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58. Biomineralization in Marine Organisms

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This chapter describes biominerals and the marine organisms that produce them. The proteins involved in biomineralization, as well as functions of the biomineralized structures, are treated. Current and future applications of bioinspired material synthesis in engineering and medicine highlight the enormous potential of biomineralization in marine organisms and the status, challenges, and prospects regarding successful marine biotechnology.

58.1 Overview

Marine biotechnology has huge potential across a broad spectrum of applications, ranging from biomedicine to the environment. However, marine biotechnology has not yet matured into an economically significant field [58.1]:

> *Fundamental knowledge is lacking in areas that are pivotal to the commercialization of biomedical products and to the commercial application of biotechnology to solve marine environmental problems, such as pollution, ecosystem disease, and harmful algal blooms.*

One of the recommendations of the 2002 report of the Ocean Studies Board and the Board on Life Sciences is that better tools should be developed for the use of marine biotechnology to help solve environmental problems such as biofouling, pollution, ecosystem degradation, and hazards to human health.

This chapter gives a functional approach to biomineralization in marine organisms. It presents the materials that are biomineralized (which include simple precipitated minerals, biologically produced perfect crystals, and composites of minerals and an organic matrix with interesting new properties) and the proteins that are important in biomineralization, gives an overview of some of the thousands of marine organisms that produce such materials, including information on the respective biomineralized structures and their functions, and finally presents current and possible future applications of bioinspired material synthesis in engineering (including mining) and medicine.

One of the amazing properties of biomineralization in organisms is that material, structure, and function are strongly correlated. Biominerals are highly controlled in structure, composition, shape, and organization, and can yield new, more benign approaches in engineering. The complex shapes of biominerals cannot be explained with simple mechanistic models of crystal growth [58.2].

Biotechnologists, material scientists, biologists, geologists, engineers, and medical doctors have long been fascinated by mineral structures in organisms. Now, with highly developed measurement devices at our disposal, we can investigate and understand biological materials, structures, and processes, and increasingly produce related bioinspired analogs [58.3].

Minerals are usually stiff, brittle, and cheap energy wise. Organic materials are soft and pliable. The synergistic combination of both yields biominerals with amazing functionalities, with a lightweight organic frame (which saves metabolic energy), filled with *cheap* inorganic material (e.g., calcium carbonate), yielding inorganic-organic hybrids (biocomposites) with well-defined mechanical properties [58.4].

Biominerals have functional structures and shapes, e.g., curved teeth and light baskets. The organic matrix acts as a meditator of mineralization and as crystal modifier. Characteristics of materials produced by controlled biomineralization are uniform particle sizes, well-defined structures and compositions, high levels of spatial organization, complex morphologies, controlled aggregation and texture, preferential crystallographic orientation, and higher-order assembly into hierarchical structures.

In contrast to most other biological transformations, biomineralization leaves far-reaching effects on the biosphere and lithosphere, including traces such as bones, shells, and fossils, but also mountain ranges and cliffs [58.5]. Biomineralization has implications on the global scale, via the Earth sciences. It is important in the global cycling of elements, in sedimentology, in fossilization (paleontology and taxonomy), in marine chemistry, and in geochemistry [58.4].

In the course of biomineralization, mineral products (biominerals) are created in organisms. Biomineralization has been around since the first Prokaryota appeared in the Archaean, the geological aeon from about 4 to 2.5 billion years ago. Biomineralization is of high interest to biologists and also to engineers, material scientists, and tissue engineers.

Biomineralization is characterized by interesting chemical reactions involving proteins, the creation of perfect crystals, the control of crystal growth and inhibition depending on the crystallographic axis, as well as the production of composite materials with properties that are of high value to engineering. Many biological fluids are supersaturated with respect to certain inorganic minerals, but crystals do not form spontaneously. An example of such crystal growth inhibition is saliva; it is supersaturated with respect to hydroxyapatite formation, yet teeth do not grow continuously. The overgrowth is prevented by phosphoprotein macromolecules that bind to enamel crystals.

Solubility controls biomineralization. Organisms produce hard parts by exceeding the solubility of the mineral component. Increased CO_2 in the oceans increases carbonate mineral solubility, making biomineralization of calcium carbonate structures more difficult. Many of these calcium carbonate biomineralizing organisms are important parts of the marine food chain.

The number of marine biomineralizers is vast. There are 128 000 species of molluscs, 700 species of calcareous green, red, and brown algae, more than 300 species of deep-sea benthic foraminifera, and 200 000 diatom species [58.6].

Biomineralization describes the formation of organized mineral structures through highly regulated cellular and molecular processes. Examples of biomineralized materials are enamel (97% mineral) and dentin (70% mineral), as well as bone (70% mineral). Crystal formation takes place in two steps: crystal nucleation (requires a high degree of saturation) and crystal growth (requires lower degree of saturation).

58.1.1 Marine Biomining

Current methods of mining are, in many cases, not environmentally sustainable. It might be interesting to focus on bio-assisted ways of obtaining resources such as Fe, Al, and Ti from marine environments (Table 58.1) [58.7]. All kinds of microbes contribute actively to geological phenomena, and central to many such geomicrobial processes are transformations of metals and minerals. Bioremediation is the use of biological systems for the clean-up of organic and inorganic pollution, with bacteria and fungi being the most important organisms for reclamation, immobilization, or detoxification of metallic and radionuclide pollutants [58.8].

Table 58.1 Concentration of transition metals and zinc in seawater (after [58.11], original references after [58.12–14])

Element	Seawater (M) × 10^8
Fe	0.005–2
Zn	8.0
Cu	1.0
Mo	10.0
Co	0.7
Cr	0.4
V	4.0
Mn	0.7
Ni	0.5

Biomining is the use of microorganisms and plants (phytomining) to aid in the extraction and recovery of metals from ores [58.9]. The microorganisms that grow in this aerobic, lithotrophic, and acidic environment are usually chemolithoautotrophic, using reduced forms of sulfur and iron, and acidophilic [58.10, p. 307].

Microorganisms themselves might be very beneficial in this kind of approach or processes inspired by biological processes that go on in biomineralizing organisms [58.15, 16]. The usage of controlled microbial cultures in order to concentrate certain minerals and ores was discussed already in 1972 [58.17]. It might be worth reconsidering such ideas, with the increased knowledge of biomineralization and environmental impact, as well as the novel methodologies that we now have at our disposal.

Bacteria that are active in marine microbial corrosion are promising with respect to marine mining. *Acidithiobacillus ferrooxidans*, for example, lives in pyrite deposits, metabolizes iron and sulfur, and produces sulfuric acid. *Acidithiobacillus thiooxidans* consumes sulfur and produces sulfuric acid. Both of these bacteria are already used as catalysts in bioleaching, whereby metals are extracted from their ores through oxidation. *Sulfobacillus* sp. are ferrous-iron and mineral-sulfide-oxidizing bacteria. *Sulfurivirga caldicuralii* is a microaerobic, thermophilic, thiosulfate-oxidizing chemolithoautotroph that is related to pyrite, arsenical pyrite, and chalcopyrite. The archaea *Sulfolobus shibitae, Metallosphaera* sp. and *Acidianus infernus* are related to chalcopyrite [58.18].

> *In low-temperature, aqueous habitats with oxygen, bacteria can affect the dissolution or precipitation of minerals through their reduction or oxidation of compounds containing Mn, Fe, S, C, U, Cu, Mo, Hg, and Cr* [58.10, p. 306].

Certain organisms are involved in the deposition of marine minerals, e.g., bacteria in deep-sea polymetallic nodules and coccoliths in seamount crusts [58.19]. Biosynthesis and bioleaching, i. e., extraction of specific metals from their ores through the use of bacteria and further organisms, are of increasing importance.

Limestone and other fixed carbonates represent 1.8×10^{22} g carbon in the Earth's lithosphere [58.20]. 40% of the Earth's limestone deposits that were previously thought to be of abiotic origin are, in fact, the consequence of heterotrophic bacterial metabolism [58.21], which thus emphasizes the role of microbial mineralization (carbonation) in the process of locking atmospheric and organic carbon as carbonate rocks back to the Earth's lithosphere, a long-term carbon storage compartment. While the precipitation of carbonate leads to CO_2 release in the ocean, this reaction must be considered in terms of final balance, as the buried sedimentary layers of carbonate, which no longer interact with the ocean water, constitute a long-term carbon sink [58.22]. The oceans absorb about half of the carbon dioxide that is generated when burning fossil fuels. As a consequence of this increased amount of carbon dioxide, the oceans are becoming increasingly acidic, which is resulting in less calcium carbonate biomineralization and a potential collapse of the marine ecosystem.

58.2 Materials – Biominerals

Many organisms build inorganic structures in various shapes and forms. The synthesis, as well as the size, morphology, composition, and location of these biogenic materials is genetically programmed and controlled. Detailed investigations and descriptions of biomineralization have only become possible with the modern methods that are now at the disposal of biologists. Many of the crystals and composite materials made up of proteins and amorphous inorganic parts are still unknown in current inorganic chemistry. Nowadays we know more than 70 minerals that are produced by organ-

Table 58.2 Non-exhaustive list of biominerals produced by marine organisms (after [58.4, 23–27])

Biomineral	Chemical formula	Marine biomineralizers of the respective biomineral
Carbonates		
Calcite	$CaCO_3$	Foraminiferans (e.g., *Rosalina leei* and *Spiroloculina hyaline*), coccolithophorids, brachiopod and mollusc shells, crustaceans, mammals, birds, corals, Archaeocyatha, bryozoans, echinoderms (brittle star, sea urchin, star fish, sand dollars, sea cucumbers. . .), Serpulidae (tube-building annelid worms in the class Polychaeta), barnacles, cyanobacteria, sponges, algae
Mg-calcite	$Mg_xCa_{1-x}CO_3$	Foraminiferans, calcareous and hypercalcified sponges, calcareous sponge spicules, octocorals, crustaceans, echinoderms, corals, bryozoans
Magnesite	$MgCO_3$	Tropical coralline alga *Hydrolithon onkodes*, cyanobacteria
Aragonite	$CaCO_3$	Hypercalcified demosponges, scleractinians, brachiopods, molluscs, teleosteans, bryozoans, Serpulidae (tube-building annelid worms in the class Polychaeta), algae, bacteria
Vaterite	$CaCO_3$	Ascidians
Monohydrocalcite	$CaCO_3 \cdot H_2O$	
Protodolomite	$CaMg(CO_3)_2$	Sea urchin teeth (protodolomite: a crystalline calcium-magnesium carbonate with a disordered lattice in which the metallic ions occur in the same crystallographic layers instead of in alternate layers as in the dolomite mineral)
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	
Amorphous calcium carbonate (at least five forms)	$CaCO_3 \cdot H_2O$ or $CaCO_3$	Vascular plants, crustaceans
Dolomite	$CaMg(CO_3)_2$	Tropical coralline alga *Hydrolithon onkodes*, sea urchin teeth, embryos of the Nudibranch gastropod *Aplysia punctata*
Strontianite	$SrCO_3$	Marine snail shells, microbes, cyanobacteria
Siderite	$FeCO_3$	Bacteria
Phosphates		
Octacalcium phosphate	$Ca_8H_2(PO_4)_6$	Vertebrates (bone/teeth precursor)
Hydroxyapatite	$Ca_5[OH\vert(PO_4)_3]$	Vertebrate bones, vertebrate teeth (enamel), brachiopods, conodonts (teeth), fish (scales), in the radular apparatus of the mollusc *Falcidens* sp.
Brushite	$CaHPO_4 \cdot 2H_2O$	Tropic bivalve species *Codakia orbicularis* and *Tivela mactroides*
Francolite	$Ca_{10}(PO_4)_6F_2$	Linguliformea (brachiopods)
Carbonated hydroxyapatite	$Ca_5(PO_4,CO_3)_3(OH)$	Bones
Carbonated apatite (dahlite, dahllite)	$Ca_5(PO_4,CO_3)_3F$	Bones, dental enamel, dentin
Whitlockite	$Ca_{18}H_2(Mg,Fe^{2+})_2(PO_4)_{14}$	Dental plaque
Struvite	$Mg(NH_4)(PO_4) \cdot 6H_2O$	Bacteria, embryos of the Mediterranean mussel *Mytilus galloprovincialis*
Vivianite	$Fe_2^{3+}(PO_4)_2 \cdot 8H_2O$	Bacteria
Amorphous calcium phosphate (at least six forms)	Variable	Vertebrates, bivalves, crustaceans, chitons (teeth), gastropods (gizzard plates)
Amorphous calcium pyrophosphate	$Ca_2P_2O_7 \cdot 2H_2O$	Granules in the hymenostomatidian ciliate *Tetrahymena pyriformis*

Table 58.2 (continued)

Biomineral	Chemical formula	Marine biomineralizers of the respective biomineral
Oxides and hydroxides		
Magnetite	Fe_3O_4	Eubacteria, Archaebacteria, teleosteans, polyplacophorans (chitons)
Amorphous ilmenite	$Fe^{+2}TiO_3$	Foraminifera, snail radulae
Maghemite	γ-Fe_2O_3	Magnetotactic bacteria
Amorphous iron oxide	Fe_2O_3	In the radular apparatus of the mollusc *Falcidens* sp.
Amorphous manganese oxide	Mn_3O_4	Bacteria
Manganese(III) oxohydroxide	$MnOOH$	Bacterial spores of the marine *Bacillus*, strain SG-1
Goethite	α-$FeOOH$	Gastropods, limpet teeth, marine sponges
Akaganeite	β-$FeOOH$	Bacteria
Lepidocrocite	γ-$FeOOH$	Polyplacophorans (chitons), marine sponges
Ferrihydrite	$(Fe^{3+})_2O_3\cdot 0.5H_2O$	Lamprey *Geotria australis*, chitons, snails
Todorokite	$(Na,Ca,K,Ba,Sr)_{1-x}(Mn,Mg,Al)_6O_{12}\cdot 3-4H_2O$	Hydrothermal vent microbes
Birnessite	$(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5H_2O$	Microbes
Sulfates		
Gypsum	$CaSO_4\cdot 2H_2O$	Cnidarians, statoliths of certain medusae, Desmidae (algae), cyanobacteria
Bassanite	$CaSO_4\cdot 0.5H_2O$	Statoliths of certain medusae
Barite	$BaSO_4$	Cyanobacteria, Spirogyra (alga), Loxididae (protozoa), *Chara fragilis* (higher alga), Xenophyophorea (large deep-sea protists), diatoms, foraminifera, Loxodes (gravity receptor)
Celestite	$SrSO_4$	Radiolarians, Acantharia, algae, foraminifera *Rosalina leei* and *Spiroloculina hyaline*, snail shell
Jarosite	$KFe^{3+}_3(SO_4)_2(OH)_6$	*Purpureocillium lilacinum* (an acidophilic fungus), *Acidithiobacillus ferroxidans*
Sulfides		
Pyrite	FeS_2	Magnetotactic bacteria
Amorphous pyrrhotite	$Fe_{(1-x)}S$ ($x = 0$ to 0.2)	
Hydrotroilite	$FeS\cdot nH_2O$	Sulphate-reducing bacteria, *Desulfovibrio* spp.
Sphalerite	$(Zn,Fe)S$	Magnetotactic bacteria
Galena	PbS	Sulfate reducing bacteria
Greigite	Fe_3S_4	Magnetotactic bacteria
Mackinawite	$(Fe,Ni)_{1+x}S$ ($x = 0$ to 0.11)	
Wurtzite	$(Zn,Fe)S$	
Cadmium sulfide	CdS nanoparticles	Marine cyanobacterium *Phormidium tenue*
Acanthite	Ag_2S	Polychaete worm *Pomatoceros triqueter*
Arsenates		
Orpiment	As_2S_3	Bacteria
Native elements		
Sulfur	S nanoparticles	
Gold	Au nanoparticles	Tropical marine yeast *Yarrowia lipolytica*, marine sponge *Acanthella elongate*, marine alga *Sargassum wightii*
Silver	Ag nanoparticles	Marine fungus *Penicillium fellutanum*, *Fusarium oxysporum* (a fungus that is reported to infect marine mammals)

Table 58.2 Continued

Biomineral	Chemical formula	Marine biomineralizers of the respective biomineral
Native Elements		
Selenium	Se nanoparticles	Bacteria *Sulfurospirillum barnesii* and *Pseudomonas marina*
Uranium	U nanoparticles	*Shewanella oneidensis* (bacterium); reduction of Uranium by *Desulfovibrio vulgaris*, a bacterium that builds marine aerobic biofilms
Silicates		
Silica (opal)	$SiO_2 \cdot nH_2O$	Radiolarians, diatoms, demosponges, hexactinellid sponges, most sponge spicules, Opal teeth in copepods and limpets, mollusc penial structures, heliozoan spines and scales
Sepiolite	$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$	Microorganisms (?)
Halides		
Fluorite	CaF_2	Vertebrate and invertebrate skeletons, fish skin, mollusc shell, gizzard plates of gastropods, statoliths of marine mysid crustaceans
Hieratite	K_2SiF_6	Gravity receptors
Amorphous fluorite	CaF_2	*Archidoris* (sea slug) spicules
Atacamite	$Cu_2(OH)_3Cl$	Jaws of the marine bloodworm *Glycera dibranchiata*
Organic minerals		
Weddellite	$CaC_2O_4 \cdot 2H_2O$	*Thalassia testudinum* (turtle grass), sea grass, vascular plants, Bornetella (marine alga) skeleton, gizzard plates of the deep water gastropod *Scaphander cylindrellus*, renal sac of the ascidian tunicate (marine filter feeder) *Mogula manhattensis*, molluscs
Whewellite	$CaC_2O_4 \cdot H_2O$	
Manganese oxalate	$MnC_2O_4 \cdot 2H_2O$	
Calcium tartrate	$CaC_4H_4O_6$	Chiton
Calcium malate	$C_4H_4CaO_5$	
Earlandite	$Ca_3(C_6H_5O_7) \cdot 4(H_2)O)$	
Guanine	$C_5H_5N_5O$ (one of the four main nucleobases found in the nucleic acids DNA and RNA)	Fish scales (fish silver), *Tetragnatha* spiders (silver color)
Uric acid	$C_5H_4N_4O_3$	
Paraffin hydrocarbon	C_nH_{2n+2}	
Wax	organic compounds that characteristically consist of long alkyl chains	
Magnesium oxalate (glushinskite)	$Mg(C_2O_4) \cdot 2(H_2O)$	
Copper oxalate (moolooite)	$Cu(C_2O_4) \cdot 0.4H_2O$	
Anhydrous ferric oxalate		
Sodium urate	$C_5H_3N_4O_3Na$	

isms in various ways (Table 58.2). Biomineralization takes place at normal temperatures and pressures, both much lower than those required to form the same mineralized structures by conventional chemical synthesis.

Biomineralized products comprise metals and alloys, ceramics, polymers, and composites. Examples are Ba, Ca, Cu, Fe, K, Mn, Mg, Na, Ni, Pb, Sr, and Zn; as hydroxides, oxides, and sulfates or sulfides, carbonates, and phosphates [58.23, p. 25]. Some bacteria (e.g., from the species *Geobacter* and *Citrobacter*) accumulate and passivate toxic metal ions, such as UO_2^{2+}, Pb^{2+}, and Cd^{2+}. Bacteria have learnt to cope with most elements of the periodic table, e.g., with encoded resistance systems for toxic metal ions. For many chemical elements, bacteria have found uses either in ultralow concentrations in functional biomolecules (e.g., vanadium), or in vast amounts (e.g., calcium for the formation of shells) [58.28]. Gold, silver, uranium, palladium and CdS nanocrystals are produced by various organisms [58.29], Chaps. 25 and 55. The size of nanocrystals strongly determines fundamental properties such as their color or the external field required to switch a magnetized particle in hard disk drives. The perfect control of the size of the biomineralized nanocrystals is one major reason why bioassisted nanocrystal production is widely viewed as highly promising regarding base materials for new man-made optical and electrical materials. Zinc (Zn) is present in the jaws of the marine worm *Nereis* sp. [58.30], and copper (in the form of the biomineral atacamite, $Cu_2(OH)_3Cl$) is present in the jaws of the marine bloodworm *Glycera dibranchiate* [58.31]. The metals reinforce protein fibres in worm jaws.

The three different types of biominerals are either produced by simple precipitation, as perfect crystals,or as composites.

58.2.1 Biominerals Produced by Simple Precipitation and Oxidation Reactions

Calcium carbonate, iron(III)-oxide hydrate (FeOOH), manganese(IV)-oxide (MnO_2), and pyrite, as well as marcasite (both FeS_2) are generated in organisms by precipitation and oxidation reactions, i. e., relatively simple reactions in which solved substances are translated into insoluble ones via the metabolism of organisms. Example: $CaCO_2$ in stromatolites that were built by autotrophic cyanobacteria as far back in time as 3.5 billion years ago.

Calcium Carbonate $CaCO_3$

$[Ca^{2+} + 2HCO_3^-]$ (carbonate) $\rightarrow$ $CaCO_3$ (stromatolite) $+$ CO_2 (insertion to the biomass) $+$ H_2O.

The advantage for the cyanobacteria might be mechanical fixation of the biofilm in water.

Iron(III)-Oxide-Hydroxide FeOOH Goethite

Gallionella ferruginea is a chemoautotrophic iron-oxidizing chemolithotrophic bacterium that has been found in a variety of different aquatic habitats. It uses the energy it obtains from oxidization, remains of its activities are drains clogged with iron depositions, iron(III)-oxide (Fe_2O_3) and iron(III) oxide-hydroxide ($HFeO_2$). This bacterium or some of its biochemicals related to the oxidization of iron might be of high interest for an alternative way of mining iron in the sea.

Manganese Dioxide MnO_2

Manganese(IV)-oxide (MnO_2) is precipitated via microorganisms such as *Leptothrix discophora* [58.32]. The sheaths of the organisms of the Sphaerotilus-Leptothrix group often are coated with $Fe(OH)_3$ or MnO_2 [58.33].

The Mn and Fe oxidizing/depositing bacteria in freshwater habitats belong to the genera *Sphaerotilus*, *Gallionella*, and *Leptothrix* [58.34, 35].

> *In marine environments, the direct evidence for Fe-oxidizing bacteria is not well documented. The one notable exception was the finding of abundant Gallionella-like stalk material and microscopic identification of putative G. ferruginea cells from a shallow water volcanic system near Santorini Island in the Mediterranean Sea.* [58.36]

Pyrite and Marcasite FeS_2

Sulfate reducing bacteria gain energy from the reduction of sulfates. When iron(II) ions are present, FeS_2 can be produced,

$$2SO_4^{2-} + 3.5C + 2H^+ + Fe^{2+}$$
$$\rightarrow FeS_2 + 3.5CO_2 + H_2O$$

(the C comes from organic substances).

58.2.2 Biological Production of Perfectly Crystallized Minerals

Ice H_2O

Ice is a mineral with a relatively low melting point. Organisms actively protect themselves against this unwanted mineral in their bodies via two strategies: either they prevent freezing of their bodily fluids via freeze protection proteins (Sect. 58.3) or they enrich ice nucleation proteins in their blood, which promote and control freezing so that their cells do not suffer. Some bacteria such as *Pseudomonas syringae* produce proteins that promote freezing; they are used for the production of artificial snow. Various organisms such as arctic fish, plants, fungi, microorganisms, and bacteria build antifreeze and ice structuring proteins. With the help of these proteins, the organisms can survive in temperatures below the freezing point of water.

Antifreeze proteins bind to ice crystals and prevent their growth and recrystallization, thereby preventing the cells of the organisms from being destroyed by ice crystals. Due to their ice binding properties, antifreeze proteins in living nature work at very low concentrations (300–500 times less than conventional man-made antifreeze agents). Frost-tolerant species survive the freezing of their body fluids [58.37].

Calcium Carbonate $CaCO_3$ (Calcite, Aragonite, and Vaterite)

Calcite is the most stable polymorph of calcium carbonate. It is transparent, with a refractive index of 1.6584 and 1.4864 (depending on the crystallographic axis). These properties make it a good material for the production of optical lenses. The brittle star *Ophioma wentii* has calcite eyes of optically corrected microlenses all over its body (Fig. 58.1).

Already 350 millions of years ago some trilobite species used calcite lenses; up to 15 000 lenses making up one single eye! Calcium carbonate is also present in the ear: zebra fish use Starmaker proteins to biomineralize aragonite otoliths for hearing and their vestibular sense [58.39].

Magnetite Fe_3O_4

Magnetite is a ferromagnetic black iron oxide that can, e.g., be found in a chain of magnetosomes, i. e., single magnetic domain crystals in magnetotactic bacteria (Fig. 58.2), e.g., *Magnetospirillum magnetotacticum*. The anaerobic bacterium uses the magnets to orient itself along the magnetic field lines of the Earth, and thereby determine up and down (it cannot do this via gravity, because as a small bacterium it lives a life at a low Reynold's number, like a piece of dust in honey – which is no way to rely on gravity). Magnetosomes were also found in migratory birds, trout, and salmon. Magnetite particles with molecular precision have even been identified in the human brain (Fig. 58.3). Biogenic magnetite in the human brain may account for the high-field saturation effects observed in magnetic resonance imaging and, perhaps, for a variety of biological effects of low-frequency magnetic fields.

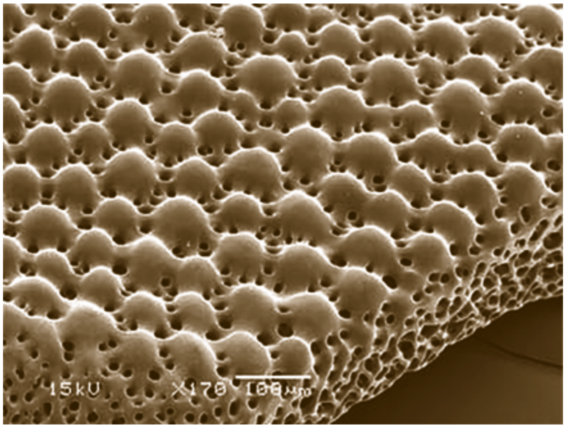

Fig. 58.1 The calcite microlenses of the brittle star. Each of the lenses is only some tens of micrometers in diameter. Scale bar 100 µm

The formation of bacterial magnetite crystals is as follows: first, the bacterium takes Fe(III) ions from the environment. Then it reduces Fe(III) to Fe(II) ions during the transport across the cell membrane. Sub-

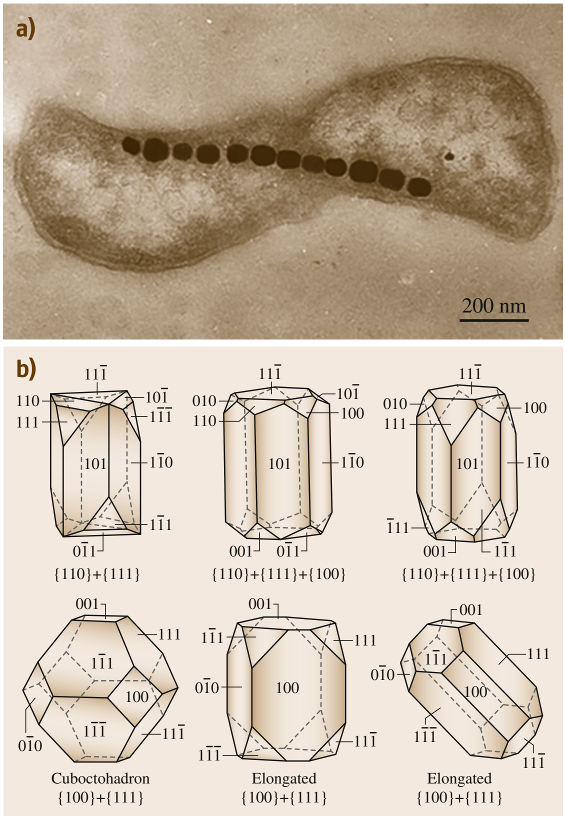

Fig. 58.2 **(a)** A magnetotactic bacterium. **(b)** Magnetosome crystal morphology. The magnetosomes are built with atomic precision (after [58.38], with permission)

sequently, Fe(II) ions are transported to and across the vesicle membrane (the magnetosome membrane), amorphous hydrated Fe(III) oxide is precipitated within the vesicle, and the amorphous phase is transformed to magnetite by surface reactions involving mixed-valence intermediates [58.40, 41].

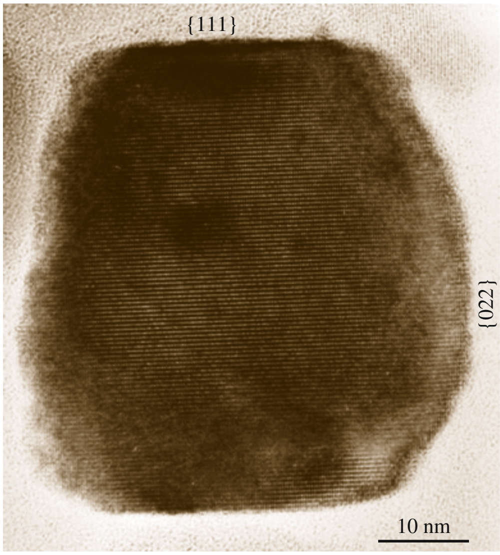

Fig. 58.3 A magnetite particle from the human brain (after [58.42], with permission)

58.2.3 Composite Biomaterials

Composite materials combine two or more materials yielding new materials with interesting properties. Many biomaterials are composites. In most cases, the functionality of the biological composites is based on nanoscale structures. Examples for such nanocomposites (also known as hybrid biomaterials) are nacre (the beautifully iridescent layer in, e.g., abalone shells or pearls, Figs. 58.4 and 58.5), bones and enamel, as well as egg or mollusc shells. In many cases, the mechanical properties of such nanocomposites are outstanding: abalone nacre, for example, has a fracture toughness that is 3000 times higher than that of calcite crystals [58.43].

Calcium Carbonate CaCO$_3$ Nanocomposites

Calcium carbonate is an important ingredient in the nanocomposite that makes up the shells of foraminifers [58.44], eggs of birds and mollusc shells. Calcium carbonate is the material that is biomineralized most: remnants of calcium carbonate biomineralizing organisms yielded whole mountain ranges. The calcium carbonate shell serves as mechanical protection for the soft bodies of the organisms, be they foraminifers, other single-celled organisms, mussels, molluscs, or other animals.

Fig. 58.4 Pearls

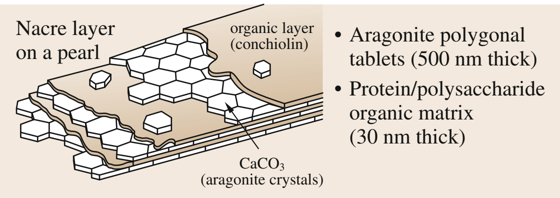

Fig. 58.5 Nacre layer on a pearl. The conchiolin protein/polysaccharide matrix is about 30 nm thick, the aragonite polygonal tablets are about 500 nm thick. The beautiful luster of the pearl comes from optical interference effects of light on the thin tablets. Permission pending

Nacre is an iridescent form of aragonite (which is a calcium carbonate with orthorhombic symmetry as opposed to the trigonal symmetry in calcite) that is made by certain marine animals. Its protein content is about 5%.

Sea urchins biomineralize calcium carbonate in their shells, teeth, and spines. Sea urchin spines can reach a length of 10 cm, with their toughness by far outnumbering the toughness of pure calcium carbonate. Sea urchin teeth are single crystal calcites [58.45].

In corals, sensitive little animals (polyps) biomineralize with the help of algae, with whom they live in symbiosis, an exoskeleton of calcium carbonate. The algae consume the CO_2 and aid in $CaCO_3$ precipitation.

Nanostructured Silicon Dioxide SiO_2 in Diatoms and Glass Sponges

Diatoms are unicellular algae that live in fresh or saltwater and on moist surfaces, and that at normal temperature and pressure biomineralize an exoskeleton of rigid, tough, and hard silica [58.46]. These exoskeletons are nanostructured and of exquisite beauty (Fig. 58.6). Sometimes, single diatom cells are connected via hinges and mechanical interconnecting devices. Such linkages have a size on the order of several hundreds of nanometers. No signs of wear in diatoms have ever been reported, not even when they fossilized and were alive tens of millions of years earlier (as is the case for the fossil diatom depicted in Fig. 58.6). Diatoms can serve as inspiring natural microsystems when it comes to tribological or mechanical aspects of microengineered devices, especially 3D microelectromechanical systems (MEMS) [58.47, 48].

Proteins that are involved in the biomineralization of silica are called silicatein, silaffin and silicase. Silicateins are high molecular weight proteins that strengthen the silica structure; silaffins are low molecular weight proteins that yield silica precipitation within minutes.

Diatomaceous earth is a natural resource that is mined in various places on the Earth. It contains the remnant shells of diatoms. Because of the porous nanostructured shell of the diatom, diatomaceous earth has huge surface area and is, therefore, used for filtering drinks such as beer and apple juice, or for the production of explosives such as dynamite.

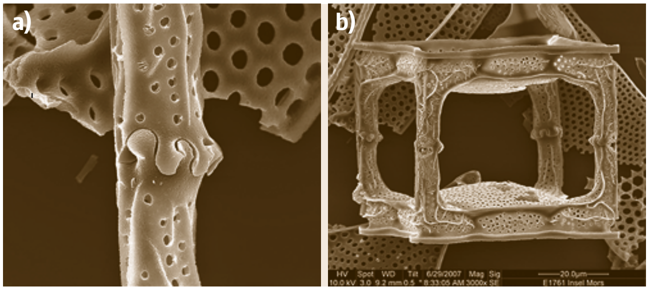

Fig. 58.6a,b Diatoms are silica biomineralizing phytosynthetic single-celled organisms. The fossil diatom *Solium exsculptum* from the island of Mors in Denmark depicted in the image lived 45 millions of years ago. It beautifully shows an expedient nanostructured shell, reinforcement ribs, connections, and primary mechanical structures. Panel **(a)** is a zoom into the most left junction in panel **(b)**. The sample is from the Hustedt Collection in Bremerhaven, Germany, # E1761 (Courtesy of F. Hinz, AWI Bremerhaven). Image reproduced with kind permission

A second type of marine organisms that biomineralize silica are the about 500 species of glass sponges (Hexactinellida) [58.50]. Glass sponges are exclusively marine organisms; they comprise about 7% of all sponges currently known. Their skeleton is made from amorphous hydrated silica needles (spicules) of exquisite shapes (Fig. 58.7). One single species can have up to 20 different types of needles. *Monorhaphis chuni* produces a silica needle of up to 3 m in length and 8 mm in diameter, which it uses to stabilize itself at the bottom of the Indian and Pacific oceans.

Glass sponges are an important ecological factor in the Antarctic; spicules of dead animals can build woolly layers up to 2 m high. The single spicules have concentric layers of silica, arranged around a hollow central canal. The spicules are a composite material of silica and proteins and are in many cases highly elastic.

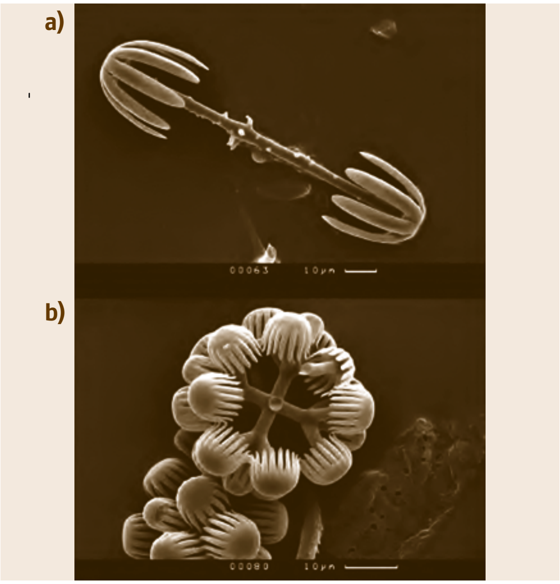

Fig. 58.7a,b Hexactinellida (glass sponge) spicules. Glass sponges consist of a network of such spicules covered by a thin layer of living cells. In this way they are heavily defended both inside and out. Single glass sponges have up to 20 different types of spicules in various shapes, some of them needle like **(a)**, some ball-like **(b)**, some in star shapes. Scale bars 10 µm

Hydroxyapatite $Ca_5[OH|(PO_4)_3]$

Animal bones consist of about 65% inorganic components, mainly hydroxyapatite (a calcium phosphate with the chemical formula $Ca_5[OH|(PO_4)_3]$), providing compressive strength, and about 35% inorganic components, mainly collagen, providing high tensile strength. Further ingredients in bones are proteins and fats. The high strength of bone is due to the fact that hydroxyapatite crystals are ordered mainly along the lines of tension and compressive stress, which results in a strut-like arrangement. See Fig. 58.8 for a drawing of the seven layers of hierarchy in bone.

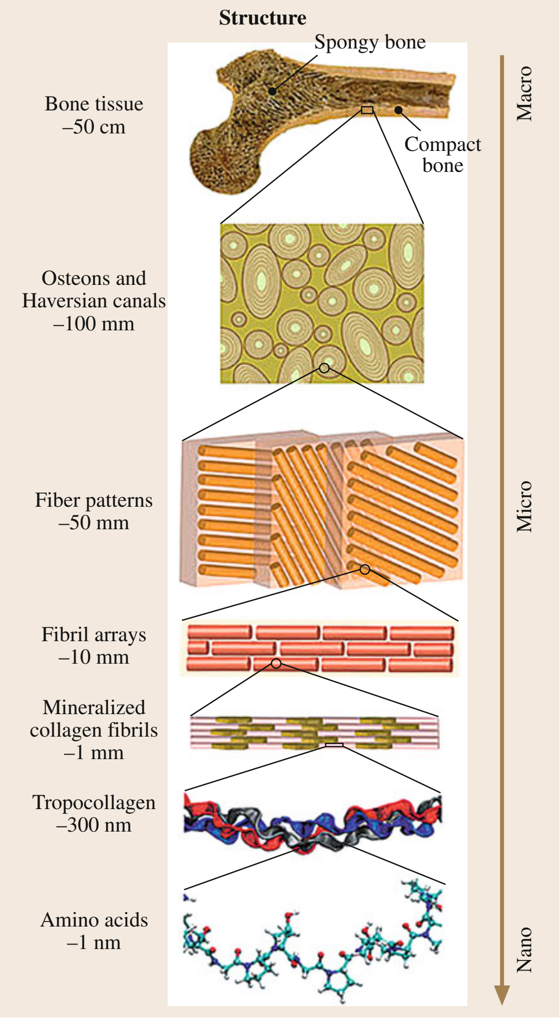

Fig. 58.8 The hierarchical levels of bone, a biomineralized structure with added functionality on each level of hierarchy, resulting in a tough and strong, yet lightweight material [58.49], with permission

Fluorapatite $Ca_5(PO_4)_3F$

Enamel has 95% inorganic components, mainly hydroxyapatite. In fluorapatite the OH group is replaced with F – this makes enamel more resistant against acids and provides a better protection against caries.

58.2.4 Example of Uptake and Conversion of a Very Rare Element: Selenium

In 1983, *Foda* et al. [58.51] described uptake and conversion of the very rare element selenium by the marine bacterium *Pseudomonas marina* in seawater containing either selenite or selenate. *Pseudomonas marina* bioconverts selenite into water-soluble non-Se(IV) metabolite(s) and subsequently releases them back into the medium. It is also capable of reducing Se(IV) to elemental Se; this pathway becomes increasingly evident at higher concentrations of selenite.

In 2011, selenium-reducing microorganisms that produce elemental selenium nanoparticles were reported [58.52]. This study identified high-affinity proteins associated with such bionanominerals and with non-biogenic elemental selenium. Proteins with an anticipated functional role in selenium reduction, such as a metalloid reductase, were found to be associated

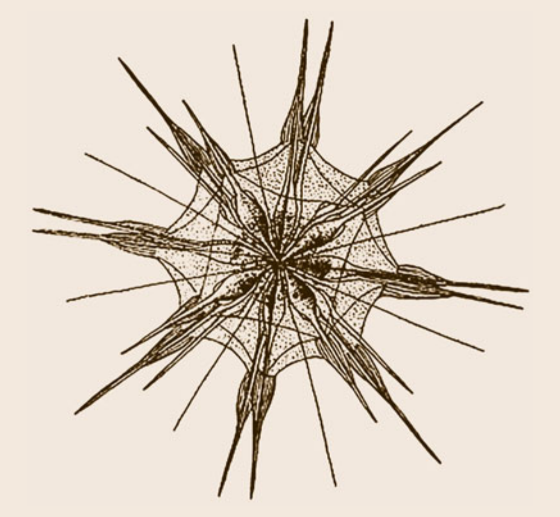

Fig. 58.9 An Acantharea exoskeleton. These planktonic, free living, exclusively marine protozoa range in size from 0.05–5 mm in diameter

with nanoparticles formed by one selenium respirer, *Sulfurospirillum barnesii*.

58.2.5 Example of Strontium Mineralization in Various Marine Organisms

Strontium is an alkaline earth metal that occurs naturally in the minerals celestine ($SrSO_4$) and strontianite ($SrSO_3$). These two minerals also occur as biominerals in radiolarians, acantharia, algae, the foraminiferae *Rosalina leei* and *Spiroloculina hyaline* [58.53], and in snail shells.

Acantharea are one of the four types of large amoebae that occur in the marine water column. Acantharea have a very regular exoskeleton and are of high importance for strontium circles in the sea. Their sizes range between 0.05–5 mm (Fig. 58.9).

58.2.6 Example of Biomineralization of the Unstable Calcium Carbonate Polymorph Vaterite

Vaterite is a polymorph of calcium carbonate and is less stable than calcite or aragonite. Vaterite occurs naturally in some organisms, such as in the spicules of sea quirts [58.54], in turtle eggshells [58.55], and in gastropod (e.g., snail, abalone, limpet) shells (e.g., [58.56]). In those circumstances, impurities such as metal ions or organic matter may stabilize the vaterite and prevent its transformation into calcite or aragonite.

58.3 Materials – Proteins Controlling Biomineralization

We are just beginning to understand the role of proteins in biomineralization [58.57]. Proteins have several important active roles in biomineralization: they inhibit spontaneous mineral formation from solution (e.g., the protein statherin in the mouth inhibits spontaneous precipitation of calcium phosphate), they inhibit the growth of existing crystals, and they are responsible for directing crystal nucleation, phase, morphology, and growth dynamics. The crystal shape is, for example, affected by proteins with specific structures and sequences that adsorb to different faces of the crystal, leading to regulation of shape (crystal faces have different charges and arrangements of atoms so proteins can selectively adsorb). Furthermore, proteins can self-assemble into ordered arrays that guide the formation of organized mineralized structures.

Proteins ultimately contribute to the extraordinary mechanical, optical, etc., properties of the biomineralized material and structures. Chitin and collagen seem to be universal and alternative templates in biomineralization.

Table 58.3 gives a non-exhaustive list of the proteins involved in biomineralization and the respective biomineralized material.

The three main organic structuring and scaffolding polymers are chitin, cellulose, and collagen. All three have common principles in their organization: they form nanofibrils with 1.5–2 nm diameter, they have the ability to self-assemble, they produce fibrillar and fiber-like structures with hierarchical organization from the nanolevel up to macrolevels, they have the ability to act as scaffolds and as templates for biomineralization, and they form rigid skeletal structures [58.23].

Certain proteins provide active organic matrices that control the formation of specific mineral structures; others act as catalysts that facilitate the crystallization of certain metal ions [58.58].

58.4 Organisms and Structures That They Biomineralize

Marine vertebrates, invertebrates, and plants biomineralize more than 70 different substances (Tables 58.2 and 58.4); some specific crystals produced by living nature cannot be produced by conventional chemical synthesis (e.g., the defect-free magnetosomes in magnetotactic bacteria or some crystal classes that obviously need proteins for their build-up – they do not exist in geological crystal formations). The number of marine biomineralizers, and with them the range of different structures, materials, processes, and functions, is tremendous: 128 000 species of molluscs have been described, 700 species of calcareous green, red, and brown algae, more than 300 species of deep-sea benthic foraminifera, and 200 000 diatoms species [58.23, p. 26].

Many biomineralized structures are built from nanostructured, hierarchical materials, and sometimes even functional gradient materials. Bone, for example,

Table 58.3 Biominerals and the respective proteins involved in biomineralization (non-exhaustive list)

Biomineral	Proteins
Apatite	Collagen (controls apatite) (in Porifera, coelenterates, molluscs, echinoderms)
Bone	Biglycan (a small leucine-rich repeat proteoglycan (SLRP) found in a variety of extracellular matrix tissues, including bone, cartilage, and tendons; essential for the structure and function of mineralized tissue) Osteonectin (a bone-specific protein linking mineral to collagen) Osteopontin (an extracellular structural protein and, therefore, an organic component of bone) Sialoprotein (BSP) (a component of mineralized tissues such as bone, dentin, cementum, and calcified cartilage) Osteocalcin, phosphophoryn, bone sialoprotein, proteoglycans, glycoproteins, glycosaminoglycans
CdS nanoparticles	C-phycoerythrin (from the marine cyanobacterium *Phormidium tenue*)
Calcium carbonate	Calcified cartilage sialoprotein (BSP) (a component of mineralized tissues such as bone, dentin, cementum, and calcified cartilage) Orchestin (a calcium-binding phosphoprotein in the calcified cuticle of a crustacean) Snail shells conchiolin (conchin) Calmodulin-like protein (from pearl oyster *Pinctada fucata*) Eggshell matrix proteins Otoconin (in octoconia, small crystals of calcium carbonate, also called statoconia, as gravity and acceleration sensors) Statherin (growth *inhibiting* protein, inhibits spontaneous precipitation of calcium phosphate in the mouth) Pancreatic stone protein (PSP) *inhibits* calcium carbonate precipitation in pancreatic fluid Starmaker proteins (in zebrafish, aragonite biomineralization)
Calcium phosphate	Serum protein fetuin-A (inhibition of calcium phosphate precipitation, *inhibiting* smooth muscle cell calcification)
Dentin	Dentin sialoprotein (BSP) (a component of mineralized tissues such as bone, dentin, cementum, and calcified cartilage)
Enamel	Amelogenin (a series of closely related proteins involved in amelogenesis, the development of Tuftelin) Enamelin and amelogenin (tooth enamel proteins) Tuftelin (enamel) Transcription factor FoxO1 (essential for enamel biomineralization) Phosphoprotein (inhibits hydroxyapatite formation)
Goethite	Chitin (in limpet teeth, as template for goethite growth)
Gold	Cytochrome C Lysosome
Ice	Antifreeze proteins (control of ice crystal growth) Ice interaction polypeptides
Magnetite	MamA (required for the activation of magnetosome vesicles) MamJ (directs the assembly and localization of magnetosomes) Mms6 (regulates magnetite crystal morphology)
Nacre	Nacre proteins (perlucin, n16N,...)
Silica	Polyamines, silicatein and silaffine (in diatoms) Frustulin, pleuralin (in diatoms)
Uranium	Cytochrome c3 (reduction of uranium, from *Desulfovibrio vulgaris*)
Vaterite	Eggshell pelovaterin (turtle eggshells, vaterite crystals)

Table 58.4 Examples for biomineralizing organisms in all six biological kingdoms

Kingdom	Examples
Plants	*Thalassia testudinum* (turtle grass), sea grass, vascular plants
Animals	Avian egg shell ($CaCO_3$) Archaeocyatha ($CaCO_3$) Brachiopod and mollusc shells ($CaCO_3$) Sea-mats (Bryozoans) ($CaCO_3$) Calcareous sponge spicules ($CaCO_3$) Calcareous tunicate (marine filter feeders) spicules ($CaCO_3$) Conodonts (apatite (phosphate carbonate)) Enamel (vertebrate teeth) (apatite (phosphate carbonate)) Echinoderms ($CaCO_3$) Corals ($CaCO_3$) Glass sponges such as the Venus flower basket *Euplectella aspergillum* (amorphous hydrated silica) Lanternshark (mineralized spines) Crystal structures in the inner ear in zebrafish Japanese pearl oyster *Pinctada fucata* Cephalopods such as the Giant Pacific octopus (beak) Sea urchins (needles, larval skeleton) Fanworms (Serpulidae) ($CaCO_3$) Vertebrate bone (apatite (phosphate carbonate)) Whale teeth Narwhal whale *Monodon monoceros* tooth (up to 9 feet long) Shells, snail shell (strontium, calcium) Rhopaliophoran medusae (Cnidaria) statoliths (calcium sulfate hemihydrate) Demosponges (silica) Brittle star crystal eyes (Calcite) Most sponge spicules (silica) Hypercalcified sponge (calcium carbonate basal skeleton in addition to their spicules) *Petrobiona massiliana* (Calcarea, Calcaronea), *Ceratoporella nicholsoni*, *Goreauiella auriculata* (Astroscleridae), *Astrosclera willeyana*, *Hispidopetra miniana*, *Stromatospongia norae* (Ceratoporellidae: Porifera), *Calcifibrospongia actinostromarioides*
Protista	Coccolithophores ($CaCO_3$) Diatoms, radiolarians and silicoflagellates (hydrated silica) Foraminifera ($CaCO_3$, $SrSO_4$)
Fungi	Fungi in corals (pearl-like skeletons)
Bacteria	Chemosynthetic marine organisms Magnetotactic bacteria (e.g., *Magnetospirillum gryphiswaldense*, *Magnetospirillum magneticum*) Cynobacteria in stromatolithes Marine bacteria ($CaCO_3$, Selenium nanoparticles)
Archaea	*Sulfolobus shibitae*, *Metallosphaera* sp., *Acidianus infernus* (iron, sulfur, uranium)

has seven layers of hierarchy, spanning from the components of collagen fibrils to the whole bone. Level 1 consists of the components themselves, including proline and hydroxyproline. On level 2, one step up in size, in hierarchy, and with added functionality, comes the mineralized collagen. On level 3 there are arrays of fibers, which on level 4 build patterns, e.g., spirals. On level 5 the osteons, cylindrical motifs in bone structure, appear. Level 6 brings in as added functionality, integrated into the whole bone structure, spongy *vs.* compact bone, and level 7 is the whole bone (Fig. 58.9).

Nature's nanostructures are built by benign chemistry and via self-assembly and templating. Human chemical synthesis is slowly reaching the efficiency and

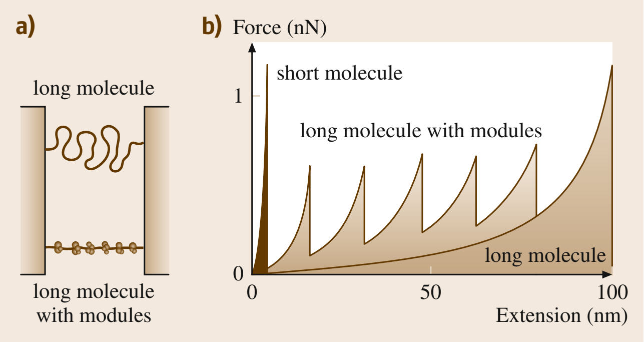

Fig. 58.10a,b Concept for a self-repairing adhesive [58.43]. **(a)** Two ways to attach two particles: with a long molecule or with a long molecule with nodules. **(b)** When stretched, a short molecule can only be extended a little and would then break. A long molecule would be stretched much more and finally break. However, a long molecule with nodules, with sacrificial bonds that break before the backbone of the molecule breaks, increases the toughness of the adhesive. Such a strategy is applied in the abalone shell and also in diatom adhesives (after [58.43], with permission) ►

purity of natural biomineralized crystals, and in terms of controlling morphology and hierarchy, there is still a lot for us to learn [58.59].

From nanometer small crystals that serve as nucleation centers up to meter-long silica spicules in certain marine glass sponges – biomineralized structures span many orders of magnitude in length.

58.4.1 Example: Molluscan Shells

The main material in molluscan shells is calcium carbonate: it amounts to about 95–99% of the weight. The remaining 1–5% are made up of proteins. The complex biocomposite (Fig. 58.10) of molluscan shells is far more fracture resistant than a calcite crystal: in the case of the abalone shell, this factor amounts to 3000 [58.43]. The proteins controlling the biomineralization (for an overview, see Sect. 58.3) allow for calcium carbonate (and/or strontianite, celestite, and fluorite, see Sect. 58.2) synthesis at ambient conditions, and control the crystal nucleation, phase, morphology, and growth dynamics. The abalone shell is an example of a biomineralized material with high fracture toughness. The blue-rayed limpet *Ansates pellucida* has a shell that shows stripes of green-blue dynamic structural coloration (photonic structures). It exerts different control over the calcium carbonate crystal phases in different parts of its shell, utilizing different proteins and making different structures. Several phases of $CaCO_3$ can exist locally next to each other, each containing its characteristic proteins [58.60].

58.4.2 Example: Coccolithophores

Coccolithophores (Fig. 58.11) are small unicellular photosynthesizing protists that produce exoskeletons of elaborate calcite plates with a size of about 1–10 μm. These microscopic organisms control the nucleation as well as the growth of the plates. Coccolithophores form a significant proportion of total marine primary production and carbon fixation; the biomineralized structures of dead coccolithophores are the largest single component of deep-sea sediments and they also make up the white cliffs of Dover [58.61, 62].

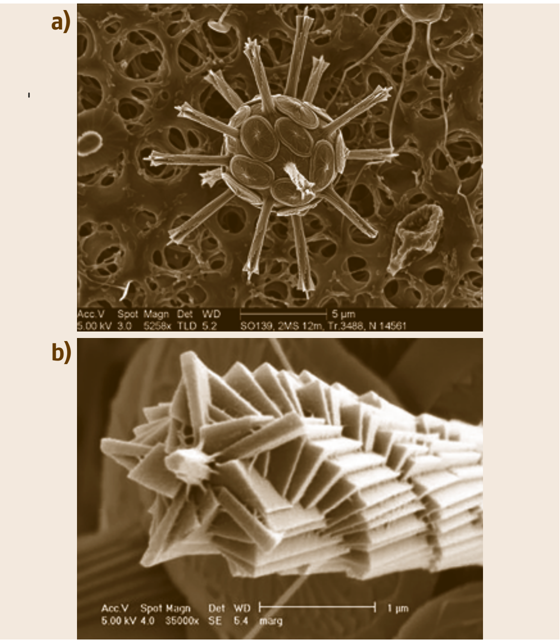

Fig. 58.11a,b The coccolithophorid *Rhabdosphaera clavigera*. **(a)** Whole organism. **(b)** Detail of the tip of a single spine showing spiral structure formed from consistently aligned crystal units with rhombic faces (after [58.61], permission pending)

58.5 Functions

Most structures in biological systems are multifunctional. Their integrated approach allows for highly compact, cheap solutions to various chemical, dynamic, structural, mechanical, or physical demands *in one go*. Structures in organisms can be great teachers for engineers and inspire novel, sometimes even revolutionary, new approaches. However, because of their intrinsic multifunctionality, not always can one single aspect of an organism be successfully isolated in pure form for man-made applications, sometimes not even concept-wise. One fascinating example of the multifunctionality of living nature is biomineralized structures and their respective functions. Especially more complex arrangements, such as the silica micro- and nanostructures in diatoms, are envisaged to provide substantial inspiration in micro- and nanotechnology, especially tribology (regarding friction, adhesion, lubrication, and wear of small rigid interacting parts in relative motion) [58.63]. Further examples of tribological optimization in biomineralized structures are chitons, where iron is stored close to their magnetite-coated teeth, and the teeth can easily be renewed as they wear [58.64], and the jaws of certain marine worms that contain copper and zinc-reinforced proteins [58.30, 31].

The generalized principle *use structure rather than material* can be identified in various organisms. Especially for micro- and nanoscale organisms with rigid interacting parts in relative motion (e.g., some diatoms) straightforward biomimetic principle transfer to novel MEMS can be envisaged [58.47, 48].

Examples of functions of biomineralized structures are given in Table 58.5 and contain, for example, the calcite cell wall scales in coccolithophorids that are used as exoskeleton, the calcite shells of foraminifera and molluscs, the aragonite cell walls of scleractinian corals, aragonite mollusc shells, and vaterite gastropod (e.g., snail, abalone, limpet) shells. Calcite was used for optical imaging in the now extinct trilobites (it constituted their eye lens), and provides mechanical strength to the cuticle of crustaceans, e.g., crabs. In eggshells it provides mechanical protection. Mg-calcite provides mechanical strength to the spicules of octocorals, and strength as well as protection to the shell and spines of echinoderms (marine invertebrates with tube feet and five-part radially symmetrical bodies, such as sea stars and sea urchins). Chitin is the material of the poison dart in certain marine gastropods. Aragonite provides buoyancy devices in cephalopod (e.g., octopus) shells, as well as gravity receptors in fish heads. Vaterite spicules provide protection for ascidians (sessile coral-looking animals, e.g., sea squirts), and amorphous calcium carbonate in the crab cuticle provides these crustaceans with mechanical strength, whereas in the leaves of marine plants it serves as calcium storage. Iron-silica biominerals provide cyanobacteria with an effective UV screen [58.65].

58.6 Applications

58.6.1 Current Applications of Bioinspired Material Synthesis in Engineering and Medicine

Micro- and nanoengineers profit from the fact that in biological systems very often structure rather than material is used to achieve certain functionalities. In many cases, the structures are solely responsible for the respective functions, allowing for simple biomimetic transfer of principles from the inspiring structure to the respective application in engineering. This is of relevance in current MEMS design (where only a handful of base materials can be used, and the MEMS designer therefore has to work with structure rather than material), and will be even more relevant in the future when we finally mass-produce various 3D MEMS.

The abundance and distribution of chemical elements in seawater is a function of their solubility, reactivity, and involvement in biotic and abiotic processes, as well as oceanic circulation; it shows similarity to the composition of the human body (Fig. 58.12). Animals have a similar composition; in plants the first four most abundant elements are the same as in people or animals (O, C, H, and N), but the fifth most abundant element is P. The elemental composition of the cell phone (which shall serve here as a representation of a technical device) is completely different (Fig. 58.12). Potential future marine biotechnology might provide materials and structures for new technologies that are less focused on plastics and metals. For each such marine biotechnology attempt, careful considerations regarding the potential benefit of

Table 58.5 Non-exhaustive list of already identified functions in biomineralized structures of marine organisms, sorted by chemical, dynamic, mechanical, physical, and structural functions

Chemical functions	Dynamic functions	Structural functions
Calcium storage High performance nanocomposites Molecular glue in composite structures Storage (biominerals are ion reservoir for cellular functions) Mineralized holdfast (byssus of the jingle shell *Anomia*) Underwater adhesives Waste disposal (inside, like some nanocrystals or pearls, perhaps also outside)	Lubrication (bearing-like structures) Mobility Motion Movable rigid parts (ensuring a certain maximum and minimum distance) Pumps	Sclerites (a component section of an exoskeleton, especially each of the plates forming the skeleton of an arthropod) Spicules Structure building (corals) Surface texturing for optimized mechanical properties

Mechanical Functions	Physical Functions
Click-stop mechanism Crack redirection Distance holder Fixation (e.g., click stop in diatoms) Fracture resistance Hinges Injection Interlocking devices Mechanical connection Mechanical fixation Mechanical protection Mechanical strength Protection Reinforcement Scaffolds Skeleton (endoskeleton, exoskeleton) Springs Stability Strength and Integrity Teeth for cutting, rasping and grinding (e.g., iron in the teeth of chitons) Toughness (abalone) Weapons (defensive: e.g., sea urchin needles, aggressive: e.g., pistol shrimp dactyl club, conch snail harpoons) Wear protection (addition of zinc or copper for reinforcement)	Buoyancy Co-orientation mechanisms in biominerals (control of crystal orientation) Dynamic colors (diatoms, polychaete worms) Electrically conductive bacterial nanowires (nanowiring in microbial communities) Energy dissipation Gravity sensing (otoconia, statoliths) Lenses (optical) Magnets (for navigation, location) Optical components (antireflective layers, lenses, transparent containers for photosynthesizing organisms) Ossicles Photonic components (e.g., light guiding in deep-sea organisms) Photoprotective coatings Reflectivity (fish silver) Gravity sensing Magnetic sensing Optical sensing Balance sensing UV protection Whiteness

biomimetic and biomineralization approaches need to be made, taking energy and other factors into account. One of the advantages of technology as opposed to functional entities in organisms is the freedom of choice in materials. Organisms are stuck with a certain material as soon as they start using it. Examples are $SrSO_4$ in the exoskeleton of Acantharea (Sect. 58.2.5), or SiO_2 in diatoms (Sect. 58.2.3) – with the abundance of Sr and Si in ocean water being about 8 and 2 ppm, respectively [58.66].

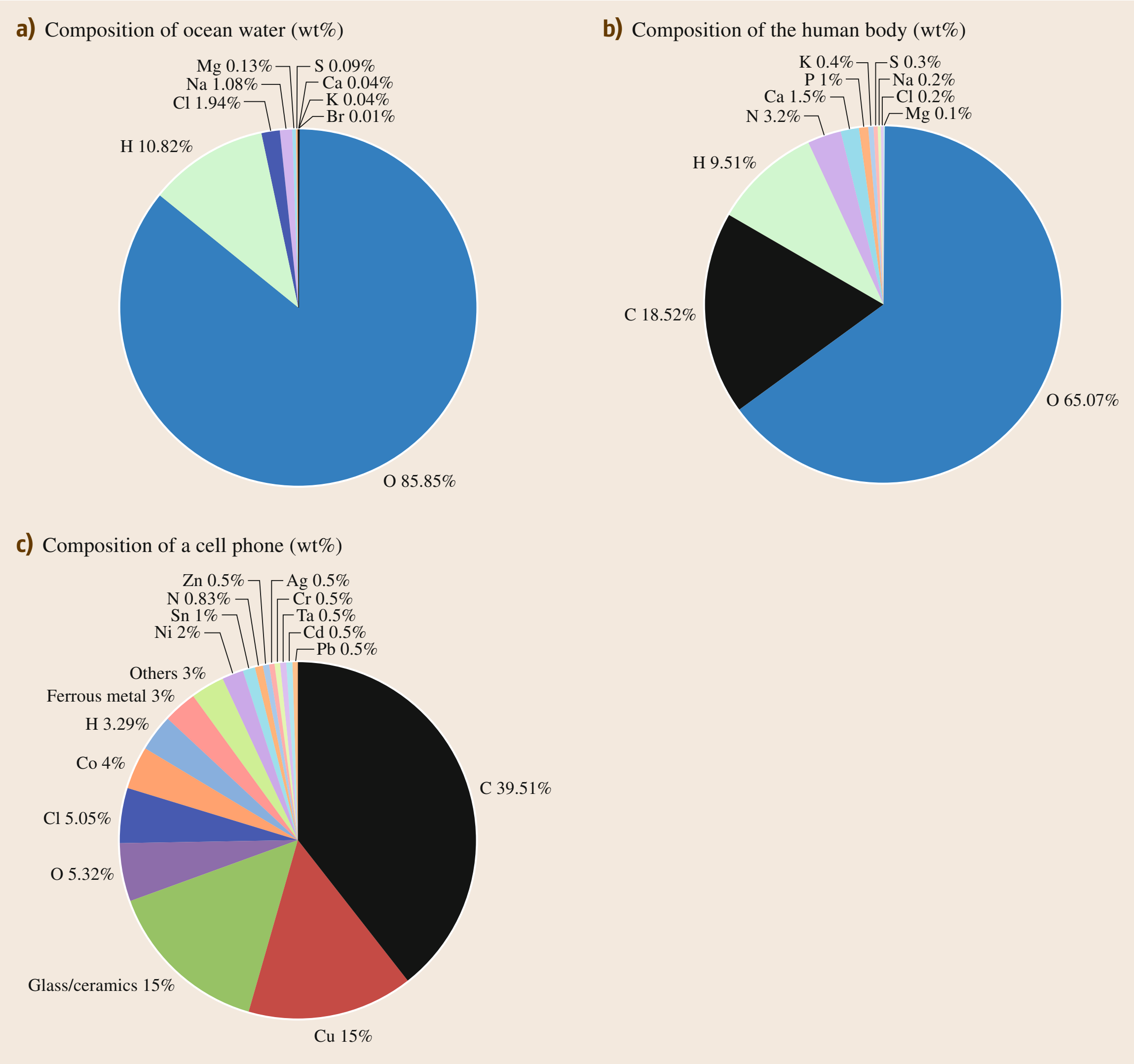

Fig. 58.12a–c The elemental compositions of ocean water, the human body, and a cell phone. The elemental composition of ocean water **(a)** is similar to the elemental composition of the human body **(b)** and very different from the composition of current engineering devices such as a cell phone **(c)**. Novel disruptive engineering approaches that learn from living nature (e.g., by using the principle *use structure rather than material*) might in the future yield marine biotechnology inspired machines and devices that need less metal and plastics, but rather achieve the needed functionality mainly from their structure (e.g., a navigation device inspired by homing sea turtles, with no dependence on satellites or metal parts)

Bioinspired material synthesis is also of increasing importance in tissue engineering, especially regarding applications for scaffolding (Chap. 53). Important factors are similar in a scaffold and in a biomineral, and relate to the chemical composition, the pore structure and architecture, the degradation rate and mechanical properties. The strength of the scaffold must be high enough to resist fragmentation before the cells synthesize their own extracellular matrix. The modulus of elasticity (i. e., the stiffness) must be high enough to resist compressive forces that would collapse the pores, must transmit stress (and strain) in the physiological range to surrounding tissues, and must prevent concentrated loading and *stress shielding*.

Also the synthesis of scaffold materials using principles and processes underlying biomineralization is of high interest. Biomineralized materials can be used as biomaterial scaffolds, either as they occur naturally or after treatment for modification. Further applications are bioinert and biodegradable materials, in medical devices, for tissue engineering, and for the coating of implants.

We have already started to initiate chemical reactions by printing reagents directly into a 3D reactionware matrix (i. e., printing of molecules and tissues with a commercially available 3D printing platform), and time will tell how far we can get with printing whole organs or machines, from basic ingredients, simple base materials, in our homes [58.67, 68].

Current biotechnology allows the usage of proteins that are important in biomineralization across species. *Natalio* and coworkers used silicatein-α (from sponges) to guide the self-assembly of calcite *spicules* similar to the spicules of calcareous sponges. As opposed to the rather brittle natural spicules, the synthetic spicules show greatly enhanced bending strength, and furthermore waveguiding properties even when they are bent [58.69].

58.6.2 Possible Future Applications of Bioinspired Material Synthesis in Engineering and Medicine – Outlook

The future of marine biotechnology is dependent upon the development of an enhanced understanding of the physical, chemical, and biological properties of marine organisms and ecosystems. Materials, structures and processes related to marine environments can provide valuable contributions to engineering, resource management, medicine, and various other fields. A prerequisite for this is the understanding of the connection between functionalities of biomineralized materials and structures from the nanoscale to the macroscale, including the effect of hierarchy and structuring. Especially interesting are models where macroscale properties can be understood from distinct functionalities at various length scales and subsequent implementation in technological processes. Efficient successful synthesis of biomineralized materials and structures, where form follows function, will pave the way towards tailored multiscale marine biotechnology, which starts at the molecular level and incorporates the hierarchical functionalities of biological materials through the length scales up to the macroscale, perfectly integrating nanotechnology and biology.

Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures as proposed by *Cölfen* and *Mann* [58.70] is a key challenge in the design of integrated materials with advanced functions. Macromolecules and surfactants could be used to significantly increase the scope for controlled materials synthesis.

Biomimetic silica biosynthesis opens a new route to semiconductor nanofabrication [58.71, 72]. In 2008, *Jeffryes* and coworkers succeeded in metabolically inserting nanostructured Ge into a patterned silica matrix of the diatom *Pinnularia* sp. at levels ranging from 0.24 to 0.97 wt % Ge [58.72]. Embedding nanoscale germanium (Ge) into dielectric silica is of high importance for optoelectronic applications. The same group succeeded in incorporating amorphous titania into the frustule, which maintained its native structure even when local TiO_2 concentrations within the nanopores approached 60 wt %. Similar to germanium-silica nanocomposites, titanium dioxide nanocomposites are of high interest for optoelectronic, photocatalytic, and solar cell applications.

Genetic approaches to engineering hierarchical scale materials, engineered virus and protein cage architectures for biomimetic material synthesis, and bone-like materials by mineralization of hydrogels are further promising areas of research and development.

Biomineralization processes will play increasingly important roles in biology, biotechnology, medicine, chemistry, interfacial science, materials science, and nanotechnology [58.73]. With cellular and genetic controls of mineral formation, we could shape the minerals exactly as we need them. In vitro models of mineralization would allow us to understand in great detail the interactions and molecular contacts between macromolecular and mineral components. Macromolecular scaffolds for materials synthesis and organization would open up new directions in tissue engineering. A detailed understanding of the complex matrix–mineral relationships from the molecular level to the skeletal tissue, its properties and structure–function relations will open completely new approaches in engineering and medicine. For jewelery applications, we might even think about growing facetted crystals by spatially controlling growth inhibition and promoting proteins (control of crystal orientation and shape by interface engineering). Just imagine crystals grown in gels, with exactly the shape and size needed!

Ehrlich proposed bamboo corals as living bone implants [58.23, pp. 195–199]. The high content of calcium carbonate scaffolds of the commonly used coral resembles bone in terms of structure and mechanical properties. The coral exoskeleton is biocompatible, osteoconductive, and biodegradable, and allows for attachment, growth, spreading, and differentiation of bone cells. Coralline hydroxyapatite can be manufactured by hydrothermal conversion of the calcium carbonate coral skeleton.

Nature can furthermore serve as a teacher concerning the nanofabrication of crystalline materials, optical structures, nanoscale attenuators (for micro- and nanoelectromechanical systems (MEMS/NEMS)), and dynamic and hierarchical structures [58.74].

Microbe–mineral interactions that lead to sedimentary structures such as microbially induced sedimentary structures (MISS) and stromatolites, banded iron formations, cherts, sandstones, and carbonate rocks might one day be reproduced in the laboratory or in the field, and allow a more benign, environmentally friendly way of mining.

Although synthetic bone replacement materials are now widely used in orthopaedics, much research and development is still needed before we will be able to replicate both the structure as well as the exquisite mechanical properties of natural bone. Synthetic biomimetic materials fabricated according to biological principles and processes of self-assembly and self-organization are promising new approaches for a new generation of biologically and structurally related bone analogs for tissue engineering [58.75]. Current strategies for bone repair have accepted limitations. Marine organisms with naturally occurring porous structures as templates for bone growth might be an inspiration for novel ex vivo bone tissue engineering approaches [58.76].

Marine invertebrate cell cultures are currently not well established. They could serve as tools for biomineralization studies [58.77] and ultimately yield a new generation of advanced, high-performance composites required for new construction materials, new microelectronic, optoelectronic and catalytic devices, chemical and biological sensors, energy transducers and harvesters, smart medical implants, and faster and higher capacity biochips. Marine biotechnology regarding applications of bioinspired material synthesis in engineering and medicine has enormous potential.

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