

CHAPTER 3

Biom mineralization on Outer Core of Coccolithophores: A Computational Modeling Study on Role of 12-Amino Acid Polypeptides on Calcite Surface Growth

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Abstract: Formation of biominerals is a complex process which is mechanized upon the interaction of various mineral surfaces on biological polymers/oligomers. Coccolithophores are a group of single celled algae found in marine environments, which produces complex calcite mineralized structures on their outer-core known as coccoliths. Formation of this exoskeleton by coccolithophores can be directly linked to the genetic information carried in their DNA pattern. Sequencing of amino acids in a protein is a direct result from the DNA base pair sequence that forms RNA via translation and then protein via transcription. This study analyses the interfacial interaction between organic matrix (polypeptide sequence on coccolithophore outer core) and calcite (104) surfaces and surface steps. Negatively charged and neutral 12-amino acid peptides are placed upon [4 8 -1], [0 1 0] and [4 2 -1] surfaces steps of Calcite (104) surfaces, and using Cerius² software (Accelrys) and Abalone 2.0 software with modified Universal 1.02 force-field, energetics was studied. It is observed that the proximity of an amino acid

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residue towards the calcite surface and steps depends largely on the nature of the R group. Energetics also revealed that complex 12-residue amino acids facilitate adsorption on calcite steps compared to simple 3-residue proteins, which may induce the growth of calcite biominerals on a particular phase in outer core.

Keywords: Biomineralization, Calcite, Computational modeling, Coccolithophores, Surface growth

Introduction

Biomineralization is a process where interfacial interactions between biological systems and inorganic materials system play major role[1]. Biological systems provide particular exoskeletons based on their soft protein pattern which serve as scaffold, on which the hard inorganic materials grow to form biominerals. Most of the minerals that form on biological systems consists of carbonates, bicarbonates, silicates, phosphates and sulphates. These minerals are abundant in marine system. During evolution of prokaryotic and eukaryotic organisms gained the ability to produce mineralized exoskeletons, where organic-inorganic system interactions occur over time. Thus, these resulting biominerals carry a significant trace of ancient marine evolution and give us an insight into how marine biological systems interacts with earth's crust.

Coccolithophores are ancient marine algae, and they originated around 208 million years ago, during the Triassic period [2]. The average atmospheric CO₂ concentration in atmosphere was 5 times higher than current atmosphere during the Triassic period. Coccolithophores produces tiny exoskeletons which forces deposition of calcium carbonates on their outer core, as biominerals. More than 50% of today's CaCO₃ deposition of the world is accounted by coccolithophores. Coccolithophores survived two huge mass extinction events one including the extinctions of dinosaur, and still currently present as floating organisms in marine systems. Coccolithophores play a major role in biogeochemical cycle of Carbon. Carbonate depositions on the exoskeleton of these marine organisms act as a source of CO₂ in upper oceanic crust, and also act as a reservoir of biogenic organic carbon produced by marine photosynthesis. The forced deposition of carbonates on oceanic coccolithophores actually balance out the exodus of CO₂ in to atmosphere by various processes including dissolution of biominerals[2,3]. Thus, presence of coccolithophores in marine biology are also important in maintaining carbon footprint in the atmosphere and reducing global warming.

The term coccolith were coined by Huxley in 1857, when deep sea deposition of mineral bodies resembling coccoid cells were observed for the first time. The term means spherical stone, and honouring the spherical shaped mineralized structure produced by organisms, Lohmann in 1902 coined the term coccolithophores. Coccoliths are biomineralized calcified scales produced by extant haptophytes, and are mainly categorized by their micro sized structure and homogeneous calcite distribution. Haptophytic coccolithogenesis requires influx of inorganic carbon and Ca²⁺ ion. Deep sea calcite mineralization also requires extreme control mechanism and compartmentalization of calcium ions, and regulation of Ca²⁺ to prevent apatite deposition. The spherical shaped exoskeleton composed of

biominerals on coccolithophores are called coccosphere. Today, there are more than 280 distinguishable and structurally different coccospheres are present in the oceans around the world. On these coccospheres, intricate calcite vesicular depositions occur, and these depositions are result of organic soft tissue matrix-inorganic calcium carbonate interactions. The deposition of biominerals on coccospheres originated back in Triassic period, when were mainly monolithic in structure with size ranging between 2-3 μm . However, with time the sizes slightly increased in late Triassic period, and nature of depositions changed. Research is being more focused on the organic structure of the soft tissues, and the biopolymeric material that not only give the coccosphere its shape, but also dictate the mechanical properties of the coccolithophores. Localization and organization of the organic matrix is important on the individual coccolithophore surface, and it is important to understand what specific matrix orientation is formed that governs specific calciferous deposition on coccoliths.

The complex morphological patterns of coccoliths at micro and nano scale suggests that they can act as novel model compounds [9]. It is necessary to understand the complexities in the crystal formation influenced by the protein matrix on the outer core of coccolithophores. This understanding will help scientists design many templates where similar biomineral deposition can take place, and which can be applied as sensors and catalysts. The understanding of calcite formation, and specifics of the calcite deposition on these protein matrices is also as important as understanding the influencing protein matrix structure. The complexities in the protein matrix structure can be attributed to the DNA pattern of specific species. Central dogma of biology follows the path of translation of DNA to RNA, and transcription of RNA to protein. Sequencing of DNA base pairs will thus dictate the final arrangement of amino acids in the protein structure in the organic protein matrix of coccolithophores. Basically, this arrangement of amino acids will further dictate the crystal morphology of the calcite formation, and effective biomineral formation on coccoliths. These amino acid sequence can form small or big polypeptide cluster which may differ in complexity at various location on the coccolith, or coccosphere, thus they will influence calcite formation in distinguishable way at various surface sites. This is an important factor in this research, as micro level analysis will reveal the actual polypeptide-calcite interaction that is taking place during the formation of coccolithophores[3,4]. *Emiliania huxleyi* is the major species among all the coccolithophore species present in modern day ocean, because of its huge numerical presence compared to other species. This species is also can be easily cultured in the laboratory, which facilitates the research on understanding organic matrix-calcite interaction for formation of biominerals. Even within the *E. Huxleyi* species, many variations in morphology have been observed owing various evolutionary aspects, grazing pressures of ocean beds, and reduced ocean pH. Diversification in morphologies of coccolithophores has also influenced diverse deposition of calcite as biominerals on coccolithophore species[4]. The principle aim of this research work is to study the various peptide-calcite interactions, which are representatives of the diverse organic templates on coccolithophore surface on which calcite biomineralizations have occurred over millions of years. The thermodynamic stability of a particular peptide-calcite (organic template-mineral) interface indicates the possibility of surviving a particular coccolithophore morphology over millions of years[5], and that particular peptide-calcite interface is representative of a particular coccolithophore surface of interest. The principal aim of this study is to establish a set of thermodynamically stable calcite-peptide interface

combinations (with varying amino acid sequences on peptides and varying surface and surface steps of calcite mineral) which will enable us to map that particular combination to existing coccolithophore morphologies [11]. This will help us in understanding the various structural and evolutionary aspects as well as the biological genomic aspects of formation of this very ancient life form on earth.

The peptides that are being studied in this research provide selective stabilization of mineral surface and surface steps. These peptides or in general organic templates on the surface of bioorganisms induce nucleation of calcite seed formation (or biomineral formation in general). There are two aspects in this study. The role of side chains and functional groups present in the side chains of amino acids in the peptides that induce the onset of mineralization, and how they help selective adsorption of the mineral surface on organic matrix. Another aspect of this study is role of calcite surfaces and their ability to orient the peptide chains in particular way to facilitate selective adsorption. The combination of both studies will give us insight in structural and functional aspects of biomineral formation on outer exoskeletons of coccolithophores.

The parallel alignment of peptide chains along the particular surface steps of calcite are the main deciding factors for controlling the shape of biominerals[13]. Structural matching at the organic-inorganic interface is key for favourable adsorption. The coordination environment of the cations and anions present in a mineral surface (Ca^{2+} and CO_3^{2-} in this case) combined with the particular arrangement of the ligands present in the peptide structure cause the nucleation of crystals that finally gives the final shape of the biomineral-combined coccolithophore exoskeleton structure[10]. The general rule of thumb for this nucleation onset is the matching the distance of repeating units of ligands on the organic matrix (adsorbate – amino acid functional groups in this case), with the repeating units between calcium ion and carbonate ions on the mineral surface (adsorbate in this case)[12]. The most favourable interfacial energy between the adsorbent and adsorbate leads to formation of a stable biominerals.

Experimental Section

As mentioned in the introduction section, the main focus of the study is on understanding the calcite mineral and protein interaction and adsorption of calcite on protein interface, that can mimic the actual deposition of calcite biominerals on coccolithophore exoskeleton. Calcite {104} family of faces are chosen as they have the exposure of most surface area, and main objective of this work is to find suitable amino acid residues that can match the interfacial structural topography and facilitate effective adsorption on calcite surfaces. These suitable amino acids, when aligning parallel to the calcite surfaces and surface steps, can start the nucleation and growth of mineral surfaces on the soft biological framework, resembling that actually happens in the outer exoskeleton of coccolithophores.

To find a suitable polypeptide chain for adsorption on calcite surfaces, we need to keep in mind that translation of DNA to polypeptide sequences via RNA involves conversion of a four-base codon (ATGC) into twenty different amino acids. The transfer of codon information into proteins (or amino acid chains) is done by t-RNA, which possesses anticodons that can base pair with codons. To avoid sterically hindrance issues within the peptide, we had studied these interactions on 3-amino acid peptides [6] and energetics from that study helped us determine the surface steps of calcite {104} surfaces on

which possible parallel alignment and favourable adsorption of larger peptide chains can happen. These calcite steps are calcite [010] and calcite [42-1] surface.

Empirical force field methods have been used to study the interaction of peptides with calcite surfaces. When we study molecular dynamics of any particular system, our main aim remains to produce results that can exceed the accuracy of real-life situations or bench top experiments. Here the peptide-calcite adsorption phenomenon, that happens in nature on coccolithophore surfaces, is being mimicked through the computational modeling study. For this, we need to have a set of force-fields based upon which the atoms and molecules will interact with each other during molecular dynamics (MD) simulation run. When any two atoms come close during any molecular dynamics simulation run, they gather information from forcefield such as bond angle, bond length, 2-body and 3-body potential energies. Based on these information, two atoms come close to each other, or move away from each other, or behave in a certain manner. Universal 1.02 force field has all these necessary information required for interaction between a biological system with other systems, but since we are studying interaction between inorganic materials and biological systems, we have modified the Universal 1.02 force field according to our need and named the force field as CALCITE 1.0 force field [Table 1]. Here, LJ potential terms between Ca atom and other atoms such as N, O, S, P, C, H present in an amino acid, has been included, and relevant bond lengths and bond angles for these Ca-O, Ca-C, etc. interactions have been included. Using Cerius software (Accelrys Inc.), calcite surface steps along periodic boundary conditions chain parallel to symmetry [010], [42-1] and [48-1] has been created.

Table 1: Potential Parameters for CALCITE 1.0 forcefield

O-O	Buckingham	Intermolecular <14Å	A = 1482.9 eV	$\rho = 0.2661 \text{ \AA}$	$C = 0 \text{ eV/ \AA}^6$
Ca-O	Buckingham	Intermolecular <14Å	A = 789.3 eV	$\rho = 0.292 \text{ \AA}$	$C = 0 \text{ eV/ \AA}^6$
O-C	Morse	Intermolecular	D= 4.9771	$r_0 = 1.232 \text{ \AA}$	$K_b = 63.233 \text{ eV/ \AA}^2$
O-C-O angle	Three-body	Intermolecular	$K_0 = 1.829$	$\theta_0 = 120^\circ$	
CO₃²⁻ plane	Umbrella	Intermolecular	$\omega_0 = 0^\circ$	$K_0 = 4402.18 \text{ eV}$	
Charges	C= +1.345	O = -1.115	Ca = +2.000		

Buckingham: $A \exp(-r/\rho) - C r^{-6}$ (C in eV/ Å⁶); **Morse:** $D [(1 - \exp\{-a(r-r_0)\})^2 - 1]$ a = (K_b/2D)^{1/2}
Three-body: $E = K_0(\theta - \theta_0)^2$ **Umbrella:** $E = K_0 (1 - \cos \omega)$ for $\omega_0 = 0^\circ$ projection on O-C-O plane. ω = Angle between the C-O bond and its projection on O-C-O plane.

The calcite cluster under study contains 700 atoms or 140 CaCO₃ units, with cations and anions arranged in a way resulting net zero dipole moments either perpendicular or parallel to calcite {104} faces. This resembles the tiny nanocluster of a calcite rhombohedron that actually grows on the

coccolithophores[7,8]. The upper layer of the created calcite cluster contains 15x16 unit cells whereas the layer below contains 15x22 unit cells. This arrangement creates the necessary surface steps on which the adsorption of peptide chains is studied. For non-polar surface steps, the unit cell arrangements are changed to 14x10 and 14x12 in upper and lower layer, respectively. Creation of two types of non—polar surface steps generate required obtuse angle for the study. The surface steps can be terminated either by calcium ion or calcite ion, depending on the position of the surface steps. Adsorption energies of peptide chains are calculated for each of these surface step types.

To find absolute minimum energy configuration for each peptide-calcite adsorption scenario, peptides are brought manually to the calcite surface steps for each calculation. For each starting position, minimizer of the Cerius software is used for the starting position of the peptide. Qeq charge equilibration of Cerius software is used to calculate charge distribution within the peptide molecules and any protons added due to adjusting deprotonation state was removed, and resulting charges were distributed over the whole molecule.

Molecular dynamics simulation using NVE ensemble and periodic boundary conditions are performed at 300K. The structure resulting from simulation is allowed to evolve over time, and Cerius software does this by solving Newton equations of motion. The dynamic time step is reduced to .001ps, and length of the run can range from 10000 to 100000 steps, depending on the evolution of the peptide structure alongside calcite surface steps.

The peptide chain that has been used this study is a 12-residue protein (Glycophorin A, also known as GPA protein). This is a known calcium binding protein present in *Emiliana Huxleyi*, this protein contains high percentage of glutamic acids, alanine and proline. This protein has repeating stretches of 35 amino acid residues for most of the protein, and this repeat unit contains a 12-amino acid residue sequence that shows strong binding affinity to Ca^{2+} ions. The 12-amino acid sequence present in this repeating unit is **Pro-Glu-Val-Pro-Glu-Gly-Ala-Val-Asp-Thr-Ala-Ile**. Using the molecular builder of Cerius software, this peptide chain is developed and minimized at every starting position, as mentioned earlier in this chapter. Aqueous equilibration for each of these peptides are done to obtain effective hydration energies of these peptide chains to mimic the natural environment present in ocean floor, before onset of MD simulations for each of the calcite step starting position.

The 12-amino acid peptide residue has complexities in the side chain position of the amino acid, and this has a chance to provide steric hindrance to the adsorption and parallel alignment of the peptide chain along the calcite surface steps. The effect of side chain is an important matter of study, as side chains of biomolecules and organic molecules can often influence surface topography and growth of the mineral surface. Here a peptide residue is chosen in such a manner that has mostly alternating Glycine (Gly) and Alanine (Ala) residues. Glycine has H-atom as side chain and Alanine has Methyl group ($-\text{CH}_3$) as side chain. These two are most simple side chain residues that provide minimal steric hindrance to the adsorption and parallel alignment of the peptide on calcite surfaces. These two are most fundamental amino acids present in biogeochemical pathways of prebiotic systems, and are expressed as

result of Guanine-Cytosine base pairing which is strongest possible base pair interactions among all possible ATGC interactions.

Results and Discussion

pH condition is varied during the MD simulation taking into account both negatively charged and neutral 12-amino acid residue peptides. The interaction of both these types of 12-amino acid residues are studied on **a)** non-polar steps parallel to step direction [48-1] (and the symmetry-equivalent [4 4-1]) with both obtuse and acute angles of carbonate ions (with respect to the calcite terrace of lower layer) **b)** polar steps terminated by Ca^{2+} ions and CO_3^{2-} ions parallel to surface step direction [010] and [42-1], and **c)** flat (104) terraces.

1) Interaction of negatively charged 12-amino acid residue peptide with multiple surface locations of calcite (104) surface

Table 2: Adsorption energies of negatively charged 12-amino acid residue peptide with complex structure and simple structure on different calcite (104) surface locations

Calcite surface locations for complex-structured peptide	Vacuum adsorption energy (eV/residue)	Calcite surface locations for simple structured peptide	Effective adsorption energy (eV/residue)
non polar steps parallel to [48-1] with CO_3^{2-} making obtuse angle	-1.94	non polar steps parallel to [48-1] with CO_3^{2-} making obtuse angle	-1.33
non polar steps parallel to [48-1] with CO_3^{2-} making acute angle	-1.71	non polar steps parallel to [48-1] with CO_3^{2-} making acute angle	-0.83
polar steps terminated by Ca^{2+} parallel to [010]	-7.16	polar steps terminated by Ca^{2+} parallel to [010]	-2.32
polar steps terminated by Ca^{2+} parallel to [42-1]	-5.53	polar steps terminated by Ca^{2+} parallel to [42-1]	-1.97
polar steps terminated by CO_3^{2-} parallel to [010]	-1.54	polar steps terminated by CO_3^{2-} parallel to [010]	-0.31
polar steps terminated by CO_3^{2-} parallel to [42-1]	-0.83	polar steps terminated by CO_3^{2-} parallel to [42-1]	-1.21
flat-terrace	-2.12	flat terrace	-0.89

The adsorption energies of the complex and simple structures (w.r.t side chain) of 12-amino acid peptides on various locations of calcite {104} surface is listed in **table 2**. The alignment of 12-amino acid residue peptide chain shown in **Figure 1** depicts a U-shaped structure at the edge of the calcite surfaces. The negatively charged side chain is heavily attracted to calcium ions present on the surface. The formation of U-shaped structure also owe to the fact that the two sets of terminating side chains are bulky residues that is causing steric hindrance during the process of adsorption. Proline and glutamine are present at one end, and Leucine and Isoleucine are present at the other end. The smaller the side chain, closer the amino acid gets to the calcite surface step. The adsorption energies are most favorable (for both complex and simple structured peptides) on polar steps terminated by Ca^{2+} ions. The adsorption energies are more favorable on step direction parallel to [010] in comparison to [42-1]. The

adsorption energy of the complex structured 12 amino acid peptide on a flat terrace of calcite surface {104} is more favorable than some of the polar and non-polar step locations.

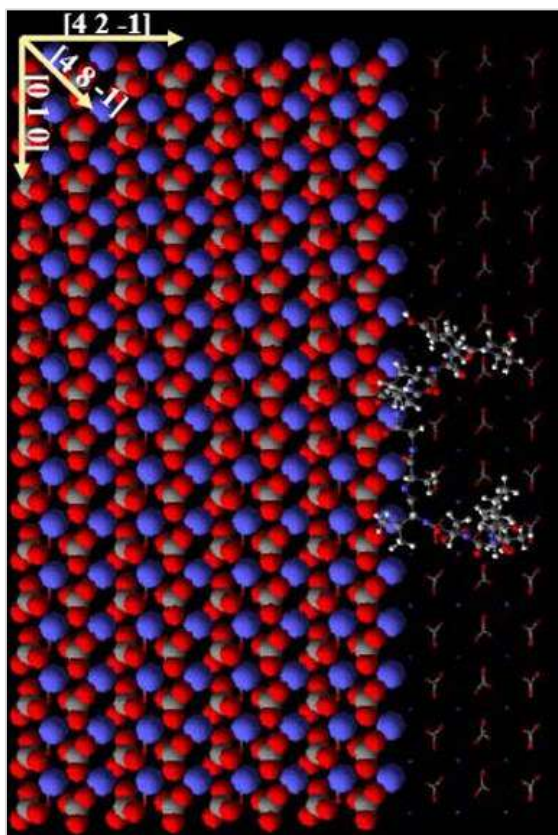


Figure 1: 12-amino acid residue peptide with complex structure aligned parallel to [010] surface step direction of calcite (104) surface

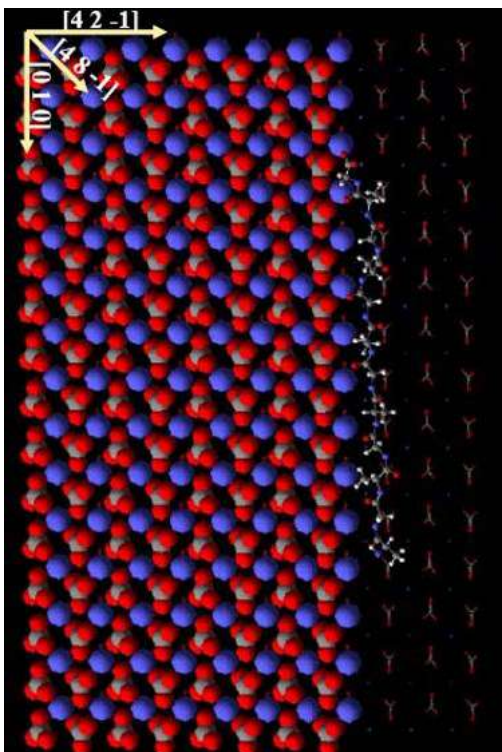
2) Interaction of neutral 12-amino acid residue peptide chain with multiple surface locations of calcite (104) surface

The adsorption energies of neutral 12-amino acid peptide residue with complex and simple structure along side calcite surfaces are listed in **table 3**.

The most favourable adsorption energies in this case are observed for peptide adsorption on polar surface steps parallel to step direction [010], terminated by negatively charged carbonate ions. Simple peptide with alternating glycine and alanine sidechains gives less favourable adsorption energies compared to the complex ones on the polar steps (**Figure 2**). The main difference between the two types (complex and simple structure 12 amino acid peptides) exists in their orientation alongside calcite surface steps, where the simple structured peptide adopts more parallel alignment compared to its complex 12-amino acid residue.

Table 3: Adsorption energies of neutral 12-amino acid residue peptide with complex structure and simple structure on different calcite (104) surface locations

Calcite surface locations for complex-structured peptide	Vacuum adsorption energy (eV/residue)	Calcite surface locations for simple structured peptide	Effective adsorption energy (eV/residue)
non polar steps parallel to [48-1] with CO ₃ ²⁻ making obtuse angle	-2.51	non polar steps parallel to [48-1] with CO ₃ ²⁻ making obtuse angle	-0.98
non polar steps parallel to [48-1] with CO ₃ ²⁻ making acute angle	-1.81	non polar steps parallel to [48-1] with CO ₃ ²⁻ making acute angle	-0.65
polar steps terminated by Ca ²⁺ parallel to [010]	-3.85	polar steps terminated by Ca ²⁺ parallel to [010]	-1.51
polar steps terminated by Ca ²⁺ parallel to [42-1]	-3.01	polar steps terminated by Ca ²⁺ parallel to [42-1]	-0.96
polar steps terminated by CO ₃ ²⁻ parallel to [010]	-7.23	polar steps terminated by CO ₃ ²⁻ parallel to [010]	-2.12
polar steps terminated by CO ₃ ²⁻ parallel to [42-1]	-1.60	polar steps terminated by CO ₃ ²⁻ parallel to [42-1]	-1.63
flat-terrace	-1.85	flat terrace	-0.53


Figure 2: 12-amino acid residue peptide with simple structure aligned parallel to [010] surface step direction of calcite (104) surface

The spacing between successive calcium ions or carbonate ions situated on calcite surface are 4.36 Å in the step direction parallel to [42-1] compared to 4.96 Å in the step direction parallel to [010]. The smaller distance in [42-1] matches better with the separation of adsorbing functional groups in the peptides investigated. As mentioned earlier, this matching of spacings between the adsorbate peptides and adsorbent calcite surface is the key for nucleation and growth of biominerals on the coccolithophore surface.

Conclusion

Long-chain peptides are more frequently observed in naturally occurring biominerals compared to short-chain peptide residues. Comparison of the adsorption energies of simple and complex structured 12-amino acid peptides reveals that simple-structured peptides are more likely to have parallel alignment at the step-edge of calcite surface. That does not necessarily mean that simple structured peptides are more common in nature. The results in this study shows that the 12-amino acid residue peptides with complex structure side chains have comparable (more thermodynamically favorable in some cases) adsorption energies on calcite surface steps with simple structured peptides. Thus, it can be concluded that the simple-structured peptides can provide structural and spatial matching with the growing calcite surface, and the complex structured peptides that have complex side chain structures are more likely to get adsorbed on calcite surface steps. The complex 12-amino acid residue peptides are more capable to form a complex with Ca^{2+} ions being central metal ion and may serve as a carrier of these ions to calcite surfaces. The complex side-chains in amino acids play a significant role in interaction with the calcite surface atoms on surface step locations.

Molecular level interactions of side-chain functional groups of amino acids with specific calcite surfaces has been discussed in this book chapter, with an aim and scope to study several other combinations of peptide-calcite interfaces that can occur during natural biomineral formation. The structural information of peptides of an organism can be deduced from protein data bank, and experimental studies can provide insight into growth phases of calcite on the exoskeleton of that particular organism. These two sets of information can help developing molecular models to study effects of functional groups present in the amino acid of the organism in natural biomineralization process. This will help to create a database on influence of various functional groups present in amino acids, on biomineral formation. To mimic the natural environment, present in ocean floor or other environmental set-ups, for biominerals formation more closely, multi-dimensional model of organic networks needs to be prepared which will provide insights into the growth of calcite crystals under the influence of such an organic framework.

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