Crystal Growth and Inhibition: Toward a General Model

M.P. ANDERSSON[3] AND S.L.S. STIPP[2]

[1]Chemical Engineering and [2]Physics, Technical University of Denmark; martan@kt.dtu.dk, stipp@dtu.dk

We honour Georges Calas for his contributions, over nearly a half century, to the understanding of mineral and glass behaviour. I wonder if Georges' experience is the same as ours … the more we learn, the less we feel we know and the more questions we have. How do solids form and dissolve? What controls their morphology? How do organisms control biomineral growth? A general model that describes growth and dissolution and the effect of enhancers and inhibitors, using only a few, physically meaningful parameters, for any mineral or glass, would be a breakthrough for mineralogists, materials scientists and advanced materials engineers.

Calcite is a good model for mineral-fluid investigations because of its simple composition and crystal form and its prevalence as a biomineral. From the past five decades of study on calcite and other minerals, combining macroscopic data with high resolution observations and molecular modelling, we now have a clearer picture of how crystals grow. We know that ions in solution and on surfaces are hydrated and that water, organic compounds and ions order themselves at the mineral-fluid interface. We know that step and kink geometry results in very different adsorption energies and dehydration frequencies, which explains why crystal growth and organic molecule adsorption also occurs on top of step edges rather than only at kink sites. Experiments in nonstoichiometric solutions and molecular modelling demonstrate that for calcite, the 16 different kink sites, each with its own adsorption energy, determine where ions and molecules adsorb, which completely controls surface energy, changing surface tension dramatically. From the thermodynamic base given to us by Lars Síllen, Werner Stumm, George Parks and many of our academic predecessors, we know that near equilibrium, the activity of ion pairs and polynuclear complexes increases. In a recently published microkinetic model, we showed that calcite growth rate could be described using only adsorption constants and the dehydration energy for the surface and solution species. The model was effective in pure systems and in systems containing inorganic (Mg, SO_4) and organic (acetate, benzoate) inhibitors over a very much wider range of conditions than any previous model. The microkinetic model provides a base upon which to build a more extensive model, that also describes precipitation and dissolution in other systems.