

Supporting information

Direct Imaging of Nanoscale Dissolution of Dicalcium Phosphate Dihydrate by an Organic Ligand: Concentration Matters

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One supporting figure and 2 supporting references.

Results and Discussion

In experiments to examine the effect of ionic strength on brushite dissolution, we adjusted the solution composition by adding NaCl as background electrolyte to the 0.1 or 1.0 mM citrate solution, which changed ionic strength. Ionic strength, in turn, may influence the step movement speed by changing the activity coefficients of ions in solution. The pit retreat rates for all three steps with NaCl at 0.01, 0.1, or 0.5 M were significantly enhanced compared to that in pure water at the same pH of 7.7 (Figure S1A). When 0.01, 0.1, or 0.5 M NaCl was introduced into 0.1 or 1.0 mM citrate solution (pH 7.7), the rates of pit retreat along the $[-100]_{Cc}$ and $[10\bar{1}]_{Cc}$ directions rapidly increased compared to that in the same concentration citrate solutions without NaCl (pH 7.7) (Figure S1B and C). However, dissolution along the $[101]_{Cc}$ steps was still not initiated in the presence of citrate (0.1 or 1.0 mM) and NaCl (0.01–0.1 M), whereas the step retreat rate of 1.48 ± 0.11 nm/s was required when NaCl concentration was increased to 0.5 M.

Previous AFM studies demonstrated that background electrolytes enhance the calcite dissolution rate,¹ and the magnitude of this enhancement is determined by the nature and concentration of the electrolytes through modifying water structure dynamics as well as solute and surface hydration.²

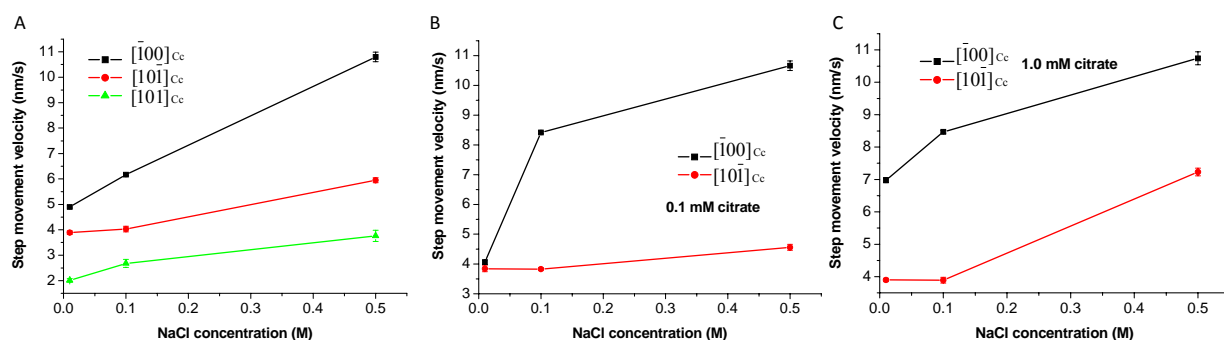


Figure S1. Retreat velocity of all three steps of etch pits on brushite (010) surfaces in (A) the absence and presence of citrate at (B) 0.1 mM or (C) 1.0 mM with three different concentrations of NaCl (0.01, 0.1 and 0.5 M) at pH 7.7.

Supporting References

- (1) Wang, L. J.; Ruiz-Agudo, E.; Putnis, C. V.; Menneken, M.; Putnis, A. Kinetics of calcium phosphate nucleation and growth on calcite: Implications for predicting the fate of dissolved phosphate species in alkaline soils. *Environ. Sci. Technol.* **2012**, *46*, 834–842.

- (2) Ruiz-Agudo, E.; Kowacz, M.; Putnis, C. V.; Putnis, A. The role of background electrolytes on the kinetics and mechanism of calcite dissolution. *Geochim. Cosmochim. Acta* **2010**, *74*, 1256–1267.