THEORETICAL INVESTIGATION OF MOLLUSK SHELLS: ENERGY LANDSCAPE EXPLORATION OF CaCO_3 POLYMORPHS AND ELEMENT SUBSTITUTION: A SHORT REVIEW

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Due to the remarkable properties achieved under ambient conditions and with quite limited components, mollusk shells are very appealing natural bio-composites used as inspiration for new advanced materials. Calcium carbonate which is among the most widespread biominerals is used by mollusks as a building material that constitutes 95-99% of their shells. Within the investigation of calcium carbonate polymorphs present in the shells, diverse theoretical and experimental studies were performed, however, further research of these crystalline forms is required. There are very little researches on the energy landscapes of biogenic calcium carbonate which can provide us information about the free energies of already known as well as newly discovered plausible structures. To investigate the structural, mechanical, elastic, or vibrational properties and to predict new possible structures of biogenic calcium carbonate, different calculation methods could be employed. Some of these studies are presented and discussed in this paper.

Keywords: mollusk shell, biogenic composite, calcium carbonate, energy landscape, bioinspired materials

Introduction

Due to their hierarchical structure, natural materials can display extraordinary performance in comparison to the materials of which they are assembled and therefore can be used as a guide to enhance the characteristics of artificial materials. It is a common belief that biological composites gather their remarkable properties by combining organic and inorganic components and arranging them in a preferred orientation over several length scales. As the hard phase in biological composites provides stiffness and mechanical stability, the matrix maintains the geometry of the structure and distributes the mechanical stress among the hard constituents, but also provides high fracture toughness and increases fatigue resistance. However, a crucial factor for the excellent mechanical properties is considered to be the arrangement of these constituents [1]. Mollusks are good examples of structural composites assembled of mineralized organic matrices made through biomolecular engineering, whereby these molecular-level interfacial designs can result in the formation of hardened materials with unique functional properties [2]. To protect themselves from predators that try to break their shells, through evolution mollusks improved their structure and mechanical properties, and considering the simple constituents they use for the formation of the shell, their properties are much better than man-made materials [3]. So, when the outer surface of a seashell is exposed to a concentrated force in the normal direction as is a predator's bite, the hard ceramic layer can prevent perforation,

while the inside layer can absorb mechanical energy that would otherwise be consumed towards more serious damage and catastrophic failure. In the case of overloading, the brittle calcite layer may fail, but experiments have demonstrated that the tough nacreous layer could delay and eventually arrest those cracks, thereby delaying the complete failure of the shell [4]. Biogenic nacre is a non-brittle bio-ceramic that is formed in an aqueous environment and under ambient conditions, and it could be used as bio-inspiration for many new sustainable materials. It is considered, that its highly controlled structural organization of mineral and organic components from macro, down to the nano- and molecular scales is guided by organic molecules, which eventually get incorporated into the material to be responsible for properties such as fracture mechanics or corrosion resistance [5]. As nacre is assembled of layers of aragonite tablets with organic matrix between them which constitute only a few percent of the shell mass, it is considered that this organic material provides a template for the nucleation of aragonite, or it gives a pre-formed framework in which the mineral growth, or both [6].

Calcium carbonate is the most widespread biomineral used by invertebrates that serves as material for shells of mollusks [7] and continues to attract much interest from both scientific and technological viewpoints [8]. In mollusk shells, calcium carbonate is composed of two dominant minerals, calcite and aragonite, that are affiliated with organic matrix, the diversity of which reflects the

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taxonomic diversity and regardless of the lack of varieties, the mineral components can be placed in a diversity of arrangements [9]. Occasionally, as a component of a shell, the rare polymorph vaterite may be included. For understanding macroscopic mechanical properties of molluscan shells, their structure-property relations at all length scales down to the molecular level should be accounted for. Consequently, as a method that can explore a wide range of properties from the atomistic scale up to the macroscale, multiscale modeling has become the most broadly used method for examining the structure-property relations of biological nanocomposites [7].

Optimization of Mollusca shells

The geometry of the shell was modeled at the macroscale as well as the micromechanics of the nacreous layer and three different failure modes were identified, depending on the morphology of the shell. Optimization of the shell concerning six multiscale parameters with the Nelder-Mead (NM) simplex search method was applied for the search of the global optimum (figure 1 and figure 2), but since this algorithm is prone to find only local optima, the NM optimization process was coupled to a probabilistic restart. To increase the chance of converging to the global optimum, the NM was started at 100 randomly picked initial simplex within the design space. Due to the presence of multiple local optima in the objective function, the algorithm converged to various points within the design space. Nevertheless, even the results did not converge to a single point, all parameters fall into a narrow range compared to the boundaries assigned to each variable [4].

Figure 1. Optimization results for the NM algorithm initiated from different points within the design space where t represents normalized shell thickness while α_c represents calcite to shell thickness ratio [4]

Parametric and optimization studies revealed that whenever two failure modes in different layers coincide, the shell shows optimal resistance to perforation by a sharp indenter. In this optimum configuration, the shell structure exploits the capabilities of the different layers

of the shell to their full extent. According to the results from the experiments performed on two shells of red abalone, there is a suggestion that the actual seashell has a microstructure design that fully exploits its material properties [4].

Figure 2. A visual map of design space for t (normalized shell thickness) and α_c (calcite to shell thickness ratio). [4]

Calcium carbonate polymorphs

Among several polymorphs of calcium carbonate, calcite and aragonite are the most important crystalline forms. The most stable form at room temperature and atmospheric pressure is calcite, which has a rhombohedral crystal structure with space group $R\bar{3}c$ and whose atomic structure is presented in figure 3. Aragonite (figure 4), which is composed of biogenic environments, has an orthorhombic crystal structure with space group $Pmcn$ and is metastable [8]. Both polymorphs can be found within the ICSD database [10,11].

Figure 3. Rhombohedral crystal structure of calcite at standard conditions. 3D visualization using hexagonal settings [12]

Vaterite, the rare polymorph of calcium carbonate that is responsible for malformations which led to the unusual tick shell in Asian clams (*Corbicula fluminea*) is rarely found in the natural environment as it is less stable in comparison to the other two calcium carbonate polymorphs, calcite, and aragonite. These shells are found in four rivers in the UK and the infrequent formation of vaterite in mollusks is considered to be related to peculiar biomineralization such as the process of regeneration in shell, generation of pearls, or formation of shell in initial stages. As fossil specimens of *Corbicula* had similar deformations as was found in these shells, it is assumed that these malformations are not related to anthropogenic impact such as pollution, but a disrupted process of biomineralization instead [13].

Figure 4. Orthonorhombic CaCO_3 aragonite structure [14]

Biogenic calcite lattice is anisotropically distorted in comparison to geological calcite and it is considered that this is a widespread phenomenon. It is suggested that lattice distortions are probably caused by intra-crystalline organic molecules, that are of the greatest importance regarding nucleation, growth, and morphological modifications of biogenic crystals [15]. Some features of a crystal, such as a habit or domain size, are affected by the formation processes so these can be beneficial to a different level of local structural order or crystallinity in calcite and aragonite. There is also a suggestion that by looking at the luminescence of crystals, defects that exist in the crystal structure of CaCO_3 could be detected [16].

Energy landscapes of calcium carbonates

In many cases where direct laboratory measurements are difficult or impossible to perform, the mechanisms of atomistic processes could be performed by simulations to evaluate materials properties. Even though simulations cannot replace experimental measurements, an atomistic model that is well-parametrized can provide a solid framework for evaluation of mechanisms and prediction of the activation energies and rates for diffusion under conditions that experimentalists cannot achieve [17]. Although thus far materials capable of existence are discovered through the experimental exploration of energy landscapes, to a priori identify the aim of synthesis, it is

necessary to apply the exploration using the theoretical methods [18]. The first step in synthesis planning is the prediction of possible structure candidates capable of existence, where a computational search of the respective potential energy landscapes for (meta)stable structures should be employed [19]. A very important issue in solid-state chemistry is considered the development of a general methodology to predict the possible meta(stable) modifications of a solid [20]. The surface geometry and energies of the calcium carbonates have been modeled using atomistic simulation techniques, which are based on the Born model of solids that assumes that the ions in the crystal interact via long-range electrostatic forces and short-range forces, including both the repulsions and the Van der Waals attractions between neighboring electron charge clouds. Considering that the surface energy is a measure of the thermodynamic stability of the surface, a low, positive value indicates a stable surface [21]. As stated [22], the (meta)stable phases capable of existence coincide with locally ergodic regions on the enthalpy landscape of the chemical system of interest. According to Gibbs [21], the equilibrium form of a crystal should possess minimal total surface free energy for a given volume. A surface with a high surface free energy has a large growth rate and this fast-growing surface will not be expressed in the equilibrium morphology of the resulting crystal, but only surfaces with low surface free energies, and hence slow growth, will be expressed. At 0K, the surface free energy is a close approximation of the surface energy as calculated by static lattice simulations because the entropy term included in the surface free energy is small compared to the enthalpy term, as the difference between the energies of the bulk and the surface is small. Thus, the surface energies can be assumed to determine the equilibrium morphology of the crystal [21].

According to Gibbs, the energy of a crystal is made up of two components: a surface component, which is important when the crystals are small, and a bulk component which becomes dominant at large volumes [21]. The bulk lattice energies of the three polymorphs express their thermodynamic stability, so the stability of calcite over aragonite is due to its higher entropy content at elevated temperatures rather than its bulk lattice energy, which favors aragonite. The relative surface contributions of the polymorphs show that in the crystal nucleation stage calcite is the most stable form, while aragonite becomes more stable when the crystal is large enough for the bulk lattice energy to outweigh the surface energy terms [21]. Within the investigation of the structural stability and electronic structure of CaCO_3 surfaces in calcite and aragonite polymorphs using the electronic structure calculations within the density functional theory, systematic calculations showed that in both calcite and aragonite surfaces, the surfaces with the same number of Ca atoms as CaCO_3 groups, have the lowest surface energy over the wide range of Ca chemical potentials. The analysis of the electronic structures clarifies that in

order to achieve stabilization, the transfer of electrons between 4s orbitals of Ca atoms into 2p orbitals of O atoms which are located near the surface, is crucial [8]. In the simulations that used a modification of Born model description of solids, which treats the ionic material as a collection of point ions with electrostatic (coulombic) and short-range forces acting between them, the calculated lattice parameters for the end-member carbonates differ from their measured lattice parameters by less than 1%. The lattice energy generally increases with increasing ionic radius, and for the carbonate minerals, lattice energy is presented in figure 5. Results obtained by these simulations indicated that the lattice energy of aragonite is less exothermic per mole than calcite at ambient pressure, consistent with the metastability of aragonite at room pressure [17].

Figure 5. Calculated lattice energies for the rhombohedral carbonate minerals as a function of the ionic radius of the divalent cation [17]

Thermodynamic phase stabilities of calcite and aragonite were also analyzed by lattice vibrational analysis based on first-principles calculations and resulted in different pressure dependences in phonon feature between two polymorphs, suggesting different physical origins of the pressure-induced phase transitions [23]. The results from ab initio DFT calculations of the band structure and carriers effective masses of CaCO_3 aragonite performed within the LDA and GGA description of the exchange correlation potential suggest that if the luminescence of scallop shells is due to band to band recombination in CaCO_3 , their thermal treatment in the 300-400 °C range will contribute to blueshift or enhance the higher energy part of their spectra due to the aragonite-calcite transformation. The LDA and GGA results for CaCO_3 aragonite exhibit very close indirect and direct energy gaps, and the computed effective masses are heavy and anisotropic [24]. A description of ab initio methods could be found in detail elsewhere [25]. Investigation of the morphology and surface stability of calcium carbonate polymorphs with atomistic simulation techniques resulted in the relaxed {1014} surface as the most stable surface,

with the lowest surface value and attachment energy. It is required to compute the equilibrium morphology of a crystal, so the relative stability of the surfaces can be measured, which is determined by the surface energy and the related growth rate for the various surfaces. It is suggested that the surface energies apparently could determine the equilibrium morphology of the crystal. Energetic stabilities of different polymorphs of calcium carbonate are presented in figure 6. [26].

Figure 6. Energetic stability of CaCO_3 polymorphs [26]

To comprehend the macroscopic mechanical properties of the tissue, it is essential to consider its structure-property relations at all length scales down to the molecular level. In the study with lobster cuticle as an example, ab initio calculations were combined with hierarchical homogenization that allowed examination of structure-property relations at all length scales. Multi-scale modeling approach that connects atomic and macroscopic scale allowed that mechanical properties at the nanoscale could be determined as well as structures that were not accessible until now, but also to follow their evolution up to the macroscale [27].

Element substitution in carbonates

As it is believed that trace elements in calcium carbonate polymorphs in marine organisms can tell us about past climates, they are receiving much attention lately [28]. There is also an assumption that different organic and inorganic impurities in biogenic minerals affect their characteristics, particularly it is considered that these impurities make the material harder and tougher [29]. The generic association is considered as the most important parameter for the control of trace elements in calcium carbonate shells, and it is suggested that snails are higher in Mg and lower in Sr and Ba in comparison to clams [30]. Even though there is a belief that the substitution of trace elements for Ca is ideal, in reality, these elements incorporate in crystal structures through structure relaxation, which is controlled by the flexibility of the surrounding structure [28]. From the investigation of manganese substitution in aragonite of mollusk shell, it

was confirmed that the present manganese in the shells of all studied species is in the form of high-spin Mn^{2+} , or in other words, manganese and calcium have the same valence. It is also experimentally observed that manganese is always coordinated by a CO_3 -octahedron, what is considered to be good evidence that manganese is predominantly present in the inorganic carbonate, but also suggests that the structure of aragonite, where it is incorporated, is locally altered so it can achieve octahedral coordination, as it does in calcite. Modification in the local symmetry at the atomic scale enables the bivalves to host larger quantities of manganese than any non-biogenic aragonite, and there is a consideration that this extraordinary characteristic is probably facilitated through the non-classical crystallization paths of bivalve shells. Figure 7. presents the density of states of the Mn substituted aragonite [31]. In these cases, manganese substitutes Ca atom, while in the case that it substitutes carbon as a second cation in $CaCO_3$, a completely different $CaMnO_3$ compound with perovskite structure is formed [32].

Figure 7. Density functional theory. A,b. The density of states for the spin-up Mn-site of rhodochrosite, projected on d- (a) and p-symmetry (b). (c) Simulated valence-to-core emission for rhodochrosite and Mn-doped aragonite. [31]

Magnesium is one of the crucial factors in calcite mineralization and is very important for carbonate growth [33]. It is also an important minor element in biogenic aragonite, although it is stated that there is considerable inter-specimen inconsistency in the temperature dependence of Mg/Ca ratio in corals and bivalves arago-

nite polymorphs [34]. Due to the consideration that real materials are not pure crystals, but instead have many defects and lattice imperfections, the particular characteristics of the crystals and minerals derive from these defects and imperfections. The presence of Mg leads to significant distortions in the structure of calcite, as well as the prevention of mineral growth, if it is present in concentrations 4-8 mol%, but also influences the character of the bond between carbon and oxygen, transforming it to more ionic bonds. Even when present in the small concentrations there is a significant distortion of the defect-closest O atoms, thus developing local microstructures that are distinguished in comparison to the original structure of calcite mineral [33]. Results obtained from step velocity and terrace width measurements also indicate the inhibition of calcite growth due to the impact of Mg^{2+} . It is suggested that the increase in mineral solubility forms the underlying physical basis for the diminished growth rates of calcite that are noted in the presence of Mg^{2+} [35]. As a crystal form of calcium carbonate in mollusks, calcite is often associated with a significant amount of Mg that has an important role in the structure and mechanical properties of these organisms. $CaCO_3$ and $MgCO_3$ crystallize under ambient conditions in the hexagonal/rhombohedral R3c phase layered structure in which CO_3^{2-} planes alternate with cation (Ca^{2+} or Mg^{2+}) ones. The equilibrium structural and elastic characteristics are summarized in Table 1 for calcite and in Table 2 for magnesite together with previously calculated values and experimental data [7]. $CaCO_3$ uptake of Mg is controlled primarily by the crystal lattice structure and depending on its Mg content, calcite is classified as low-Mg or high-Mg calcite and this polymorph of calcium carbonate preferentially incorporates small divalent cations such as Mg, Fe, and Mn, whereas aragonite is more likely to incorporate larger cations such as Sr, Pb, and Ba. Due to the ionic radius of Mg that is suitable for incorporation into the calcite crystal lattice, it preferably coprecipitates with calcite. Hence, it is suggested that the presence of a significant amount of structurally substituted Mg in all biogenic calcite indicate that partial thermodynamic controls have a definite effect on the biogenic calcite final chemical composition [34].

Table 1. Theoretically predicted structural and elastic parameters of $CaCO_3$ in comparison with values obtained in previous theoretical studies and experiments (the equilibrium volume V (Å) of the 30-atom (6 formula units) supercells, corresponding bulk modulus B_0 , its pressure derivative B'_0 and C–O and Ca–O interatomic distances (Å) [7].

$CaCO_3$	$V/6$ f.u.(Å ³)	B_0 (GPa)	B'_0	C-O (Å)	Ca-O (Å)
This work	383.7	69.6	4.54	1.300	2.396
Previous calculations	364-386	73-75	4.63	1.270	2.415
	[36,37]	[36,37]	[37]	[37]	[37]
Exp.	367.8	80	-	1.283	2.354
	[38,39]	[38]	-	[12]	[12]

Table 2. Theoretically predicted structural and elastic parameters of MgCO_3 [7].

MgCO_3	$V/6 \text{ f.u. (}\text{\AA}^3\text{)}$	$B_0 \text{ (GPa)}$	B_0	C-O (Å)	Mg-O (Å)
This work	293.4	96	4.97	1.297	2.15
Previous	279.2	124	3.08	1.286	2.11
	[40]	[40]	[40]	[40]	[37]
Exp.	278.5	117		1.287	2.10
	[38]	[41]		[12]	[12]

In terms of the interatomic distances, it is claimed that within the CO_3^{2-} groups, distances are almost independent of the composition of the actual carbonate. The C-O distance differs only by 0.23% in CaCO_3 and MgCO_3 , with a bit smaller distance in the latter. Contrary, it is predicted that interatomic distances Ca-O or Mg-O differ substantially (10.82%), which can be explained because of the larger atomic radius of a Ca atom in comparison to an Mg atom. This is outlined in Table 3 as the volume per atom in the face-centered cubic (fcc) Ca ground state is almost two times larger than the corresponding volume in the experimentally observed ambient-condition ground state hexagonal close-packed (hcp) Mg. This difference in atomic radii also explains the growth of the bulk modulus with increasing Mg content at a slope of 0.3 GPa/at% Mg [7]. Different atomic radii are considered to be the cause of the isomorphous substitution of Ca and Mg atoms in the crystal lattice of biogenic aragonite that leads to the contraction of lattice parameters and is the same in both, biogenic as well as geologic calcite [42].

Table 3. Theoretically predicted equilibrium lattice parameters (in Å) and corresponding bulk moduli B (GPa) of fcc Ca and hcp Mg in comparison with (i) values obtained in previous theoretical studies employing both the VASP code and the all-electron full-potential WIEN2k package and (ii) experimental data [7].

	This study	WASP	WIEN2k	Exp.
α^{Ca} (Å)	5.53	5.49	5.55	5.59
		[43]	[43]	[44]
B^{Ca} (GPa)	17.3	-	-	17.0
V^{Ca} (Å ³ /atom)	42.3	41.4	42.7	43.7
		[43]	[43]	[44]
α^{Mg} (Å)	3.20	3.18	3.19	3.21
		[43]	[43]	[45]
c^{Mg} (Å)	5.18	5.17	5.18	5.21
		[43]	[43]	[45]
B^{Mg} (GPa)	35.5	34.8	-	35.4
		[46]		[47]
α^{Mg} (Å ³ /atom)	22.98	23.03	22.85	23.25
		[46]	[43]	[45]

All of the biogenic calcite spectra, regardless of the Mg content, suggested no drop in point symmetry when it comes to the substitution of Mg into Ca sites of the lattice. Regardless of the minor amount of organically bound Mg within the biogenic calcite, both the theoretical and experimental XANES spectra indicate that in each biogenic calcite, magnesium is mostly structurally substituted [34]. Calculated predictions suggest that Mg atoms in low concentrations do not lead to a destabilization of calcite crystals. Based on the ab initio results, it is suggested that in bio-composites that contain calcite within their structures, additions of Mg take place, because of their stiffening impact on the mechanical properties that unfortunately occurs at the expense of structural and thermodynamic stability [7]. There is a belief that biogenic calcite tends to be tougher and harder in comparison to geological calcite and the experimental results suggest that on the particular plane {001} biogenic calcite is 50 to 70% harder compared to geological calcite [49]. Even at low Mg concentrations, this element has a large impact on the increase of hardness of the calcite [29] and there is a suggestion that hardening mechanisms based on hindered dislocation motion could be responsible for the higher hardness and increased anisotropy in biogenic calcite [49]. It is suggested that within the crystallites, there are intra-crystalline organic molecules that are distributed in a regular way to be arranged with certain atomic groups and not randomly, as impurities. There is a consideration that these molecules improve crystal growth and possibly serve as calcium carbonate nucleation centers [42].

Conclusion

Due to their extraordinary features, shells of marine organisms were used as an inspiration for many novel materials. They are composed of calcium carbonate crystals interleaved with layers of viscoelastic proteins, having dense, tailored structures that yield excellent mechanical properties [48]. However, even though there are successfully created highly specialized, high-performance composite materials, replication of complexity, and elegance of most biological composites are still far away [1]. In order to study fundamental biological mechanisms and structures on the atomic scale, first-principles calculations based on quantum mechanics and density functional theory (DFT) as a versatile and accurate tool have recently evolved [27]. Theoretical investigations can be used as a supplement to experimental results and are especially valuable for exploring the properties of materials in cases when experimental work cannot be performed. However, as there is a lack of theoretical studies of biogenic carbonates present in mollusk shells, further work is needed, especially as these structures have a great potential for many applications within technology or medicine and can be used as a bioinspiration for new advanced materials.

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Izvod

TEORIJSKO ISTRAŽIVANJE LJUŠTURI MEKUŠACA: ISTRAŽIVANJE ENERGETSKIH PEJZAŽA POLIMORFA CaCO_3 I SUPSTITUCIJA ELEMENATA: KRATAK PREGLEDNI RAD

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Zbog izuzetnih svojstava koje postižu pri ambijentalnim uslovima i sa dosta ograničenim sastavnim elementima, školjke mekušaca su veoma privlačni prirodni biokompoziti koji se koriste kao inspiracija za nove napredne materijale. Kalcijum karbonat koji je među najrasprostranjenijim biomineralima, mekušci koriste i kao gradivni materijal koji čini 95-99% njihove ljuštore. U okviru ispitivanja polimorfa kalcijum karbonata prisutnih u ljušturama, rađena su različita teorijska i eksperimentalna ispitivanja, međutim, dalja istraživanja ovih kristalnih formi su neophodna. Postoji veoma malo istraživanja energetskog pejzaža biogenog kalcijum karbonata koji nam može pružiti informacije o slobodnim energijama već poznatih, kao i novo-otkrivenih mogućih struktura. U cilju ispitivanja strukturnih, mehaničkih, elastičnih ili vibracionih karakteristika, kao i u cilju predviđanja novih mogućih struktura biogenih kalcijum karbonata, mogu se primeniti različite metode proračuna. Neke od ovih studija su predstavljene i razmatrane u ovom radu.

Ključne reči: ljuštore mekušaca, biogeni kompoziti, kalcijum karbonat, energetski pejzaž, bioinspirisani materijali