# Calcite growth disruption by small organic molecules

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Organic molecules can control calcite growth and dissolution, as well as crystal morphology and size. In biomineralisation, organisms produce organic molecules to direct the nucleation and growth of their biominerals. These organic molecules are composed of multiple functional groups and are often complex proteins or polysaccharides, that inhibit or template calcite crystal growth.

We have studied the effect of small organic molecules, containing a single functional group on calcite growth using a constant composition setup, maintaining constant supersaturation and pH constant at 8.3. Concentration of $Ca^{2+}$ and $HCO_3^-$ ranged between 2 mM and 5 mM, in a NaCl 0.1 M background solution. Ethanol, acetate, benzoate and hexanoate were added at concentration ranging between 1 mM to 100 mM.

Ethanol has no effect or slightly promotes calcite growth. For the carboxylate functional groups, we observed 2 regimes: at low concentration, below 15 mM, they have no effect or they slightly promote growth while at higher concentration, between 15 mM and 100 mM, inhibition increases with increasing concentration.

Using PHREEQC calculations, we showed that inhibition is mainly caused by decreased saturation index, resulting from carboxylate group complexing with $Ca^{2+}$ in solution. These results fit well with a recent model of calcite growth that takes into account the existence of ion pairing in solution [1]. The calcite growth promoting effect, observed at concentrations below 15 mM, can be explained by disruption of the hydration layer at the calcite-fluid interface.

Our results show that organic molecules containing a single alcohol or carboxylate group do not inhibit calcite growth through strong surface interactions and inhibition at high concentration is mainly a result of solution complexation. Thus larger molecules with several functional groups are needed for surface control of calcite growth, such as those used by organisms during biomineralisation.

1: Andersson M.P. *et al.*, 2016, A Microkinetic Model of Calcite Step Growth, *Angewandte Chemie*, 55 (37), 11086-11090.