are substituted for by other ligands, as in $CaCO_3^0$. However, at pH above 9, Ca^{2+} incorporation at $>CaHCO_3^0$ sites also contributes to calcite growth as a result of increased frequency of water exchange in calcium hydration shells due to the presence of strongly hydrated OH^-. The decrease in calcite growth rate is a consequence of decreasing surface concentration of growth active sites (i.e. $>CaHCO_3^0$) with increasing pH in our experimental conditions. Changes in 2D island morphology were observed at high pH (12), possibly due to the stabilization of polar scalenohedral faces by the presence of OH^- ions.

References

Hoch, A.R.; Reddy, M.M.; Aiken, G.R. Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. *Geochim. Cosmochim. Acta* **2000**, 64, 61-72.

Nehrke, G.; Reichart, G. J.; Van Cappellen, P.; Meile, C.; Bijma, J. Dependence of calcite growth rate and Sr partitioning on solution stoichiometry: Non-Kossel crystal growth. *Geochim. Cosmochim. Acta* **2007**, 71, 2240–2249

Nilsson O.; Sternbeck J. A mechanistic model for calcite crystal growth using surface speciation. *Geochim. Cosmochim.Acta* **1999**, 63, 217–225.

Perdikouri, C.; Putnis, C.V.; Kasioptas, A.; Putnis, A. An Atomic Force Microscopy Study of the Growth of a Calcite Surface as a Function of Calcium/Total Carbonate Concentration Ratio in Solution at Constant Supersaturation. *Cryst. Growth Des.* **2009**, 9, 4344-4350.

Zuddas, P.; Mucci, A. Kinetics of Calcite Precipitation from Seawater: II. The Influence of the Ionic Strength. *Geochim. Cosmochim. Acta* **1998**, 62, 757-766.