

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



A Biomimetic Nano-Scale Aggregation Route for the Formation of Submicron-Size Colloidal Calcite Particles

Ivan Sondi^{*a}, and Srečo D. Škapin^b

^(a) *Laboratory for Geochemistry of Colloids, Center for Marine and Environmental Research, Ruđer Bošković Institute, Zagreb, Croatia (sondi@irb.hr)*

^(b) *Department for Advanced Materials, Jožef Stefan Institute, Ljubljana, Slovenia (sreco.skapin@ijs.si)*

1. Introduction

Carbonates are minerals that are frequently encountered in Nature, occurring as the main mineral constituents in rocks and sediments, and as the most common constituents of the bio-inorganic structures of the skeletons and tissues of many mineralizing organisms. The presence of bio-inorganic structures of calcium carbonate polymorphs within organisms has been intensively investigated in biology, mineralogy, chemistry, and material science (Addadi & Weiner, 1992; Ozin, 1997; Stupp & Braun, 1997; Meldrum & Cölfen, 2008) as well as in biological fields, primarily in zoology (Taylor et al., 2009) and evolutionary biology (Stanley, 2003).

The complex biomineral structures are formed through biomineralization processes, defined as the formation of inorganic crystalline or amorphous mineral-like materials by living organisms in ambient conditions (Mann, 2001; Bäuerlein, 2007). Many organisms have, during hundreds of millions of years of adaptation to the changing environment, developed their own evolutionary strategy in the formation of biominerals (Knoll, 2003). As a result, biomineralization has been a key to the historical existence of many species.

During the past decade, a number of published studies have shown that mineralizing organisms utilize the capabilities of macromolecules to initiate the crystallization process and to interact in specific ways with the surfaces of growing crystals (Mann, 1993; Falini et al., 1996; Stupp & Braun 1997; Falini, 2000; Tambutté et al., 2007). Several studies report evidence that many mineralizing organisms selectively form either intra- or extracellular inorganic precipitates with unusual morphological, mechanical, and physico-chemical properties (Falini et al., 1996; Mayers et al., 2008). These solids have surprisingly sophisticated designs, in comparison with their abiotic analogues, in particular, taking into account that they were formed at ambient pressure and temperature (Ozin, 1997; Skinner, 2005; Meldrum & Cölfen, 2008; Mayers et al., 2008). Their formation process is highly controlled, from the nanometer to macroscopic levels, resulting in complex hierarchical

architectures and shapes, providing superior multifunctional material properties (Stupp & Braun, 1997; Meldrum, 2003; Aizenberg, 2005).

The formation of biogenic calcium carbonate is controlled by organic molecules, mostly peptides, polypeptides, proteins, and polysaccharides, which are directly involved in regulating the nucleation, growth, and shaping of the precipitates (Elhadj et al., 2006a; DeOliveira & Laursen, 1997; Sondi & Salopek-Sondi, 2004). Recently published studies have shown that mineralizing organisms utilize the capabilities of such macromolecules to interact in specific ways with the surfaces of the growing crystals, manipulating their structural and physical properties (Teng et al., 1998; Volkmer et al., 2004; Tong et al., 2004). These materials are inspiring a variety of scientists who seek to design novel materials with advanced properties, similar to those produced by mineralizing organisms in Nature.

The mechanisms of the formation of unusual bio-inorganic mineral structures have been a discussion topic for years. Lately, a new concept, the particle-mediated, non-classical crystallization process in the formation of bio-inorganic, mesoscopically structured mesocrystals, was promoted (Cölfen & Antonietti, 2005; Wang et al., 2006). These structures are composed of nanoparticle building units, and characterized by a well-faceted appearance and anisotropic properties. This microcrystal concept is much more common in biomineralization processes than has been assumed up to now, while the number of new examples of the significance of mesocrystals in biomineral formation has significantly increased in recent years.

Precipitated calcium carbonate (PCC) solids have a wide variety of important uses in numerous industrial applications. They have long been recognized as versatile additives for use in a wide range of plastic and elastomeric applications, and in many medical and dietary applications and supplements. Presently, there is a need for new approaches to the preparation of high-activity, submicron-size PCC materials with desirable physical and chemical properties, using environmentally friendly materials and methods.

So far, only modest attention has been devoted to the formation of uniform and nearly spherical calcium carbonate colloidal particles, devoid of crystal habits and anisotropic properties, but still maintaining a crystal structure (Sondi et al., 2008). The aim of this chapter is to describe recent advances in the formation of well-defined and uniform submicron-size, nanostructured colloidal calcium carbonate particles, through the non-classical *biomimetic nanoscale aggregation route* and to identify some of the problems that still need to be addressed.

2. Bioinorganic structures - learning from Nature

A large number of organisms in Nature produce, either intracellularly or extracellularly, inorganic materials, mostly modified calcium carbonate polymorphs. The number of reported studies on their function, structure and morphology has recently been increasing. A comprehensive coverage of all such studies and of biomineral structures would be impractical in this chapter. Instead, an example of functional biomineralization will be given by presenting structures of coccolithophores and their inorganic coccosphere and coccoliths, some of the remarkable and omnipresent types of marine phytoplankton assemblies in Nature (March, 2007). These are characterized by intriguing structures that can offer an answer to the question of how organisms govern the formation of complex bioinorganic structures, and how these structures are adapted to the functions of these organisms.

The aim of the present contribution is to highlight the internal structures and surface morphology of coccolith at the nano-level. Figure 1 shows a scanning electron photomicrograph (SEM) of coccosphere from the sediments of a marine lake (Malo Jezero, in the island of Mljet, Adriatic Sea). Coccolith shows its typical complex morphological feature characterized by pervasive and consistent chirality and radial symmetry (Figure 1A). However, a fairly unique observation at higher magnification is that the structural elements of coccolith are built up of much smaller, nanosize subunits (Figure 1B-D). This finding suggests that some organisms have the ability to use neoclassical mechanisms in the formation of their biomineral structures, based on the aggregation of preformed nanosize particles.

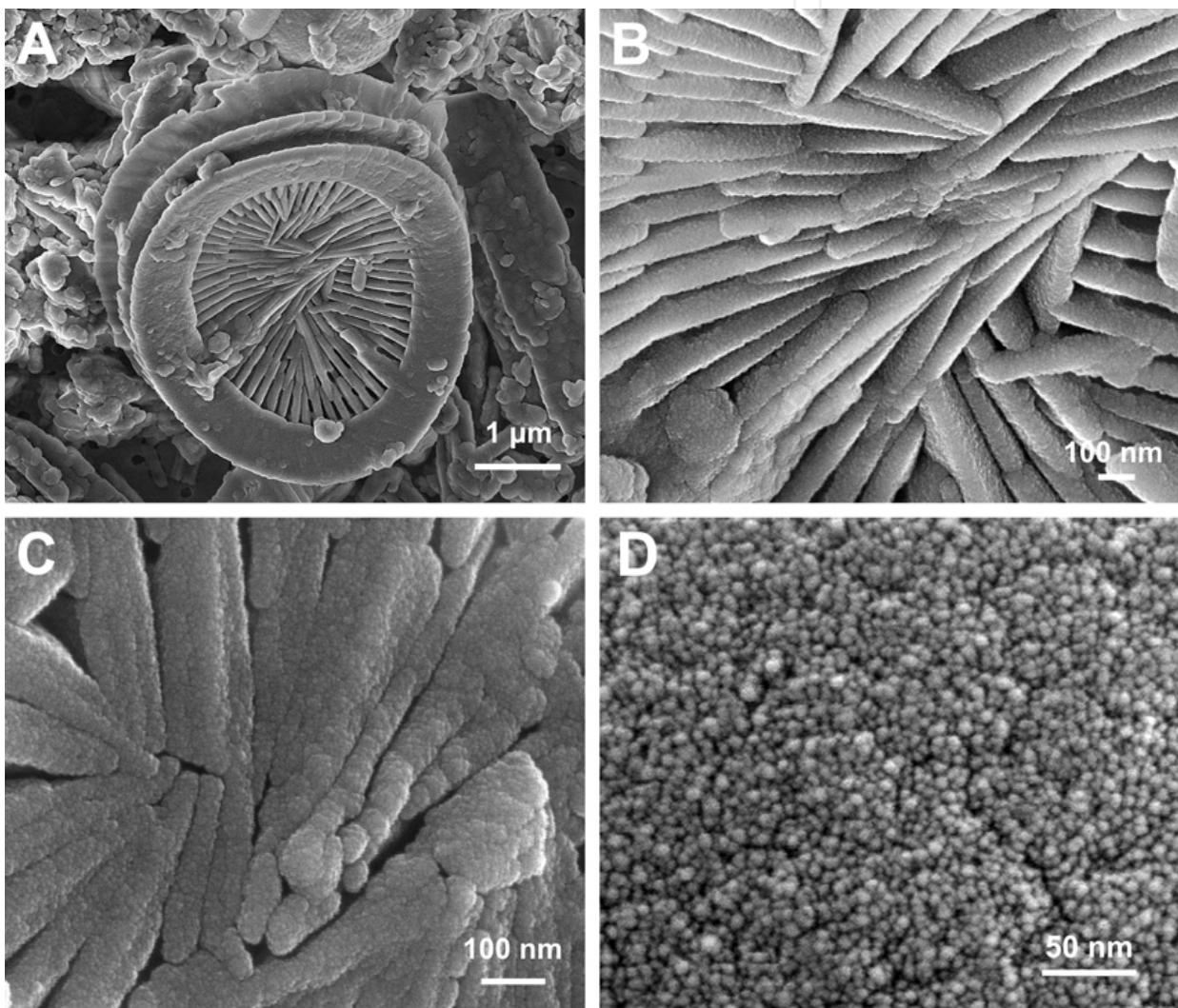


Fig. 1. SEM photomicrographs of coccosphere showing their (A) typical shape and morphology and (B-C) the composite nature of coccoliths at higher magnification. The sample originate from sediment from the marine lake of Malo Jezero on the island of Mljet, (Adriatic Sea). Unpublished illustrations.

The appearance of nanostructured biominerals in Nature is the rule rather than a chance event. Various other organisms base the functionality of their structural components on the

formation of nanostructured materials, functionally adapted to the living environment. Figure 2 shows an example of heterotrophic protozoa that build up their lorica from highly organized and nanostructured calcium carbonate solids.

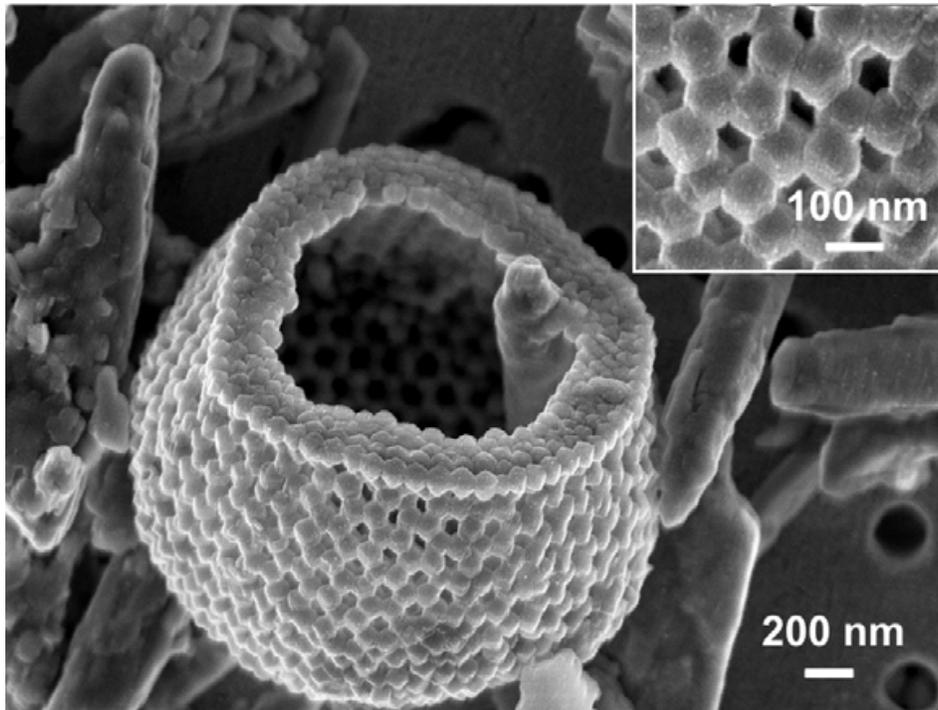


Fig. 2. SEM photomicrographs of heterotrophic protozoa showing the nanostructured shape of their lorica (the samples originate from the sediment of the marine lake of Malo Jezero on the island of Mljet, Adriatic Sea). Unpublished illustrations.

The findings obtained in natural systems have instigated laboratory experiments in producing carbonate materials by biomimetic precipitation processes. The methodology of the precipitation process, based on the aggregation of the preformed nanosize particles, is a way to produce uniform colloidal calcium carbonate solids.

3. Biomimetic formation of calcite particles

During recent decades tremendous progress in the preparation of a variety of colloids of simple and composite natures has been made. The general principles regarding the conventional formation of colloids of different structural, physical, and chemical properties have been established (Matijević, 1993). The search for innovative processing strategies to produce uniform precipitates of calcium carbonate of controlled size was advanced using the concepts and methodologies of biomimetic materials chemistry. This concept was defined by Mann (1993), who stated that *“the systematic fabrication of advanced materials will require the construction of architectures over scales ranging from the molecular to the macroscopic. The basic constructional processes of biomineralization - supermolecular pre-organisation, interfacial molecular recognition (templating) and cellular processing - can provide useful archetypes for molecular-scale building, or molecular tectonics in inorganic material chemistry”*. Some of the recent reviews have, in detail, described the biomimetic formation of carbonate solids, using

new concepts of microstructural processing techniques that either mimic, or are inspired by, biological systems (Meldrum, 2003; Cölfen, 2003; Yu & Cölfen, 2004; Xu et al., 2007).

A number of new methods and approaches, based on biomimetic processes and techniques, have been investigated and used in the preparation of calcium carbonate precipitates of different structural, morphological and surface properties. Some of them have been focused on exploring the promoting effect of matrices (templates) on the crystals' nucleation and growth (Popescu et al., 2007; Tremel et al., 2007). Several procedures have been developed, depending on the structural complexity of the templates used, such as self-assembled monolayers (Aizenberg et al., 1999; An and Cao, 2008), Langmuir monolayers (Heywood & Mann, 1994; Pichon et al., 2008), and gelatin films (Martinez-Rubi et al., 2008). Several studies have also shown that the formation of biogenic calcium carbonate structures is controlled by organic macromolecules (matrix proteins), mostly peptides and proteins, which are directly involved in regulating the nucleation, growth, and morphology of the precipitates. A variety of macromolecular additives, including proteins (Sarashina & Endo, 1998; Falini, 2000; Sondi & Salopek-Sondi, 2004), and designed peptides (DeOliveira & Laursen, 1997; Elhadj et al., 2006b; Gebauer et al., 2009), were reported. The bio-inspired production of calcium carbonates could also be accomplished by using soluble polymeric additives (Meldrum, 2003). Recently, a new class of additives was used, the double-hydrophilic block copolymers, for the effective control of the morphogenesis of inorganic precipitates in aqueous solutions, offering the possibility to obtain solids of uncommon morphologies (Sedlak & Cölfen, 2001; Cölfen, 2006).

Recently, following the protein templating concept, significant progress in the study of the bioinspired formation of calcium carbonates was accomplished through the use of catalytically active proteins, such as urease enzymes (Sondi & Matijević, 2001; Sondi & Salopek-Sondi, 2004). It was shown that during the homogeneous precipitation of carbonate solids by the urease-catalyzed reactions in aqueous solutions of calcium salts, nanosize calcite particles appeared during the early stages of the precipitation process. Following up on this work the new, bioinspired strategies for the preparation of uniform, nanostructured and submicron-size calcium carbonate solids were developed (Škapin & Sondi, 2005; Sondi et al., 2008).

Comprehensive coverage of this entire field of biomimetic material science would be impractical in this chapter. Rather, the main focus of this contribution is the role of catalytically active proteins. The complex biomimetic mechanism, acting on the crystal growth of initially formed nanocrystallites and subsequent aggregation that, finally, governs the formation of nanostructured submicron-size colloidal carbonate solids, will be discussed.

3.1. The use of urease in the formation of CaCO₃ precipitates - an overview

The first microbiological precipitation of calcium carbonate induced by urease (urea amidohydrolase, EC 3.5.1.5.), a multi-subunit, nickel-containing enzyme that converts urea to ammonia and CO₂, was described by Stocks-Fischer et al. (1999). The activity of urease in microbiologically induced calcite precipitation was also reported (Bachmeier et al., 2002). This enzyme, generated by many bacteria, certain species of yeast, and a number of plants, which allows these organisms to use exogenous and internally generated urea as a nitrogen source (Dixon et al., 1975). The chemical, structural, and surface properties and the mode of action of urease in the decomposition of urea have been described (Mobley & Hausinger,

1989; Estiu & Merz, 2004). It also appears that urease participates in systemic nitrogen-transport pathways and possibly acts as a toxic defense protein (Mobley & Hausinger, 1989). Urease, generated by certain pathogenic bacteria, during urinary tract infections, plays a significant role in the formation of intracellular urinary stones (Edinliljegren et al., 1994).

Recently, it was demonstrated that calcium carbonate polymorphs of different sizes and shapes can be obtained by homogeneous precipitation in solutions of calcium salts through the enzyme-catalyzed decomposition of urea by urease (Sondi & Matijević, 2001; Sondi & Salopek-Sondi, 2004). The role of urease in the formation of strontium and barium carbonates and their mixed compounds was also investigated (Sondi & Matijević, 2003; Škapin & Sondi, 2005). In addition to a catalytic function in the decomposition of urea, ureases also exert significant influence on the crystal-phase formation and shaping of carbonate precipitates. A recent study by the authors of this chapter has illustrated the role of the primary protein structures (amino acid sequences) of ureases on the phase formation and morphological properties of the obtained solids. As model substances, two ureases, the plant (*Canavalia ensiformis*) and the bacterial (*Bacillus pasteurii*) urease, were used in this study (Sondi & Salopek-Sondi, 2004). It was shown that despite a similar catalytic function in the decomposition of urea, these ureases exerted different influences on the crystal-phase formation and on the development of the unusual morphologies of calcium carbonate polymorphs. These differences were explained as a consequence of the dissimilarities in the amino acid sequences of the two examined ureases, causing their different roles in nucleation and physico-chemical interactions with the surface of the growing crystals. These studies have illustrated the diversity of the proteins produced by different organisms for the same function, and the drastic effects of subtle differences in their primary structures on the crystal-phase formation and the growth morphology of calcium carbonate precipitates.

3.2. Precipitation of nanostructured colloidal calcite particles by a biomimetic nanoscale aggregation route - the use of the urease enzyme as a protein-template model

Advances in the understanding of the physical and chemical principles of the formation of colloidal particles have greatly contributed to the scientific aspects of material science. It is interesting to point out, for example, that many forms of uniform colloids, built up of nanosize subunits, have been found in Nature. In considering the mechanisms of formation of colloidal materials over the range of the modal size, aggregation processes should be recognized as one of the common mechanisms (Petres et al., 1969; Lasic, 1993; Zukoski et al., 1996; Brunsteiner et al., 2005). This finding contradicts the commonly accepted classical precipitation mechanism, according to which uniform colloidal particles are formed when nuclei, arising from a short-lived burst, grow by the attachment of constituent solutes (Matijević, 1993).

Recently, a number of studies were carried out in order to employ the aggregation concept in the formation of inorganic colloids (Chow & Zukoski, 1994; Privman et al., 1999; Sondi et al., 2008). The significance of the aggregation process, in the formation of uniform colloidal particles from preformed nano-crystallites, was already observed by Težak and co-workers, in the late 1960s (Petres et al., 1969). However, this finding has long remained neglected. Recently, it has been theoretically and experimentally established that many colloids, prepared by precipitation from homogeneous solutions, are built up of nanosize subunits (Nakayama et al., 1995; Privman et al., 1999; Sondi & Matijević, 2001; 2003). Therefore, this mechanism was shown to be quite common in the formation of colloidal particles that show

crystalline characteristics. Nevertheless, there are only a few references dealing with the role of this mechanism in the precipitation of carbonates (Sondi et al., 2008; Song et al., 2009). This contribution underscores the importance of nanoscale aggregation processes in the formation of colloidal carbonate particles in the presence of model organic macromolecules (ureases), a situation commonly encountered in biomineralizing systems.

The processes of formation of bio-inorganic phases in biological systems are complex mechanisms that, almost as a rule, are characterized by several simultaneous events. An example of the complexity and of the importance of aggregation processes in the bio-inspired formation of calcium carbonate in simplified, laboratory conditions can be found in previously reported cases dealing with the role of catalytically active ureases (Sondi & Matijević, 2001; Sondi & Salopek-Sondi, 2004; Škapin & Sondi, 2005). This unique process of the biomimetic precipitation of uniform nanostructured colloidal calcite additionally explains the precipitation process based on the aggregation of preformed nanosize particles (Sondi et al., 2008).

The question is: how does the presence of urease macromolecules and of magnesium ions in the reacting solutions influence the formation of nearly spherical, submicron-size colloidal calcite particles? Obviously, the conditions under which such solids can be obtained are rather restrictive in terms of the concentration of urease, the reaction time, and the presence of magnesium and calcium salts. Details of the concentrations and methodologies used can be found elsewhere in the open literature (Sondi & Salopek-Sondi, 2004; Škapin & Sondi, 2005; Sondi et al., 2008).

In general, the process started by the rapid formation of the nanosize amorphous precursor phase is followed by simultaneous crystallization via the solid-state transformation pathway and the nanoscale aggregation processes. Three major phenomenological features, excluding the amply described decomposition of urea by urease, should be relevant in order to determine this process: (i) the role of urease macromolecules in the nucleation of the solid phase (templating), and their subsequent interaction with the inorganic phase at the solid-liquid interface, directing the growth of inorganic structures; (ii) the inhibitory effect of magnesium ions on the growth of nascent solids; and (iii) the subsequent aggregation of nanosize particles that governs the formation of submicron-size colloids.

Available reports indicate that protein macromolecules initiate the solid-phase formation, and control the crystalline nature and morphology of inorganic precipitates (Falini et al., 1996; Feng et al., 2000; Sondi & Salopek-Sondi, 2004; Xie et al., 2005; Yamamoto et al., 2008). These phenomena are the consequence of physico-chemical interactions between the active functional groups of organic macromolecules at their surface with the "building components" (ions, complexes) of the forming solids. The carboxyl-rich character of a protein, resulting from the abundance of negatively charged aspartic (*Asp*) and glutamic (*Glu*) acid residues is probably the most important factor in their biomineralization reactivity. Numerous studies have shown that these amino acids act as nucleation agents in solution and as primary active sites at the interface of organic/inorganic biomineralizing structures (Teng et al., 1998; Orme et al., 2001). The distribution of *Asp* and *Glu* on the surface of *C. ensiformis* urease is shown in the CPH model (Figure 3). Its amino acid sequence contains 12.8 % *Asp* and *Glu* residues. The initial formation of a nanosize, amorphous and metastable precursor phase may be the result of a strong interaction between the Ca^{2+} and *Asp* and *Glu* at the urease surface, forming $\text{Ca}^{2+}/\text{Asp}$ and $\text{Ca}^{2+}/\text{Glu}$ multi-carboxyl chelate complexes (Tong et al., 2004). This is in agreement with previous

studies which have shown that the *Asp* residue controls the rate of nucleation, inhibits the growth of solids and favors the formation of the amorphous phase (Aizenberg et al., 2001; Addadi et al., 2003).

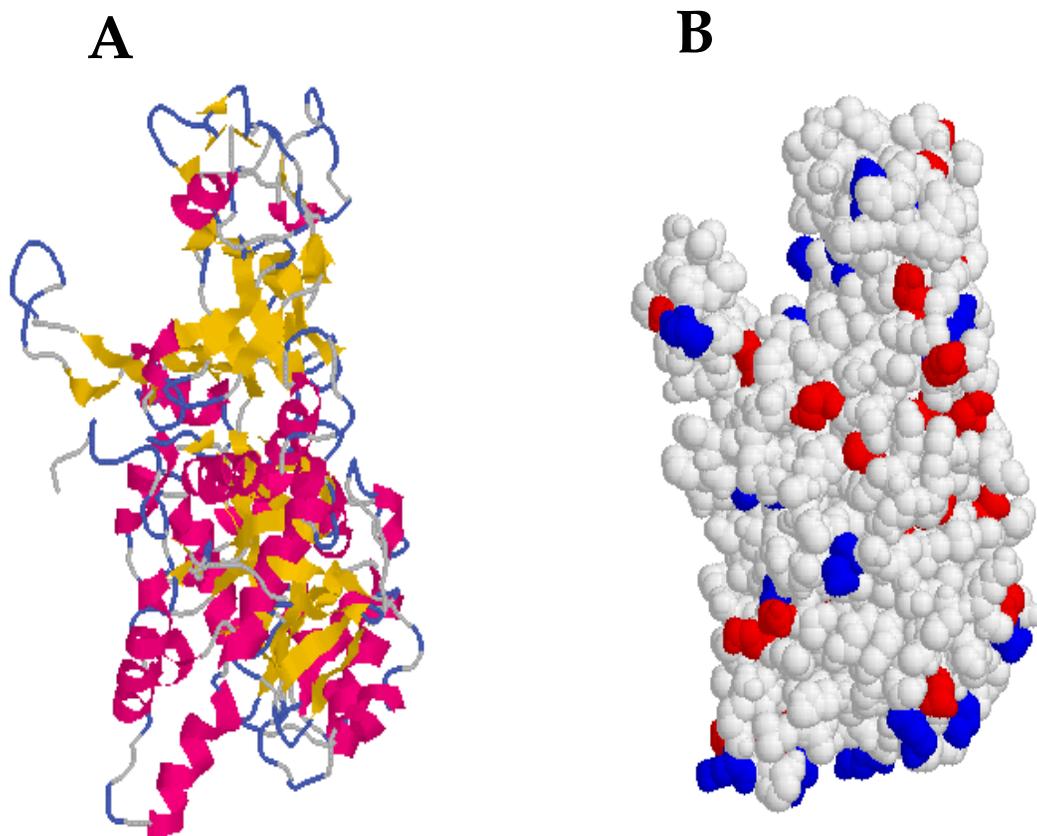


Fig. 3. CPH model of *C. ensiformis* urease (protein ID: AAA83831.1) showing (A) the tertiary structure of the protein displayed and colored according the secondary structure; (B) the distribution of *Glu* (blue) and *Asp* (red) residues on the surface of the urease molecule. The model was generated by using the Exspasy on-line program: CPH models - 2.0 for prediction of the protein tertiary structure and visualized by the RasWin 2.6 program. (Figure adapted from Sondi et al., 2008).

The presence and the activity of *Asp* and *Glu* are not sufficient to inhibit the future growth of the initially formed nanoparticles. Prolonged reaction times result in the formation of micron-size near-spheres and sequential-growth rhombohedra of calcite solids occurs (Figure 4 A-C). This observation is also corroborated by findings that, under what were otherwise the same experimental conditions, the growth of the initially formed nanoparticles was inhibited by magnesium ions (Figure 4D-F). This highlights the importance of the presence of magnesium ions during the formation of nanosize precipitates. Magnesium ions act as the main modifier of the calcite morphology in many natural environments (Davis et al., 2004). Meldrum and Hyde (2001) reported that magnesium ions, in combination with organic additives, affect the calcite morphology by adsorption to specific crystal faces, altering the nucleation and so inhibiting crystal growth.

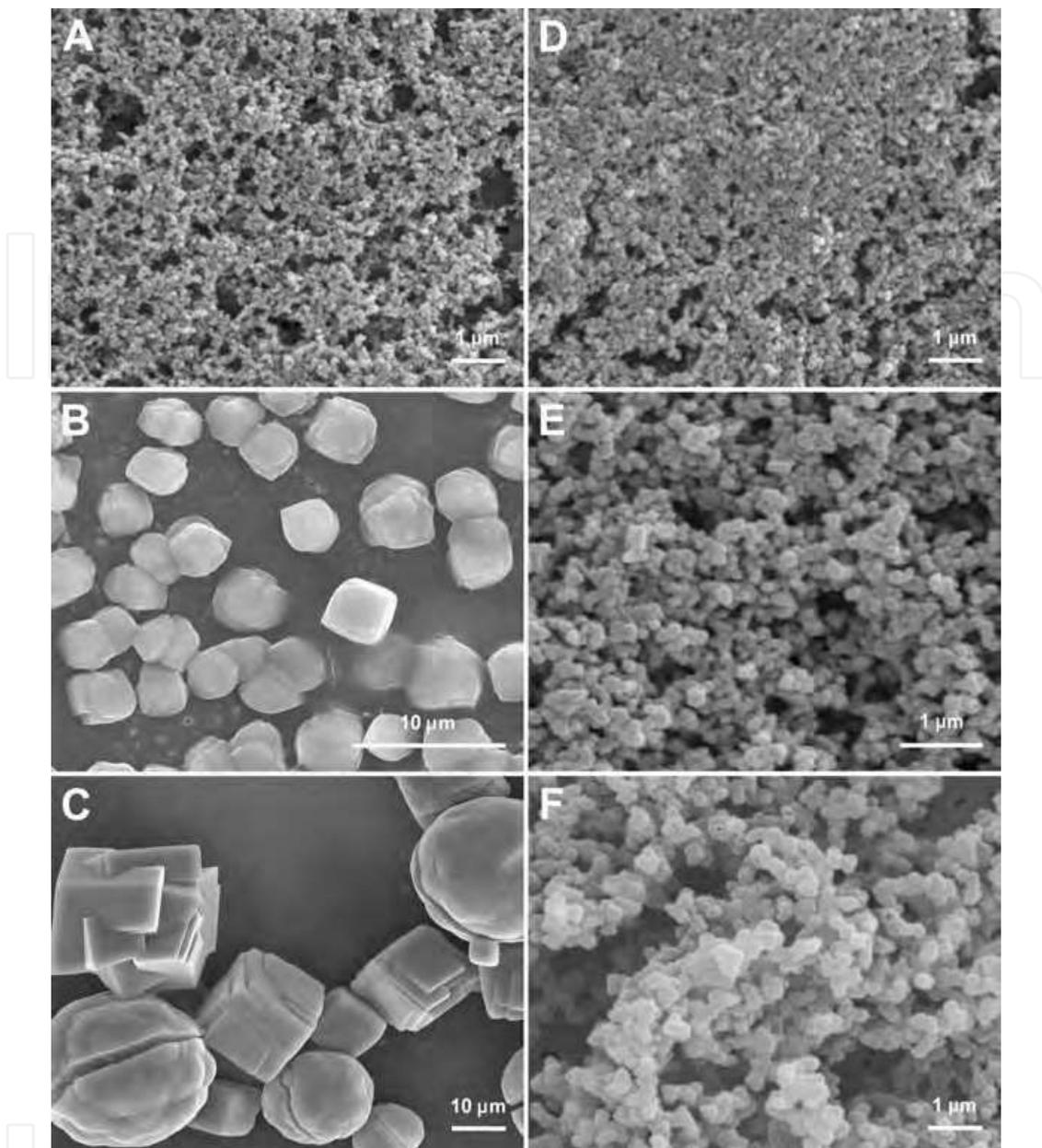


Fig. 4. Scanning electron micrographs (SEM) of calcium carbonate particles obtained by aging a solution containing 0.5 mol dm^{-3} urea, 0.25 mol dm^{-3} CaCl_2 , and 1 mg cm^{-3} *C. ensiformis* urease at $25 \text{ }^\circ\text{C}$ for (A) 10 min, (B) 30 min, and (C) 60 min, and precipitates obtained under the same experimental conditions and for the same aging time, but with the addition of 0.25 mol dm^{-3} MgCl_2 to a reacting solution (D-E). (Figure adapted from Sondi et al., 2008).

Molecular dynamic simulations (de Leeuw, 2002) are supporting evidence for the inhibitory effect of magnesium ions on calcite crystal growth. The above-described mechanisms determine the initial formation of nanosize calcium carbonate particles and inhibit their further growth.

In the final stage, the aggregation of preformed nanoparticles occurs in the reacting system. More detailed morphological and structural analyses of the obtained calcium carbonate spheroids, taken at a higher TEM magnification (Figure 5), show them to be built of slightly textured nanosize subunits that, according to the XRD data, exhibit the calcium carbonate

structure. Recently, a number of experimental and theoretical studies have dealt with mechanisms of the formation of colloidal particles by the aggregation of preformed nanosize precursors. In spite of the significant contributions of these research results, most of these models have been based on a number of simplifying assumptions (Privman et al., 1999). Often, the role of the surface charge of the particles was neglected. For nanoparticles, the charge and the extent of their electrical double layer should be a major initiator of the aggregation processes (Kallay & Žalac, 2002). Our studies have shown that a negative charge, measured on the precipitates, can be assumed to originate from the charge of the same sign on the nanoparticles (Sondi et al., 2008). Since the aggregation obviously does occur, the conclusion is that the prevailing electrostatic barrier is ineffective for preventing the aggregation of the initially formed nanoparticles, the number of which in the reacting solution is continuously increasing. Indeed, it has also been shown that nanometer-scale particles cannot be stabilized by the electrostatic repulsion barrier, at the same mass, but at a higher number concentration (Kallay & Žalac, 2002). The reason for this is that these aggregate more rapidly than the larger colloidal particles. Theoretically, the main reason is the small size of the nanoparticles in comparison to the extent of their diffuse double layers. These diffuse layers overlap entirely, and the interaction between the nanoparticles can be considered as an interaction between ions. The consequence is a rapid aggregation of the preformed nanoclusters, and the formation of complex nanostructured submicron-scale spheres.

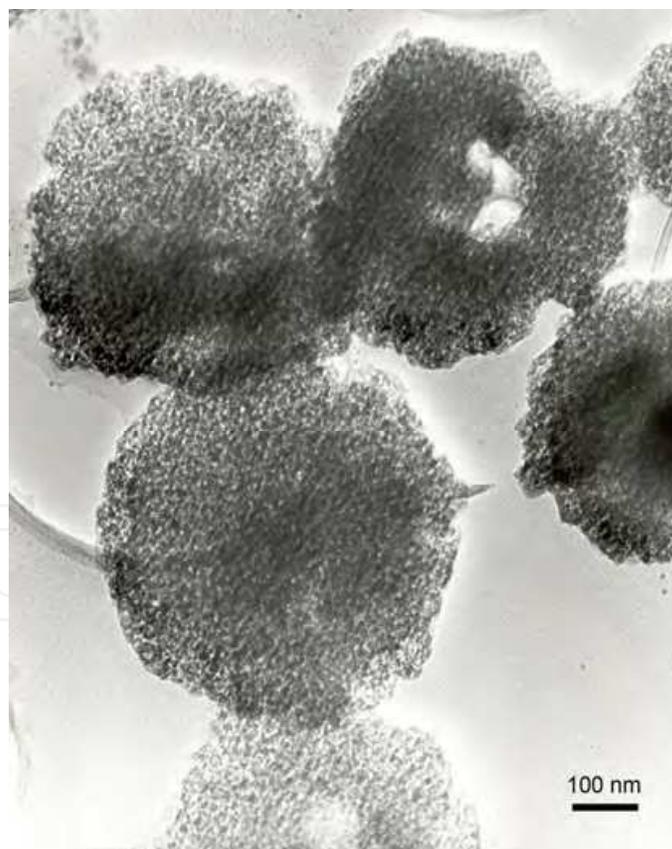


Fig. 5. Transmission electron micrograph (TEM) of spherical calcium carbonate particles obtained by aging a solution containing 0.5 mol dm^{-3} urea, 0.25 mol dm^{-3} CaCl_2 , 0.25 mol dm^{-3} MgCl_2 , and 1 mg cm^{-3} *C. ensiformis* urease at $25 \text{ }^\circ\text{C}$ for 60 min (corresponding SEM micrographs are shown in Figure 4F). (Figure adapted from Sondi et al., 2008).

4. Conclusion

This chapter aims to contribute to the understanding of the biomimetic mechanism for the synthesis of uniform and submicron-size colloidal particles of calcium carbonate. A novel, bio-inspired precipitation strategy, designated as the *biomimetic nano-scale aggregation route*, in the formation of these precipitates was discussed. This concept involves: (i) the use of functional templates, proteins, which are implicated in controlling the nucleation of solids; (ii) the inhibitory effect of magnesium ions on the crystal growth of initially formed nanocrystallites; and (iii) the subsequent aggregation of these particles that governs the formation of submicron-size and nanostructured hierarchical structures of colloidal carbonates. Understanding these mechanisms may lead to new strategies for the synthesis of novel calcium carbonate solids and to an improved insight into the sequestration of the inorganic components in the skeletons and tissues of mineralizing organisms.

5. Reference

- Addadi, L. & Weiner S. (1992). Control and design principles in biological mineralization. *Angewandte Chemie International Edition in English*, 31, 153-169, ISSN 0570-0833.
- Addadi, L., Raz, S., & Weiner, S. (2003). Taking advantage of disorder: Amorphous calcium carbonate and its roles in biomineralization. *Advanced Materials*, 15, 959-970, ISSN 0935-9648.
- Aizenberg, J. (2005). A bio-inspired approach to controlled crystallization at the nanoscale. *Bell Labs Technical Journal*, 10, 129-141, ISSN 1089-7089.
- Aizenberg, J., Black, A.J. & Whitesides, G.H. (1999). Oriented growth of calcite controlled by self-assembled monolayers of functionalized alkanethiols supported on gold and silver. *Journal of the American Chemical Society*, 121, 4500-4509, ISSN 0002-7863.
- Aizenberg, J., Lambert, G., Weiner, S. & Addadi L. (2001). Factors involved in the formation of amorphous and crystalline calcium carbonate: A study of an Ascidian skeleton. *Journal of American Chemical Society*, 124, 32-39, ISSN 0002-7863.
- An, X.Q. & Cao, C.B. (2008). Coeffect of silk fibroin and self-assembled monolayers on the biomineralization of calcium carbonate. *Journal of Physical Chemistry C*, 112, 15844-15849, ISSN 1932-7447.
- Bachmeier K.L., Williams, A.E., Warmington, J.R. & Bang S.S. (2002). Urease activity in microbiologically-induced calcite precipitation. *Journal of Biotechnology*, 93, 171-181, ISSN 0168-1656.
- Bäuerlein, E. (2007). Growth and form: What is the aim of biomineralization?, In: *Handbook of Biomineralization - Biological Aspects and Structure Formation*, E. Bäuerlein (Ed.), 1-20, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN 978-3-527-31804-9.
- Brunsteiner, M., Jones, A.G., Pratola, F., Price, S.L. & Simons, S.J.R. (2005). Toward a molecular understanding of crystal agglomeration. *Crystal Growth & Design*, 5, 3-16, ISSN 1528-7483.
- Chow, M.K. & Zukoski C.F. (1994). Gold sol formation mechanisms-role of colloidal stability. *Journal of Colloid and Interface Science*, 165, 97-109, ISSN 0021-9797.
- Cölfen, H. (2003). Precipitation of carbonates: recent progress in controlled production of complex shapes. *Current Opinion in Colloid and Interface Science*, 8, 23-31, ISSN 1359-0294.

- Cölfen, H. (2007). Bio-inspired mineralization using hydrophilic polymers. *Topics in Current Chemistry*, 271, 1-77. ISBN 978-3-540-32151-4.
- Cölfen, H. & Antonietti, M. (2005). Mesocrystals: Inorganic superstructures made by highly parallel crystallization and controlled alignment. *Angewandte Chemie-International Edition*, 44, 5576-5591, ISSN 1433-7851.
- Davis, K.J., Dove, P.M., Wasylenki, L.E. & De Yoreo, J.J. (2004). Morphological consequences of differential Mg^{2+} incorporation at structurally distinct steps on calcite. *American Mineralogist*, 89, 714-720, ISSN 0003-004X.
- de Leeuw, N.H. (2002). Molecular dynamic simulations of the growth inhibiting effect of Fe^{2+} , Mg^{2+} , Cd^{2+} , and Sr^{2+} on calcite crystal growth. *Journal of Physical Chemistry B*, 106, 5241-5249, ISSN 1089-5647.
- DeOliveira, D.B. & Laursen, R.A. (1997). Control of calcite crystal morphology by a peptide designed to bind to a specific surface. *Journal of American Chemical Society*, 119, 10627-10631, ISSN 0002-7863.
- Dixon, N.E., Gazzola, C., Blakeley, R.L. & Zerner, B. (1975). Jack-bean urease (EC 3.5.1.5)-matalloenzyme - simple biological role for nickel. *Journal of American Chemical Society*, 97, 4131-4133, ISSN 0002-7863.
- Edinliljegren, A., Grenabo, L., Hedelin, H., Pettersson, S. & Wang, Y.H. (1994). Long-ter, studies of urease-induced crystallization in humane urine. *Journal of Urology*, 152, 208-212, ISSN 0022-5347.
- Elhadj, S., De Yoreo, J.J., Hoyer, J.R. & Dove, P.M. (2006a). Role of molecular charge and hydrophilicity in regulating the kinetics of crystal growth. *Proceedings of the National Academy of Science of the United States of America*, 103, 19237-19242, ISSN 0027-8424.
- Elhadj, S., Salter, E.A., Wierzbicki, A., De Yoreo, J.J. & Dove, P.M. (2006b). Peptide controls on calcite mineralization: Polyaspartate chain length affects growth kinetics and acts as a stereochemical switch on morphology. *Crystal Growth & Design*, 6, 197-201, ISSN 1528-7483.
- Estiu, G. & Merz K.M. (2004). Enzymatic catalyses of urea decomposition: Elimination or hydrolysis? *Journal of the American Chemical Society*, 126, 11832-11842, ISSN 0002-7863.
- Falini, G. (2000). Crystallization of calcium carbonates in biologically inspired collagenous matrices. *International Journal of Inorganic Chemistry*, 2, 455-461, ISSN 1466-6049.
- Falini, G., Albeck, S., Weiner, S. & Addadi, L. (1996). Control of aragonite or calcite polymorphism by mollusk shell macromolecules. *Science*, 271, 67-69, ISSN 0036-8075.
- Feng, Q.L., Pu, G., Pei, Y., Cui, F.Z., Li, H.D. & Kim, T.N. (2000). Polymorph and morphology of calcium carbonate crystals induced by proteins extracted from mollusk shell, *Journal of Crystal Growth*, 216, 459-465. ISSN 0022-0248.
- Gebauer, D., Verch, A., Borner, H.G. & Cölfen, H. (2009). Influence of selected artificial peptides on calcium carbonate precipitation - A quantitative study. *Crystal Growth & Design*, 9, 2398-2403, ISSN 1528-7483.
- Heywood, B.R. & Mann, S. (1994). Molecular construction of oriented inorganic materials-controlled nucleation of calcite and aragonite under compressed Langmuir monolayers. *Chemistry of Materials*, 6, 311-318, ISSN 0897-4756.

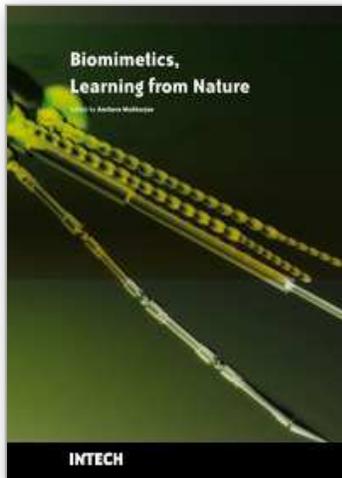
- Kallay, N. & Žalac S. (2002). Stability of nanodispersions: A model for kinetics of aggregation of nanoparticles. *Journal of Colloid and Interface Science*, 253, 70-76, ISSN 0021-9797.
- Knoll, A.H. (2003). Biomineralization and evolutionary history. *Reviews in Mineralogy and Geochemistry*, 54, 329-356, ISSN 1529-6466.
- Lasic, D.D. (1993). On the formation of inorganic colloid particles. *Bulletin of the Chemical Society of Japan*, 66, 709-713, ISSN 0009-2673.
- Loste, E., Wilson, R.M., Seshadri, R., & Meldrum, F.C. (2003). The role of magnesium in stabilizing amorphous calcium carbonate and controlling calcite morphology. *Journal of Crystal Growth*, 254, 206-218, ISSN 0022-0248.
- Mann, S. (1993). Molecular tectonics in biomineralization and biomimetic material chemistry. *Nature*, 365, 499-505. ISSN 0028-0836.
- Mann, S. (2001). *Biomineralization-principles and concepts in bioinorganic material chemistry*. Oxford University Press, ISBN 0-19-850882-4, New York.
- March, M. E. (2007). Regulation of Coccolith calcification in *Pleurochrysis carterae*. In: *Handbook of Biomineralization- Biological Aspects and Structure Formation*, E. Bäuerlein (Ed.), 211-226, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN 978-3-527-31804-9.
- Martinez-Rubi, Y., Retuert, J., Azdani-Pedram, M., Barbosa, M. & Arias, J.L. (2008). Nucleation and selective growth of polymorphs of calcium carbonate on organic-inorganic hybrid films. *Journal of the Chilean Chemical Society*, 53, 1353-1357, ISSN 0717-9324.
- Matijević, E. (1993). Preparation and properties of uniform size colloids. *Chemistry of materials*, 5, 412-426, ISSN 0897-4756.
- Mayers, M.A., Chen, P.-Y., Lin, A. Y.-M. & Seki, Y. (2008). Biological materials: structure and mechanical properties. *Progress in Materials Science*, 53, 1-206, ISSN 0079-6425.
- Meldrum, F.C. & Cölfen, H. (2008). Controlling mineral morphologies and structures in biological and synthetic systems. *Chemical Reviews*, 108, 4332-4432, ISSN 1520-6890.
- Meldrum, F.C. & Hyde, S.T. (2001). Morphological influence of magnesium and organic additives on the precipitation of calcite. *Journal of Crystal Growth*, 231, 544-558, ISSN 0022-0248.
- Meldrum, F.C. (2003). Biomimetic control of calcification. *International Materials Reviews*, 48, 187-224, ISSN 0950-6608.
- Mobley, H.L.T. & Hausinger, R.P. (1989). Microbial ureases-significance, regulation, and molecular characterization. *Microbiological Reviews*, 53, 85-108, ISSN 0146-0749.
- Nakayama, T., Nakahara, A. & Matsushita, M. (1995). Cluster-cluster aggregation of calcium carbonate colloid particles at the air-water interface. *Journal of the Physical Society of Japan*. 64, 1114-1119, ISSN 0031-9015.
- Orme, C.A. Noy, A., Wierzbicki, A., McBride, M.T., Grantham, M., Teng, H.H., Dove, P.M. & DeYoreo, J.J. (2001). Formation of chiral morphologies through selective binding of amino acids to calcite surface steps. *Nature*, 411, 775-779, ISSN 0028-0836.
- Ozin, G.A. (1997). Morphogenesis of biomineral and morphosynthesis of biomimetic forms. *Accounts of Chemical Research*, 30, 17-27, ISSN 0001-4842.
- Petres J.J., Dežalić, Gj. & Težak B. (1969). Monodisperse sols of barium sulfate. 3. Electron-microscopic study of internal structure of particles. *Croatica Chemica Acta*, 41, 183-198, ISSN 0011-1643.

- Pichon, B.P., Bomans, P.H.H., Frederik, P.M. & Sommerdijk, N.A.J.M. (2008). A quasi-time-resolved CryoTEM study of the nucleation of CaCO₃ under Langmuir monolayers. *Journal of the American Chemical Society*, 130, 4034-4040, ISSN 0002-7863.
- Popescu, D.C., Smulders, M.M.J., Pichon, B.P., Chebotareva, N., Kwak, S.Y., van Asselen, O.L.J., Sijbesma, R.P., DiMasi, E. & Sommerdijk, N.A.J.M. (2007). Template adaptability is a key in the oriented crystallization of CaCO₃. *Journal of the American Chemical Society*, 129, 14058-14067, ISSN 0002-7863.
- Privman, V., Goia, D.V., Park, J. & Matijević, E. (1999). Mechanism of formation of monodispersed colloids by aggregation of nanosize precursors. *Journal of Colloid and Interface Science*, 213, 36-45, ISSN 0021-9797.
- Sarashina, I. & Endo, K. (1998). Primary structure of soluble matrix protein of scallop shell: Implication for calcium carbonate biomineralization. *American Mineralogist*, 83, 1510-1515, ISSN 0003-004X.
- Sedlak, M. & Cölfen, H. (2001). Synthesis of double-hydrophilic block copolymers with hydrophobic moieties for the controlled crystallization of minerals. *Macromolecular Chemistry and Physics*, 202, 587-597. ISSN 1020-1352.
- Skinner, H.C.W. (2005). Biominerals. *Mineralogical Magazine* 69, 621-641, ISSN 0026-461X.
- Sondi, I. & Matijević E. (2001). Homogenous precipitation of calcium carbonate by enzyme catalyzed reactions. *Journal of Colloid and Interface Science*, 238, 208-214, ISSN 0021-9797.
- Sondi, I. & Matijević, E. (2003). Homogeneous Precipitation by enzyme-catalyzed reactions. 2. Strontium and barium carbonates. *Chemistry of Materials*, 15, 1322-1326, ISSN 0897-4756.
- Sondi, I. & Salopek-Sondi, B. (2004). The influence of the primary structures of urease enzyme on the formation of CaCO₃ polymorphs: A comparison of plant (*Canaavia ensiformis*) and bacterial (*Bacillus pasteurii*) ureases. *Langmuir* 21, 8876-8882, ISSN 0743-7463.
- Sondi, I., Škapin, S.D. & Salopek-Sondi B. (2008): Biomimetic precipitation of nanostructured colloidal calcite particles by enzyme-catalyzed reactions in the presence of magnesium ions. *Crystal Growth & Design*, 8, 435-441, ISSN 1528-7483.
- Song R.Q., Cölfen, H., Xu, A.W., Hartmann, J. & Antonietti, M. (2009). Polyelectrolyte-directed nanoparticle aggregation: Systematic morphogenesis of calcium carbonate by nonclassical crystallization. *ASC Nano*, 3, 1966-1978, ISSN 1936-0851.
- Škapin, S.D. & Sondi, I. (2005). Homogeneous precipitation of mixed anhydrous Ca-Mg and Ba-Sr carbonates by enzyme-catalyzed reactions. *Crystal Growth & Design*, 5, 1933-1938. ISSN 1528-7483.
- Stanley, D.G. (2003). The evolution of modern corals and their early history. *Earth-Science Reviews*, 60, 195-225, ISSN 0012-8252.
- Stocks-Fischer, S., Galinat, J.K. & Bang, S.S. (1999). Microbial precipitation of CaCO₃. *Soil Biology and Biochemistry*, 31, 1563-1571, ISSN 0038-0717.
- Stupp, S.I. & Braun, P.V. (1997). Molecular manipulation of microstructures: Biomaterials, ceramics, and semiconductors. *Science*, 277, 1242-1248, ISSN 0036-8075.
- Takeuchi, T., Sarashina, I., Lijima, M. & Endo, K (2008). In vitro regulation of CaCO₃ crystal polymorphism by the highly acidic molluscan shell protein Aspein. *FEBS Letters*, 582, 591-596, ISSN 0014-5793.

- Tambutté, S., Tambutté, E., Zoccola, D. Allemand, D. (2007). Organic matrix and biomineralization of scleractinian corals. In: *Handbook of Biomineralization - Biological Aspects and Structure Formation*, E. Bäuerlein (Ed.), 243-259. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN 978-3-527-31804-9.
- Taylor, P. D., James, N.P., Bone, Y., Kuklinsky, P. & Kyser, T. K. (2009). Evolving mineralogy of Cheilostome bryozoas. *Palaios*, 24, 440-452, ISSN 0883-1351.
- Teng, H.H., Dove, P.M., Orme, C.A. & De Yoreo, J.J. (1998). Thermodynamics of calcite growth: Baseline for understanding biomineral formation. *Science*, 282, 724-727, ISSN 0036-8075.
- Tong, H., Ma, W.T., Wang, L.L., Wan, P., Hu, J.M. & Cao, L.X. (2004). Control over the crystal phase, shape, size and aggregation of calcium carbonate via L-aspartic acid including process. *Biomaterials*, 25, 3923-3929, ISSN 0142-9612.
- Tremel, W., Küther, J., Balz, M., Loges, N. & Wolf, S.E. (2007). Template surfaces for the formation of calcium carbonate. In: *Handbook of Biomineralization- Biomimetic and Bioinspired Chemistry*, P. Behrens & E. Bäuerlein (Eds.), 209-232, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN 978-3-527-31804-9.
- Volkmer, D., Fricke, M., Hubar, T. & Sewald, N. (2004). Acidic peptides acting as growth modifiers of calcite crystals. *Chemical Communications*, 16, 1872-1873, ISSN 1359-7345.
- Wang, T.P., Antonietti, M. & Cölfen, H. (2006). Calcite mesocrystals: "Morphing" crystals by a polyelectrolyte. *Chemistry-A European Journal*, 12, 5722-5730, ISSN 0947-6539.
- Xie, A.J., Shen, Y.H., Zhang, C.Y., Yuan, Z.W., Zhu, X.M. & Zang, Y.M. (2005). Crystal growth of calcium carbonate with various morphologies in different amino acid systems. *Journal of Crystal Growth*, 285, 436-443, ISSN 0022-0248.
- Xu, A.-W., Ma, Y. & Cölfen, H. (2007). Biomimetic mineralization. *Journal of Material Chemistry*, 17, 415-449, ISSN 0959-9428.
- Yamamoto, Y., Nishimura, T., Sugawara, A., Inoue, H., Nagasawa, H. & Kato, T. (2008). Effects of peptides on CaCO₃ crystallization: Mineralization properties of an acidic peptide isolated from exoskeleton of cryfish and its derivatives. *Crystal Growth & Design*, 8, 4062-4065, ISSN 1528-7483.
- Yu, S.-H. & Cölfen, H. (2004). Bio-inspired crystal morphogenesis by hydrophilic polymers. *Journal of Material Chemistry*, 14, 2124-2147, ISSN 0959-9428.
- Zukoski C.F., Rosenbaum, D.F. & Zamora, P.C. (1996). Aggregation in precipitation reactions: Stability of primary particles. *Chemical Engineering Research & Design*, 74, 723-731, ISSN 0263-676

IntechOpen

IntechOpen



Biomimetics Learning from Nature

Edited by Amitava Mukherjee

ISBN 978-953-307-025-4

Hard cover, 534 pages

Publisher InTech

Published online 01, March, 2010

Published in print edition March, 2010

Nature's evolution has led to the introduction of highly efficient biological mechanisms. Imitating these mechanisms offers an enormous potential for the improvement of our day to day life. Ideally, by bio-inspiration we can get a better view of nature's capability while studying its models and adapting it for our benefit. This book takes us into the interesting world of biomimetics and describes various arenas where the technology is applied. The 25 chapters covered in this book disclose recent advances and new ideas in promoting the mechanism and applications of biomimetics.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Ivan Sondi and Sreco D. Skapin (2010). A Biomimetic Nano-Scale Aggregation Route for the Formation of Submicron-Size Colloidal Calcite Particles, *Biomimetics Learning from Nature*, Amitava Mukherjee (Ed.), ISBN: 978-953-307-025-4, InTech, Available from: <http://www.intechopen.com/books/biomimetics-learning-from-nature/a-biomimetic-nano-scale-aggregation-route-for-the-formation-of-submicron-size-colloidal-calcite-part>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen