Chemical Science Review and Letters ISSN 2278-6783

Research Article

Formation of Calcite Seed Crystal by Interaction with Langmuir Film: A Computational Modeling Approach to Study Biomineral Formation in Nature

Subhashis Biswas*[1] and Udo Becker[2]
[1]Narula Institute of Technology, Westbengal University of Technology, Kolkata-700109, INDIA.
[2]University of Michigan, Ann Arbor, MI 48109, USA.

Abstract
Formation of calcite seed nucleus under the influence of biofilms is studied in this paper. Peptides act as host for biomineral formations in nature. Under various pressure and surface area, biofilms are prepared to mimic the biomineral-forming peptides in nature, and calcite seed formation takes place under Langmuir film of fixed pressure and surface area. Hydration plays a major role in the nucleus seed formation for calcite. Adsorption energies of different calcite crystal faces vary under variable biofilm orientation. Computational modeling and Molecular Dynamics simulation study using CALCITE-WATER forcefield, derived from Universal 1.02 force-field is performed to obtain the most suitable calcite surface (100), in Cerius^2 software. This study will enhance understanding process of natural biomineral formation.

***Correspondence**
Dr. Subhashis Biswas, Narula Institute of Technology,
Email: subhashis.7@gmail.com

Keywords Calcite, Biomineralization, Langmuir Film, Computational Modeling.

Introduction

The peptides act as host organic molecules or organic complexes in the biomineralization process. The transportation of inorganic ions to the growth site and the subsequent adsorption/crystal growth has to be controlled. Organic molecules that adsorb to the growth nuclei in concert with ordered organic templates determine the morphology of the biominerals. These two-dimensional growth island-organic template interactions are stronger, when the interface energy (per unit surface area) between the organic template and the growth island is more negative. Generally, if the periodicity between the functional groups of organic molecules matches with the periodicity of Ca^{2+} ions in a particular calcite surface, then the organic-inorganic interfacial interactions become very stronger. The periodic relationship between templating biomolecular substrate and organic phase can be controlled by various laboratory experiments. [1,3]. Such approaches include the use of synthetic templates such as polymers [2], and Langmuir films [4]

Computational modelling study in this paper describes the growth of most suitable calcite surface under Langmuir film template depicting the actual process of biomineral formation under natural condition. The Langmuir monolayer is made up of Benzyl(-)-(2*S*)-3-Phenoxy-2octadecylaminopropan-1-yl methylphosphate (compound 1) with a polar phosphonate group (on the left in the structure above) and an aliphatic chain ($C_{17}H_{35}$). The growth of calcite seed nucleation under these Langmuir films at different pressure/ (surface area) conditions was evaluated.

Experimental

Computational Modeling Methods

Using the Cerius2 software package, compound 1 is aligned in a two-dimensional array to create the Langmuir film. The elongated hydrocarbon chain is pointed upwards and the amide-containing phosphate head group points downwards in contact with the inorganic mineral surface. The calculation is started with area of 46 Å^2 (per 8 phospholipid molecules in the Langmuir film) when the external force applied is 0 N/m. Then the pressure is slowly increased, and the virtual pistons placed on both sides of the Langmuir film are moved towards the center of the array. The entire Langmuir film is allowed to move during MD simulations at each particular force and surface area points. The limiting area and force of the Langmuir film is found out to be 29.011 Å^2 and 25.4 N/m. Different calcite faces are placed under the Langmuir film at a particular force and surface area condition. Molecular dynamics and energy minimizations are performed for each face. Three different calcite faces, (001), (100), and (104), were studied in such a way. In each of the interactions, both the organic compounds in the Langmuir film and the calcite lattice beneath it are free to relax to form the most stable interface during energy minimization and molecular dynamics simulation. It was observed that the the organic compounds do not affect the calcite structure beyond the fourth layer. The final interface energy per unit area provides an estimate on which face would be energetically favourable for the onset of calcite seed formation under a Langmuir film consisting of amide-containing phospholipids. Both the surface and interfacial energy in each case of organic-

calcite interaction are calculated, and the sum of these energies is used as a criterion to decide on which would be the most likely interface. CALCITE-WATER force-field is used to study the interactions within the organic molecules and for interactions between the organic molecule and the substrate, to account for the interactions of water molecules with the calcite surface. We also included non bonding van der Waals interaction terms in the force-field to account for the interactions between Ca^{2+} and $CO3^{2-}$ and water molecule. Interactions within the organic molecules and between the calcite and the organic molecules are based on the UNIVERSAL1.02 force field.

Results and Discussion

Of the three calcite faces under the Langmuir film, the (100) face yielded the lowest interfacial energy (-0.05 eV/Å2) and the (104) face (this rhombohedral face is the most stable one if calcite is grown naturally, without the influence of organic matrix) the most unfavourable one. The hydrophilic head group of the organic compounds present in the Langmuir film consists of phosphate group, benzene ring and amide bond. Deprotonated phosphate group is chosen due to its low pKa values for the interaction with the calcite surface and these phosphonate groups are attracted to the Ca^{2+} ions at the crystal surface. A close look at the orientation of the organic molecules in the Langmuir film rationalizes the favourable interaction between the organic lattice and Inorganic calcite. The hydrophobic part of each organic compound in the film, the long 63 hydrocarbon chain and the benzene ring, are aligned at an angle of 45^{o} with respect to the interfacial surface of organic and inorganic lattice. The hydrophilic part, the amide bond and the phosphate group are aligned almost perpendicular to the interface. This allows maximum interaction between the hydrophilic parts of the organic molecule and the calcium and carbonate ions on the calcite surface. The spacing, stoichiometry and the favourable chemical interaction between the hydrophilic end or the organic template and the calcite (100) face promote the calcite seed formation, as shown in figure 2. Spacing between Ca^{2+} ions in the top layer of calcite (100) plays an important role in calcite seed formation as it matches the distance between polar head-groups in Langmuir film.

Hydration plays a major role in the formation of seed nucleus during crystallization. Thermodynamically hydration counteracts the seed formation process, but the hydration actually favours the seed formation process by deviating the Ca^{2+} and carbonate ions to its final adsorption sites. The close packing of the polar head groups of the film forms a unit with the water molecules to form a "combined" hydration atmosphere, which in turn shapes the seed of crystallization in Calcite.

Table 1. Interfacial energies between various calcite surface and Langmuir film

Calcite Surface	E(surface) (eV/Å2)	E(interface) (eV/Å2)	Etotal (Esurface+ Einterface) (eV/Å2)
Calcite (100)	0.06	-0.05	0.01
Calcite (104)	0.0	2.1	2.1
Calcite (001)	0.3	-0.02	0.28

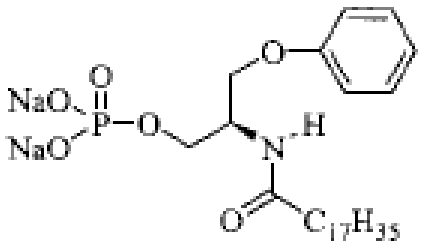

Fig. 1. Building block of the Langmuir film: amphiphilic molecule consisting of an amide-containing phospholipid**.**

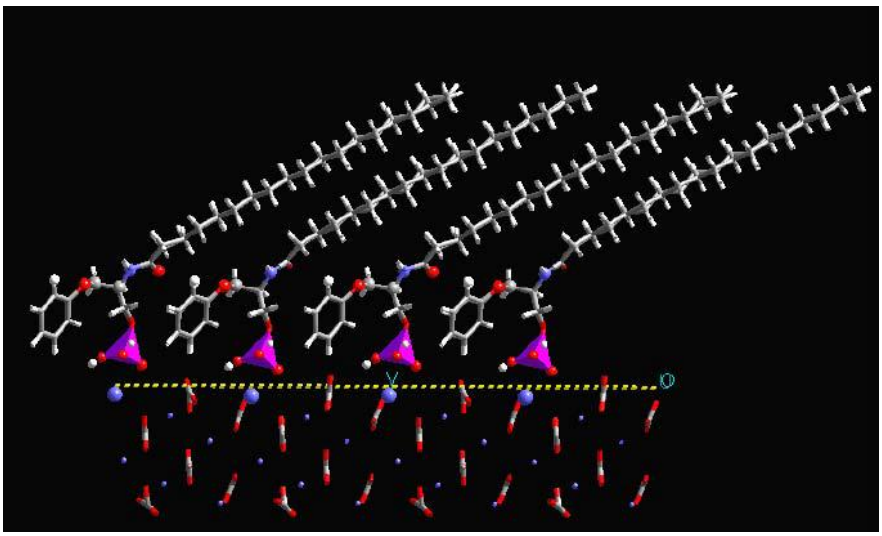

Fig. 2. Calcite (100) surface under Langmuir film

Conclusions

Formation of crystals under natural conditions in the environment is a difficult and complex process to mimic. This study follows the footsteps of experimentalists to create a model where biomineral crystal seed formation in environment can be mimicked effectively under surface area and pressure constraints. This study also shows that specific biomineral surfaces in nature can be formed under specific biological membranes, following the pathway of adsorption in vacuum. This will help us to better understand the diversification in biomineral formation natural world, and will help us to understand the general pattern of biomineral formation.

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Publication History
Received 28th Nov 2013
Revised 25th Dec 2013
Accepted 15th Feb 2014
Online 29th Apr 2014