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Ion-specific effects on spiral growth of calcite

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The mechanisms by which background electrolytes affect the kinetics of non-equivalent step propagation during calcite growth were investigated using Atomic Force Microscopy (AFM) at constant driving force and solution stoichiometry. Spiral growth, seen as growth hillocks, was directly observed and growth steps measured to record the growth in-situ. The results of this work suggest that the rate of dehydration of carbonate surface sites for cation attachment and subsequent kink nucleation control the velocity of acute step propagation in calcite cleavage planes, while the velocity of obtuse step advancement is mainly determined by hydration of calcium ions in solution. Both velocities can be altered in the presence of different background ions in solution. Overall calcite growth rates increase with increasing hydration of calcium in solution (i.e. increasing ion separation in a solution of sodium-bearing salts) and with decreasing hydration of the carbonate surface site (i.e. increasing ion-pairing of chloride-bearing salts). The different sensitivity of obtuse and acute step propagation kinetics to cation and surface hydration could be the origin of the reversed geometries of calcite growth hillocks (i.e. rate of obtuse step spreading $<$ rate of acute step spreading) observed in concentrated (IS = 0.1) KCl and CsCl solutions. At low IS (0.02), ion-specific effects are mainly associated with changes in the solvation environment of calcium ions in solution. With increasing electrolyte concentration, the stabilization of surface water by weakly paired salts becomes increasingly important in determining step spreading rate. Changes in growth hillock morphology were observed in the presence of F^-, SO_4^{2-} and Li^+ and are ascribed to stabilization of polar $(01\bar{1}2)$ and (0001) faces due to increased hydration. These forms are commonly found in biomineralized calcite, suggesting that relatively simple inorganic ions may have similar effects on mineral growth at the atomic scale as more complex organic molecules. The conclusions of this study increase our ability to predict crystal reactivity in fluids in natural systems, which often contain significant and variable amounts of solutes.