

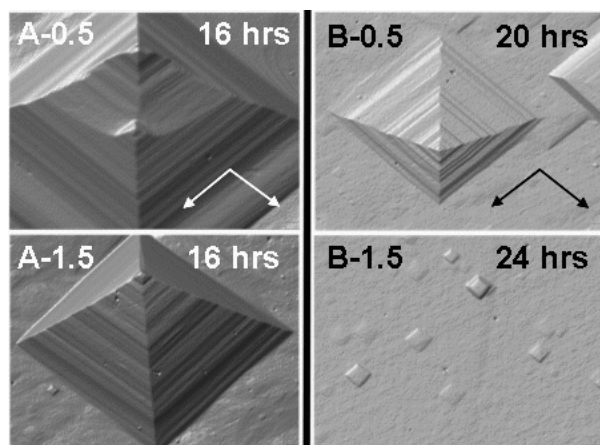
General model for impurity metal control of carbonate mineral reaction kinetics

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During carbonate mineral growth, the interaction of impurity cations is strongest for those species that achieve inner sphere coordination at energetically favorable surface sites, and secondarily mediated by steric geometry and charge distribution. Incorporation also leads to important feedback effects: once coordinated at a step edge, an impurity cation can inhibit growth rate, influencing the development of surface topography and the distribution of the impurity within the growing crystal lattice. Given these potential feedbacks and possible links between dissolution and growth kinetics [1], it is important to examine if inhibition of dissolution versus growth reflects unique roles for impurity metals.

Here we present experimental work involving inhibition of calcite dissolution by common divalent metals. In brief, our results suggest that the potential for inhibition can be described in terms of a balance between (1) the penalty for partial removal of waters of hydration versus the (2) benefit that accrues from carbonation. These results suggest a number of possible reaction paths involving both dissolved and surface carbonate complexes. These trends are used to compose and constrain a general model for metal inhibition on carbonate surfaces during both dissolution and growth.



(A) Calcite dissolution in carbon-free solutions at 0.5×10^{-6} M (top) and 1.5×10^{-6} M (bottom) Mn. (B) Effect of added dissolved carbon in otherwise identical conditions as in (A).

References

[1] Dove P.M., Han N., and DeYoreo J.J. (2005) *PNAS* **102**, 15357-15362.