Chapter 4
The Circle: Biomineralization-Demineralization-Remineralization in Nature

Abstract The mineral-biomacromolecule cycle can be divided into three fundamental stages namely: (i) biomineralization; (ii) demineralization and (iii) remineralization occurring in various organisms and environments. It is obvious that equilibrium between demineralization and biomineralization is required. Therefore, in the biomineralogy these two processes should be considered as two sides of the same coin. Interestingly, the reagents of both natural and artificial origins, mechanisms and principles of chemical dissolution that have been reported to exist in natural environments discussed in this chapter comparatively.

In biological systems which are involved in biomineralization, the alternative process known as demineralization also occurs. Demineralization remains to be one of the fundamental processes in nature (Ehrlich et al. 2008, 2009, 2010). It takes place both in organisms as well as in the surrounding environment (Liu and Lim 2003).

Demineralization is based on removing mineral ions from hard tissues of organisms (physiological and pathological demineralization) and from the hard substrates (rocks) in the case of bioerosion. Artificial demineralization deals with the dissolution of mineral phases under laboratory conditions with the aim to isolate corresponding organic matrix using chemical reagents. Physiological demineralization has been well studied in animal and human organisms, including marine invertebrates. Traditionally, significant attention has been paid tooth development, resorption of bone tissue and fracture healing (Ehrlich et al. 2008, 2009). For example, tooth caries and bone remodeling in vivo share the same initial step – "dissolution of the inorganic phase by the generation of low pH solutions" (Collins et al. 2002), nevertheless the origin of demineralization processes in both hard tissues are diverse.

It is well recognized that bioerosion in marine environment, which is based on mechanical abrasion, biologically mediated demineralization and physicochemical dissolution, has history as long as that for biomineralization (Wisshak et al. 2005; Davidson et al. 2018). Consequently, both ancient and modern bioerosion of limestones, shells and corals (including coral reefs) remains to be in trend.

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Three routes of demineralization in the natural environment with respect to biomineralized structures have been recognized as follows:

- *Chemical deterioration of the organic phase;*
- *Chemical deterioration of the mineral phase*
- *Biological (microorganisms, enzymes) attack of the composite*. (Collins et al. 2002)

The first of these three pathways occurs in environments that are geochemically stable for the inorganic component due it is extremely difficult to dissolve or alter the organic phase without first or simultaneously effecting the closely associated mineral phase. Although this kind of biocomposite destruction may yield useful biomolecular information because rates of biomolecular deterioration in the burial environment are rather slow. In the majority of environments, biocomposites undergo total chemical deterioration what is related with the lack of thermodynamic equilibrium with the soil solution. The dissolution of mineral "shield" reveals the biomacromolecules to deterioration by microbes (biodeterioration), thus in most cases after the dissolution of the initial phase microbial attachment occurs (the third pathway).

The phenomenon of dark decalcification is another example of naturally occurring demineralization (Tentori and Allemand 2006). Kawaguti and Sakumoto (1948) observed "output of Ca^{2+}" in all scleractinian corals exposed to dark and in "intake of Ca^{2+}" all corals exposed to light. Authors claimed that the formation of skeleton occurs preferentially at alkaline pH (8.84–9.15). The decrease of pH to 8.00–7.80 under exclusion of light resulted in "*resolution of the* skeleton [sic]" (Kawaguti and Sakumoto 1948). Phenomenon of dark decalcification, which has been observed in coralline algae located at various depths Chisholm (2000). It was suggested that this is the result of acidification caused by cell respiration or the previous light exposure. It is also possible that the decalcification was due to tissue injury as well as tissue recovery verified visually underwater was overestimated. It was proved that such soft corals species as *Sinularia* sp. and *Sarcophyton* sp.) possess dark decalcification. According to Tentori and Allemand (2006), "diurnal calcification–decalcification cycles may be responsible for controlling coral sclerite shape and size in both species".

However, principles, mechanisms as well as the agents of chemical dissolution that take place or are found in natural environments described above appear parallel to clarification of demineralization which takes place in vitro. According to Ehrlich and co-workers, understanding of the mechanisms underlying of natural demineralization will give us possibility to develop subtle demineralization techniques for identification of biomacromolecules involved in biomineralization and understand the mechanism of this fascinating phenomenon (Ehrlich et al. 2008).

Diverse biological systems "*seem to create specialized environments in together with the biomineralized tissues formations and probably have been doing so since life first appeared*" (Skinner 2005). It is to note that both biomineralization and demineralization are rather two components of the mineral–biomacromolecule cycle which has been founded in these specialized local environments in nature (Fig. 4.1). Consequently, remineralization remains to be the third component of this biochemical cycle.

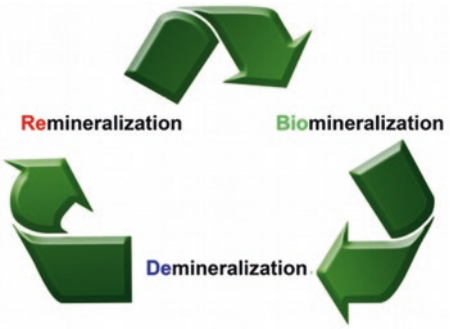

Fig. 4.1 Schematic representation of "biomineralization–demineralization–remineralization" circle which occurs in natural environment

According to our definition, "*remineralization is the process of rebuilding the solid minerals – throughout the transfer of cations and anions– to sites of nucleation where the lattices leading to mineral structures are generated. Remineralization usually follows demineralization and can be observed both in vivo in a host of natural environments*" (Ehrlich et al. 2009).

Interesting example of remineralization of foraminiferan tests in natural environments has been described by Le Cadre et al. (2003). If a specimen of *Ammonia beccarii* with a partially demineralized test was put to a solution at normal pH, organism was capable to regenerate this structure. Remineralization was accompanied, in most cases, by morphological abnormalities, which was the main difference for original calcification (e.g. different chamber sizes, wall with concave structure, abnormal expansions). Such structural abnormalities can be also caused by ocean acidification including anthropogenic impacts. Recalcification phenomenon has been also described for the spicules of gorgonian coral *Leptogorgia virgulata* (Watabe et al. 1986). It was reported that under selected conditions, exposed organic matrices from demineralized spicules, may induce the remineralization with respect to ($CaCO_3$) and impact on the mineral form (Watabe et al. 1986).

Also the formation of crystalline hydroxylapatite structures in the remineralized human enamel has been observed (Tohda et al. 1990). Recently, Neel et al. (2016) made a review on dynamics of demineralization-remineralization in bone and teeth.

The understanding of the driving forces and mechanisms of biomineralization–demineralization–remineralization related processes at the molecular level will open the way to evaluate more advanced methods for the developing of new medical tools and approaches.

4.1 Principles of Demineralization: Isolation of Organic Matter

Traditionally, scientists who have the task to isolate some organic matrix from biomineral-based structure (i.e. bone, teeth, shells, spicules, etc.) take the decision with respect to some "quick and deep" demineralization technique. However such

kind of demineralization is usually based on aggressive chemicals (i.e. HF) which led to partial, or complete destruction of both mineral as well as organic phases and to obtaining of artifacts (Ehrlich et al. 2010). For instance according to remark made by Croce and co-workers, using of hydrofluoric acid for dissolution of biosilica might have strong impact on the molecular structure of spicular proteins from Hexactinellida (Croce et al. 2004). Consequently, in 2008 we have proposed the following strategy: "*the isolation of an organic component from any natural biomineralized material whether mineralized with silica- or calcium-containing compounds is crucial, however in our minds the most effective and efficient method should be based on a slow, biomimetically inspired process that could spare the organic component in the biomineral-based naturally occurring composites and not result in artefacts, instead of fast dissolution of the inorganic component*"(Ehrlich et al. 2008, 2009, 2010).

Interestingly that Nature uses similar, long-term strategy of gentle biological demineralization. For example, diverse unicellular (Garcia-Pichel 2006) and metazoan organisms show so called *calcibiocavicole* activity (Carriker and Smith 1969) with respect to calcium carbonate-based substrates to get access for the organic nutrients hidden under the mineral cover (Carriker and Smith 1969). Diverse aerobic heterotrophic bacteria as well as nitrifying and sulphide-oxidizing strains can synthesize carbonic, organic, nitric, and sulphuric acids, respectively, and in this way may dissolve acid-labile minerals (Ehrlich 1996). Diverse organic acids are secondary metabolites produced by fungi and lichens in soils could change pH in weathering solutions and in result inhibit or promote etching (Kalinowski et al. 2000).

Organic compounds may act as chelators for metal cations in solution, lowering the saturation index in solution and inhibit precipitation or enhance dissolution. Diverse organic ligands can also adsorb onto the surface of corresponding minerals (rock). So called ligand-promoted dissolution has been reported for oxides (Pokrovsky et al. 2005), carbonates (Pokrovsky and Schott 2001; Jordan et al. 2007) and silicates (Golubev et al. 2006; Golubev and Pokrovsky 2006).

Boring marine foraminiferans are reported for bioeroding capability to infest various organic and inorganic substrates (Venec-Peyre 1996; Venec-Peyre 1987; Wisshak and Rüggeberg 2006).

Also some species of sponges (Porifera) are related to bioeroding organisms. According to Zundelevich and co-workers the biological reason of bioeroding activity of poriferans is based on "*the strategy to carve into the carbonate subgrade that is unreachable for majority of predators, with the subsequent advantage of using a space out of reach to their competitors*" (Zundelevich et al. 2007). Especially representatives of the Clionidae family, which bore in the calcareous rocks, valves of living and dead molluscs, as well as corals, remain to be typical bioeroders (Cobb 1969; Risk et al. 1995; Calcinai et al. 2000; Schönberg 2002a, b, 2006). As reported by Cobb special type of amebocytes possess that are able for etching of calcareous materials forming cavities and tunnels (Cobb 1969). It has been suggested (Pomponi 1980) that in bioeroding sponges such enzymes as carbonic anhydrases and phosphatases are involved in this process. It cannot be excluded that also symbiotic zooxanthellae (Vacelet 1981; Schönberg 2006), however Zundelevich and co-

authors suggested that these unicellular organisms have no impact on the boring rate of sponges (i.e. *Pione cf. vastifica* (Zundelevich et al. 2007).

Annelids have been also reported as bioeroders (Lunz 1940; Haigler 1969; Blake and Evans 1973; Liu and Hsieh 2000). For example, a small polychaete *Polydora websteri* known also as „*a pest of bivalves"* (Lunz 1940) lives in the shells of oysters and is able to penetrate "*all layers of the oyster shell*"(Haigler 1969). Blake and Evans proposed following mechanisms for *Polydora* caused bioeroding: (i) chemical – involving specific glands able for secreting of acidic solutions and in consequence dissolving the substrates; and (ii) mechanical, where the modified setae on the 5th setiger scrape the substrate. Both chemical and mechanical mechanisms can occur synergistically (Blake and Evans 1973).

Another polychaete, *Polydora villosa* has been reported habituating only in living corals colonies (Liu and Hsieh 2000). This species are able to produce so-called the U-sharped passages (Williams and Margolis 1974).

Some gastropod species are known as bioeroders of the bivalves (Carriker (1961); Carriker and Williams (1978); Carriker et al. (1967, 1974). According to Carriker and his group, the bioeroding mechanism includes two alternating phases:

(i) *chemical, in which an accessory boring organ (ABO) or demineralization gland, secretes an uncharacterized substance that etches and weakens the shell at the site of penetration;*
(ii) *mechanical, during which the radula rasps off and swallows some of the weakened shell as minute flakes*. (Ehrlich et al. 2009)

Troschel (1854) described, for the first time the ABO in *Dolium galea* (Naticidae). Schiemenz (1891) first proposed that this ABO excretes an acid. Ankel (1937), hypothesized the presence of a *calcase*, special enzyme with location within ABO. According to Carriker and Williams "*a combination of various chelating agents, enzymes and HCl in a hypertonic mucoid secretion discharged by the ABO dissolve shell during boring of hole*" (Carriker and Williams 1978).

In these experiments, the fine structure of shell etched by the excretion was compared with shell artificially solubilized and normal shell. As a standard for ultrastructural interpretations of the dissolution pattern, a synoptic series of scanning electron photographs of model regions of the normal shell of *Mytilus edulis* were prepared (Carriker 1978). It was proposed that, ABO excretion, which leads to favored dissolution of the shell matrix is functionally beneficial to boring gastropods what is related to increasing of the surface area of mineral phase exposed to the etching and enables discharge of shell units from surface of the borehole by the radula.

Scleractinians mostly located in shallow-water subtropical to tropical reefs. Majority of them calcify promptly and are present on reefs as a consequence of symbiosis with zooxanthellae. They are one-celled algal symbionts, which exist in the endodermal tissues of their coral host. Their existence is responsible for stimulating promptly calcification (Stanley 2003). Lately, approach of coral dissolution and physiological response for increased atmospheric CO_2 was presented by Fine and Tchernov (2007). Thirty coral fragments of the scleractinian Mediterranean species from the five coral colonies, were cultivated in the seawater (pH equaled 7.3–7.6 or 8.0–8.3 (ambient)) for 12 months, at the temperature of seawater, in the flow-through indoor system with photoperiod. After 30 days in acidic environment,

the changes in morphology of corals were well visible, especially the elongation of the polyp, as well as the colony dissociation followed by total dissolution of the skeleton. Interestingly, after 1 year, and moving back to the natural conditions, the investigated polyps were able to calcify and rebuild the colonies.

Furthermore, Johnston (1980) notified that a contradistinction could be done between "skeletal organic material" as well as "skeletal organic matrix", and implied that the first is related to the skeletal organic matrix and all other contaminating components like trapped tissues and endoliths. Therefore, to prevent this kind of contamination, the corals chemical treatment was rigorously carried out using powders of skeletons (usually prepared with bleach and/or sodium hydroxide) in attempt to obtain only the skeletal organic matrix. Cuif et al. (1999) described the common procedure. In this study they used 24 species of corals from different environments, including deep and/or cold seas and tropical lagoons of Polynesian atolls. Coral samples were exactly washed using sodium hypochlorite, cleaned with water, and dried in oven (40 °C) overnight. Then, samples were powdered. The obtained powder was thoroughly calibrated in order to adjust the decalcification, which was carried out in standardized conditions. To conduct the characterizations of full sequence of mineralizing matrix, powder (3 g) was suspended in ultrapure water (25 ml) under constant magnetic stirring, and in next step ultra-pure acetic acid under permanent pH control was added to begin decalcification. After the complete dissolution of inorganics, a low-speed centrifugation was applied to separate soluble and insoluble matrices. The desalination of soluble components was carried out using low-pressure standard system on Sephadex G25 gel-based, which allows removing the low molecular organic compounds. These two succeeding preparation steps have an important role in obtaining reliable biochemical information, because this method leads to remove majority of the insoluble external contaminants as well as low-weight soluble compounds (Cuif et al. 1999).

In comparative study on *Stylophora pistillata* leafy complex coral, widely known as *Pavona cactus*, branched robust coral, or hood coral, the same decalcification method was applied (Puverel et al. 2005). It was proved that soluble organic matrix of both coral species consist of high amounts of glycine and other acidic amino acids. Although, the results of the proteins SDS–PAGE analysis obtained from soluble organic matter and proportions of glycosaminoglycans differed from each other. For each species, sequences of internal peptide of two matrix proteins were obtained. However, *S. pistillata* sequence is extraordinary because it is consisted of a long poly-aspartate domain, as noticed for proteins from molluscan species and proteins belonging to the calsequestrin family.

Nowadays, it is recognized that such enzymes as carbonic anhydrase (Chave 1984), phosphoprotein phosphatase (Kreitzman et al. 1969; Kreitzman and Fritz 1970), vacuolar-type H+-ATPase (Ziegler et al. 2004) as well as alkaline phosphatase, play crucial roles in biomineralization/demineralization/remineralization phenomena. Alkaline phosphatase detaches phosphorous from organophosphorous compounds, while carbonic anhydrase increases the rate in the CO_2–H_2O reactions system. Both of them can be commonly found in phosphate and carbonate sites of mineralization, as well as in the majority of noncalcifying sites and organisms.

Recently, it has been discovered that *Didymosphenia geminata* nuisance diatoms are able to biosynthesize a network of calcite nanofibers within their adhesive stalks (Ehrlich et al. 2016). The nanofibrous framework in the mineralized polysaccharide matrix is responsible for the mechanical support to the stalks. Biomineralization is controlled by periplasmic carbonic-anhydrases (CAs). CAs in microalgae are mainly responsible for the regulation of carbon concentrating mechanisms and respiratory functions in response to environmental CO_2 changes, but in multicellular organisms their additional functions of decalcification were described (for review see Ehrlich et al. 2009; Meyran et al. 1987; Tresgurres et al. 2013). The activity of external carbonic-anhydrase was identified to be more than 50% of the total CAs activity; this highlights its role in anchoring this bioeroding diatom on hard surfaces and controls availability of calcium ions. Therefore, it has been suggested that the formation of $CaCO_3$ (calcite) within the adhesive stalks of *D. geminata* is driven by the activity of external CAs (Ehrlich et al. 2016).

Enzymatic demineralization is not only limited to calcium carbonates and phosphates, surprisingly enzymatic desilicification is also occurring in natural environments. Indeed, demineralization of biosilica on the surface of the spicules of *Suberites domuncula* marine demosponge can be observed using SEM (Fig. 4.2.). It has been suggested that special enzyme termed as silicase remains to be able to depolymerise amorphous SiO_2 (Schröder et al. 2003).

Based on its intriguing ability to dissolve or to etch siliceous substrates, the silicase is of interest for biotechnology. Isolation, purification as well as cloning of the gene encoding silicase are patented (Müller et al. 2007).

Thus, the natural mechanisms of demineralization are discussed above. Below I will describe briefly the present state of the art with the man-made approach.

Application of aqueous solutions of HF for chemical wet etching of silicate glasses is an important issue which has been evaluated for many years. The first report derives from the HF discovery by Scheele in 1771 (Scheele 1771). The presence, in solution of HF, the fluorine-containing species such as HF_2, HF, and F^-, are responsible for attack and etching the glass surface. The mechanism of dissolution, and the role of the various fluorine-containing species are excellently described and discussed by Spierings (1991, 1993).

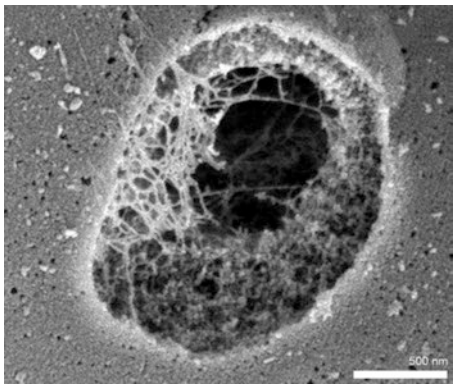

Fig. 4.2 Naturally occurring desilicification of the surface of *Suberites domuncula* demosponge spicule. (SEM image courtesy Carsten Eckert)

HF has been used in dissolution of biosilica since nineteenth century. As pointed out early by Bütschli (1901), this express method may produce artifacts (Kono et al. 1992; Croce et al. 2004; Schröder et al. 2006). However, the structural organic matrix was described for *Euplectella* sp. spicules that had been treated using HF gas (Travis et al. 1967). Also, silicateins were isolated from siliceous spicules of *Tethya aurantia* by treatment with the HF/NH_4F (Cha et al. 1999). Despite the reported formation of artefacts, the HF-based deminieralization protocols are still in use (Weaver and Morse 2003).

The use of HF to dissolve biosilica of the diatoms (Brunner et al. 2009) (Fig. 4.3) and sponges origin is represented in details in few reviews (Ehrlich et al. 2010; Ehrlich 2011; Wysokowski et al. 2018). Remarks on corresponding "collateral damages" due to the use of HF for isolation of organic matrices from skeletal structures of diverse biological objects are also to be found in these works.

In order to overcome diverse possible obstacles which could be related to HF-based dissolution of biosilica, alternative, slow-etching approach with the use of alkaline (mostly 2.5 M NaOH) solutions has been developed in 2006 (Ehrlich et al. 2006).

The following mechanism can be put forth on the basis of the reaction of alkaline desilicification of organic-silicon materials (Fig. 4.4.). Hydroxyl ions primarily attack and subsequently break the stronger siloxane bonds (Si–O–Si) located on the surface of the siliceous component.

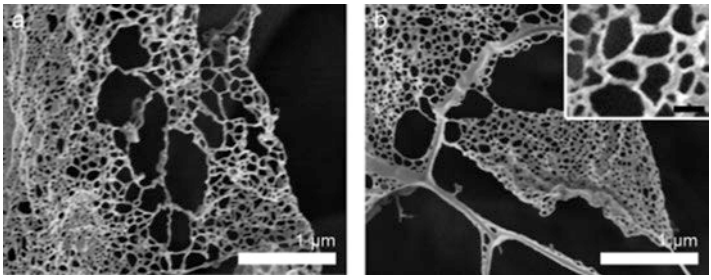

Fig. 4.3 SEM imagery: NH_4F-based demineralization in vitro of the *T. pseudonana* diatom frustule leads to isolation of filigree network (**a**, **b**) made of chitin nanofibers

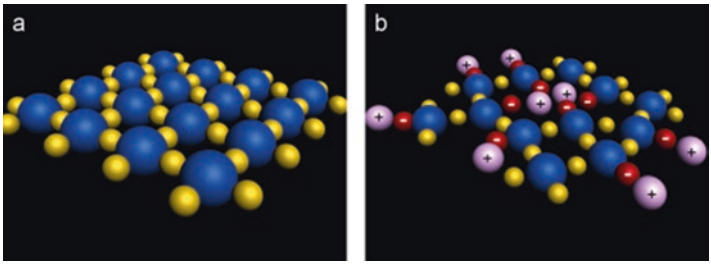

Fig. 4.4 Schematic view of the alkali-silica-reaction (left – crystalline, right – amorphous silica)

The positively charged alkali cations are able to balance the negative charge which is a consequence of bond breakage:

$$\mathrm{Si-O-Si+2NaOH \rightarrow 2Si-O-Na+H_2O}$$

The mechanism of alkaline desilicification reaction is related to the penetration of SiO_2 particles by hydroxide ions, which lead to lessening of the latter structure. This kind of the lattice disintegration using alkaline solution is practically impossible for the highly crystallized structures such as quartz; but, the amorphous silicates (likeopal A) can be easily digest because of the presence of particles with irregularly open structure and increased surface area (Ferraris 1999).

4.2 Conclusion

The process of demineralization is related to removal of inorganic part of the biominerals in organisms, and takes place in nature via chemical, physiological or pathological pathways. Naturally occurring demineralization known as bioerosion provides chemical deterioration of the mineral and organic phase using organic and inorganic acids, chelators as well as diverse specialized enzymes. Bioeroders are represented by endolithic unicellular (bacteria, cyanobacteria, fungi) and multicellular (sponges, annelids, mollusks, echinoids and fish. Artificial demineralization (in vitro) is aimed to obtain understanding of location, structure, nature and possible role of the organic matrix within skeletal structures as biocomposites (Fig. 4.5). Today, development of especially effective but gentle methods of demineralization remains to be still in trend.

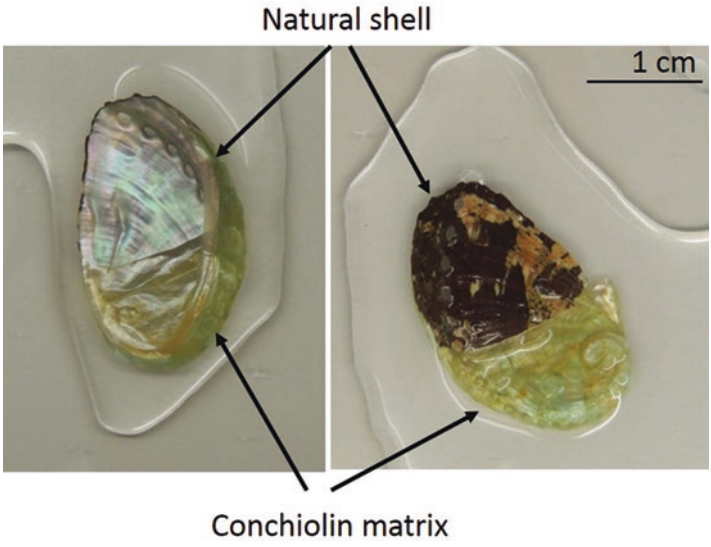

Fig. 4.5 Partial demineralization of the abalone shell using EDTA-solution at room temperature leads to visualization of the mineral-free organic matrix

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