

# Simulation of the Nucleation of Calcite Crystals

# Introduction

- Living organisms control the size, shape, and crystallographic orientation of growing crystals to form minerals with unusual morphologies and functional properties.
- This process of *biomineralization* has inspired attempts to reproduce such control in the laboratory where ordered arrays of organic molecules are used to modify and control crystal growth.
- Early experiments used Langmuir monolayers, such as the long-chain carboxylic acids.

- The calcite crystals grown from aqueous solution on these monolayers nucleate on the (10.0) face, whereas calcite crystals nucleate on the (10.4) face on the surface of pure water.
- Self-assembled monolayers have been used as substrates for calcium carbonate crystal growth, and it was found that different headgroups, and even different metal substrates, tended to nucleate different crystal faces.
- The common explanation for these effects is that the organic layer is acting as a "template" to control the growth of the mineral.

- The good geometrical matching between the arrangement of ions on a given face of the crystal and the ordering of the functional groups attached to the aliphatic chains.
- The aliphatic chains are close-packed.
- This argument has been used to explain the different orientation produced by carboxylates.

- Self-assembled monolayers of carboxylate-terminated alkanethiols nucleate crystals with different orientation on monolayers with odd and even chain lengths
- The "odd-even" effect has also been attributed to templating.
- Various types of polymers have also been used as templates. Dendrimers of polyamidoamine induce the growth of spherical or disklike crystals and polypentacosadiynoic acid (PDA) promotes nucleation of the (01.2) face of calcite.

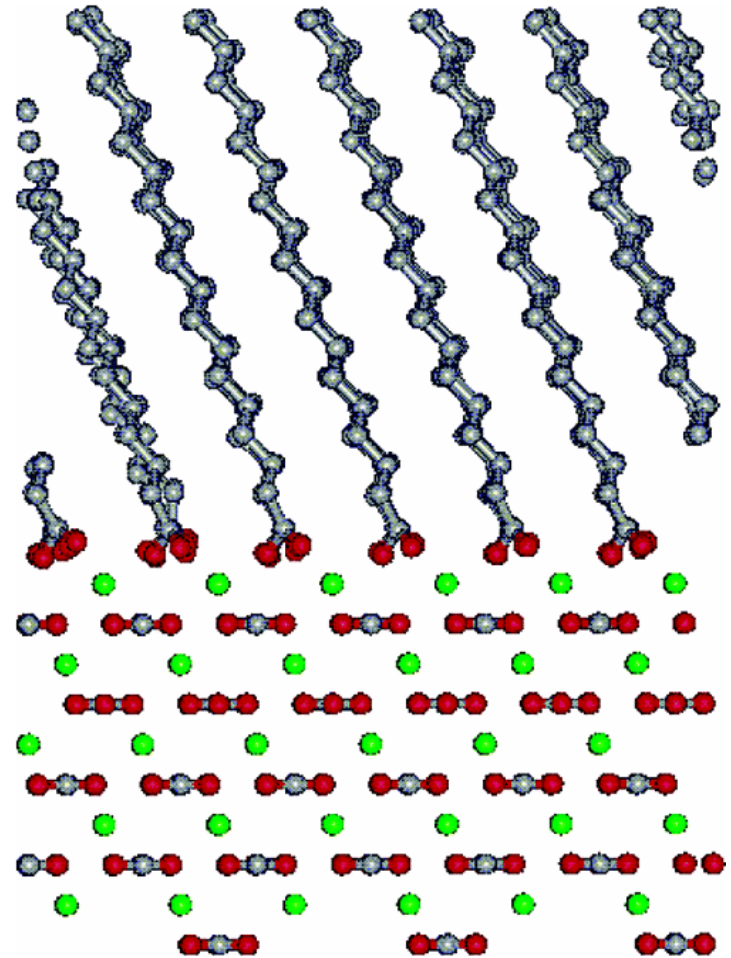
# Simulation model

- Models of interfaces between Langmuir monolayers of stearic (octadecanoic) acid and calcite surfaces.
- Both neutral (un-ionized) and fully dissociated (ionized) monolayers were considered.
- There was very good matching between the calcite surface structure and the monolayers and the magnitudes of the adhesion energies were comparable with the surface energies.

- The calculations suggested that the nucleation rate for all surfaces would be enhanced significantly on stearic acid monolayers and no particular face appeared to be favored.
- Such models can explain why calcite crystals should grow preferentially on organic layers but not why a specific morphology should be favored.
- These simulations are conceptually similar to template models where only the matching of the pattern of carboxylate groups in the template array to the structure of possible calcite surfaces is considered.

# Observations

Interface between a calcium terminated (00.1) surface of calcite and an ionized monolayer of stearic acid. The gray spheres represent C, red represents O, and green represents Ca.





- There is very good matching between the carboxylate groups of the monolayer and the carbonate ions of the crystal.
- On neutral crystal surfaces charge neutrality is maintained by replacing one carbonate ion in the surface plane with two stearate molecules.
- In practice this is only possible when the spacing between the surface carbonate ions is large enough to accommodate two monolayer molecules, that is for surfaces with large surface unit cells.

- Nucleation of calcite crystals on organic substrates is influenced by a range of factors, notably the degree of ionization and competition between the interactions of the crystal and water with the substrate.
- The simple model of an organic template controlling the growth of minerals by a lock-and-key mechanism must be modified to take account of this.

- The competition between the interaction of water and the interaction of the substrate with the crystal plays a crucial role in limiting the number of crystal faces that are nucleated on a given substrate.
- The degree of ionization of the substrate is also significant. Fully ionized substrates have stronger adhesion to the crystal surfaces than neutral substrates and therefore they should be better at promoting nucleation.
- Hence the pH of the solution is an important factor in promoting nucleation. This also controls crystal shape since the ionized and neutral monolayers stabilize different surfaces, (10.4) for the neutral case and (10.0) or (00.1) for the ionized case.

- A further factor controlling the nucleation of neutral surfaces on ionized substrates is the density of the surface carbonate ions. This must be low enough to permit the substitution of each ion by charge groups of the substrate to create a neutral interface.
- The question of stereochemical matching only comes into play after these factors have been taken into account. Perhaps the best way to consider the template is in the context of a self-assembly process.

- The organic template is not a pre-existing rigid structure onto which the mineral must fit, rather the interface between organic substrate and mineral assembles as the mineral grows.
- The constraint of stereochemical matching is then, other things being equal, likely to pick out a stable interface structure. Even so, the flexibility of the template may complicate this simple argument.
- In living systems, for example, thermal fluctuations and entanglement of biomolecules may disrupt the ideal substrate.

- If the template were made more rigid, by cross-linking the organic molecules into lines or sheets, stereochemical matching might be more important.
- Persuading the water to leave the surface is as important as persuading a mineral to grow there.