

# A microkinetic model of calcite growth

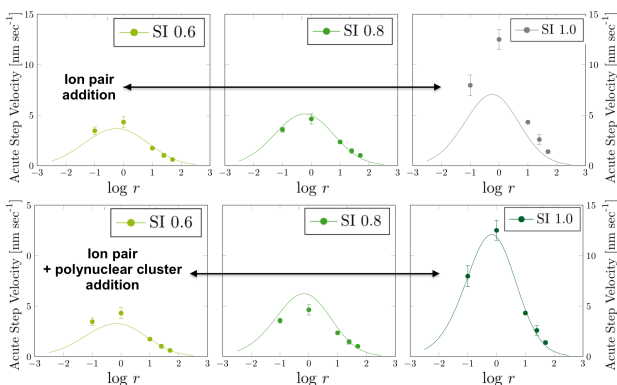
M. P. ANDERSSON\*, S. DOBBERSCHÜTZ, K. K. SAND,  
D. J. TOBLER AND S. L. S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (\* ma@nano.ku.dk)

In spite of the simple composition of calcite,  $\text{CaCO}_3$ , its growth rate over a range of supersaturation levels and  $\text{Ca}/\text{CO}_3$  ratios cannot accurately be simulated with existing models. If mineral growth could be described at the molecular level, it would help the interpretation of biomineralization processes and aid in the design of mineral growth inhibitors.

We made a microkinetic model for calcite growth, based on concepts from heterogeneous catalysis. First, we assumed that step growth occurs by addition of single ions or ion pairs and that kink nucleation is the rate limiting step. We obtained an excellent fit to our experimental data for low saturation index (SI) (Fig. 1, top). The parameters are easily interpreted in terms of ion free adsorption energies on the steps and dehydration free energy barrier. The results are consistent with complimentary density functional theory calculations.

We then extended our model by assuming the presence of polynuclear clusters [1], which have recently been called prenucleation clusters or DOLLOPS, which join the surface in the same way as ion pairs. This addition reproduces the experimental data for higher SI (Fig. 1, bottom). Our results imply that polynuclear clusters contribute to regular calcite growth, through kink nucleation on steps.



**Figure 1.** Experimental growth rates for calcite acute steps (y axis, data points) and the best model fit (lines) at various SI and  $\log r$  ( $\log(\text{Ca}/\text{CO}_3$  ratios)) (x axis).

[1] Sillen, L. G. *Acta Chem. Scand.* **8**, 299-317, doi:10.3891/acta.chem.scand.08-0299 (1954).