

# Biomineralization

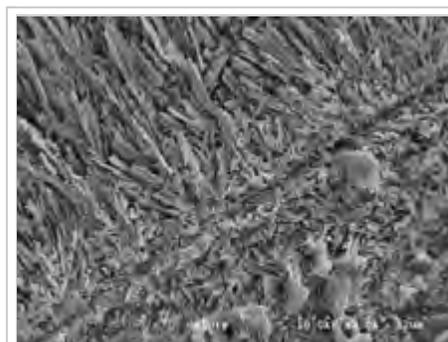
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**Biomineralization** is the process by which living organisms produce minerals,<sup>[2]</sup> often to harden or stiffen existing tissues. Such tissues are called mineralized tissues. It is an extremely widespread phenomenon; all six taxonomic kingdoms contain members that are able to form minerals, and over 60 different minerals have been identified in organisms.<sup>[3][4][5]</sup> Examples include silicates in algae and diatoms, carbonates in invertebrates, and calcium phosphates and carbonates in vertebrates. These minerals often form structural features such as sea shells and the bone in mammals and birds. Organisms have been producing mineralised skeletons for the past 550 million years. Other examples include copper, iron and gold deposits involving bacteria. Biologically-formed minerals often have special uses such as magnetic sensors in magnetotactic bacteria ( $\text{Fe}_3\text{O}_4$ ), gravity sensing devices ( $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{BaSO}_4$ ) and iron storage and mobilization ( $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$  in the protein ferritin).

In terms of taxonomic distribution, the most common biominerals are the phosphate and carbonate salts of calcium that are used in conjunction with organic polymers such as collagen and chitin to give structural support to bones and shells.<sup>[6]</sup> The structures of these biocomposite materials are highly controlled from the nanometer to the macroscopic level, resulting in complex architectures that provide multifunctional properties. Because this range of control over mineral growth is desirable for materials engineering applications, there is significant interest in understanding and elucidating the mechanisms of biologically controlled biomineralization.<sup>[7][8]</sup>



Calcitic skeletal parts of belemnites (Jurassic of Wyoming)



*Glomerula piloseta* (Sabellidae), longitudinal section of the tube, aragonitic spherulitic prismatic structure

## IUPAC definition

*Mineralization* caused by cell-mediated phenomena.<sup>[1][a]</sup>

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## Biological roles

Biominerals perform a variety of roles in organisms, the most important being support, defense and feeding.<sup>[9]</sup>

## Biology

If present on a super-cellular scale, biominerals are usually deposited by a dedicated organ, which is often defined very early in the embryological development. This organ will contain an organic matrix that facilitates and directs the deposition of crystals.<sup>[9]</sup> The matrix may be collagen, as in deuterostomes,<sup>[9]</sup> or based on chitin or other polysaccharides, as in molluscs.<sup>[10]</sup>

### Shell formation in molluscs

The mollusc shell is a biogenic composite material that has been the subject of much interest in materials science because of its unusual properties and its model character for biomineralization. Molluscan shells consist of 95–99% calcium carbonate by weight, while an organic component makes up the remaining 1–5%. The resulting composite has a fracture toughness ~3000 times greater than that of the crystals themselves.<sup>[11]</sup> In the biomineralization of the mollusc shell, specialized proteins are responsible for directing crystal nucleation, phase, morphology, and growths dynamics and ultimately give the shell its remarkable mechanical strength. The application of biomimetic principles elucidated from mollusc shell assembly and structure may help in fabricating new composite materials with enhanced optical, electronic, or structural properties.

## Chemistry

Because extracellular<sup>[12]</sup> iron is strongly involved in inducing calcification,<sup>[13][14]</sup> its control is essential in developing shells; the protein ferritin plays an important role in controlling the distribution of iron.<sup>[15]</sup> The most common mineral present in biomineralization is hydroxyapatite (HA), which is a naturally occurring mineral form of calcium apatite with the formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Hydroxyapatite crystals are found in many biological materials including bones,<sup>[16]</sup> fish scales,<sup>[17]</sup> and cartilage.<sup>[18]</sup> Each material has a mineral content which corresponds with the required mechanical properties, where increasing HA content typically leads to increased stiffness but reduced extensibility.<sup>[19]</sup>

## Evolution

The first evidence of biomineralization dates to some 750 million years ago,<sup>[20][21]</sup> and sponge-grade organisms may have formed calcite skeletons 630 million years ago.<sup>[22]</sup> But in most lineages, biomineralization first occurred in the Cambrian or Ordovician periods.<sup>[23]</sup> Organisms used whichever form of calcium carbonate was more stable in the water column at the point in time when they became biomineralized,<sup>[24]</sup> and stuck with that form for the remainder of their biological history<sup>[25]</sup> (but see <sup>[26]</sup> for a more detailed analysis). The stability is dependent on the Ca/Mg ratio of seawater, which is thought to be controlled primarily by the rate of sea floor spreading, although atmospheric CO<sub>2</sub> levels may also play a role.<sup>[24]</sup>

Biomineralization evolved multiple times, independently,<sup>[27]</sup> and most animal lineages first expressed biomineralized components in the Cambrian period.<sup>[28]</sup> Interestingly, many of the same processes are used in unrelated lineages, which suggests that biomineralization machinery was assembled from pre-existing "off-the-shelf" components already used for other purposes in the organism.<sup>[29]</sup> Although the biomachinery facilitating biomineralization is complex – involving signalling transmitters, inhibitors, and transcription factors – many elements of this 'toolkit' are shared between phyla as diverse as corals, molluscs, and vertebrates.<sup>[30]</sup> The shared components tend to perform quite fundamental tasks, such as designating that cells will be used to create the minerals, whereas genes controlling more finely tuned aspects that occur later in the biomineralization process – such as the precise alignment and structure of the crystals produced – tend to be uniquely evolved in different lineages.<sup>[9][31]</sup> This suggests that Precambrian organisms were employing the same elements, albeit for a different purpose — perhaps to *avoid* the inadvertent precipitation of calcium carbonate from the supersaturated Proterozoic oceans.<sup>[30]</sup> Forms of mucus that are involved in inducing mineralization in most metazoan lineages appear to have performed such an anticalcifatory function in the ancestral state.<sup>[32]</sup> Further, certain proteins that would originally have been involved in maintaining calcium concentrations within cells<sup>[33]</sup> are homologous to all metazoans, and appear to have been co-opted into biomineralization after the divergence of the metazoan lineages.<sup>[34]</sup> The *galaxins* are one probable example of a gene being co-opted from a different ancestral purpose into controlling biomineralization, in this case being 'switched' to this purpose in the Triassic scleractinian corals; the role performed appears to be functionally identical to the unrelated pearl gene in molluscs.<sup>[35]</sup> Carbonic anhydrase serves a role in mineralization in sponges, as well as metazoans, implying an ancestral role.<sup>[36]</sup> Far from being a rare trait that evolved a few times and remained stagnant, biomineralization pathways in fact evolved many times and are still evolving rapidly today; even within a single genus it is possible to detect great variation within a single gene family.<sup>[31]</sup>

The homology of biomineralization pathways is underlined by a remarkable experiment whereby the nacreous layer of a molluscan shell was implanted into a human tooth, and rather than experiencing an immune response, the molluscan nacre was incorporated into the host bone matrix. This points to the exaptation of an original biomineralization pathway.

The most ancient example of biom mineralization, dating back 2 billion years, is the deposition of magnetite, which is observed in some bacteria, as well as the teeth of chitons and the brains of vertebrates; it is possible that this pathway, which performed a magnetosensory role in the common ancestor of all bilaterians, was duplicated and modified in the Cambrian to form the basis for calcium-based biom mineralization pathways.<sup>[37]</sup> Iron is stored in close proximity to magnetite-coated chiton teeth, so that the teeth can be renewed as they wear. Not only is there a marked similarity between the magnetite deposition process and enamel deposition in vertebrates but some vertebrates even have comparable iron storage facilities near their teeth.<sup>[38]</sup>

Type of mineralization	Examples of organisms
<b>Calcium carbonate</b> (calcite or aragonite)	<ul style="list-style-type: none"> <li>▪ foraminifera</li> <li>▪ coccolithophores</li> <li>▪ calcareous sponge spicules</li> <li>▪ corals</li> <li>▪ Archaeocyatha</li> <li>▪ bryozoans</li> <li>▪ brachiopod and mollusc shells</li> <li>▪ Echinoderms</li> <li>▪ Serpulidae</li> </ul>
<b>Silica</b>	<ul style="list-style-type: none"> <li>▪ radiolarians</li> <li>▪ diatoms</li> <li>▪ most sponge spicules</li> </ul>
<b>Apatite</b> (phosphate carbonate)	<ul style="list-style-type: none"> <li>▪ enamel (Vertebrate teeth)</li> <li>▪ Vertebrate bone</li> <li>▪ conodonts</li> </ul>

## Astrobiology

It has been suggested that biom minerals could be important indicators of extraterrestrial life and thus could play an important role in the search for past or present life on Mars. Furthermore, organic components (biosignatures) that are often associated with biom minerals are believed to play crucial roles in both pre-biotic and biotic reactions.<sup>[39]</sup>

On January 24, 2014, NASA reported that current studies by the *Curiosity* and *Opportunity* rovers on the planet Mars will now be searching for evidence of ancient life, including a biosphere based on autotrophic, chemotrophic and/or chemolithoautotrophic microorganisms, as well as ancient water, including fluvio-lacustrine environments (plains related to ancient rivers or lakes) that may have been habitable.<sup>[40][41][42][43]</sup> The search for evidence of habitability, taphonomy (related to fossils), and organic carbon on the planet Mars is now a primary NASA objective.<sup>[40][41]</sup>

## Potential applications

Most traditional approaches to synthesis of nanoscale materials are energy inefficient, requiring stringent conditions (e.g., high temperature, pressure or pH) and often produce toxic byproducts. Furthermore, the quantities produced are small, and the resultant material is usually irreproducible because of the difficulties in controlling agglomeration.<sup>[44]</sup> In contrast, materials produced by organisms have properties that usually surpass those of analogous synthetically manufactured materials with similar phase composition. Biological materials are assembled in aqueous environments under mild conditions by using macromolecules. Organic macromolecules collect and transport raw materials and assemble these substrates and into short- and long-range ordered composites with consistency and uniformity. The aim of biomimetics is to mimic the natural way of producing minerals such as apatites. Many man-made crystals require elevated temperatures and strong chemical solutions, whereas the organisms have long been able to lay down elaborate mineral structures at ambient temperatures. Often, the mineral phases are not pure but are made as composites that entail an organic part, often protein, which takes part in and controls the biomineralisation. These composites are often not only as hard as the pure mineral but also tougher, as the micro-environment controls biomineralisation.

## Biomineralization of Uranium contaminants in groundwater

Biomineralization may be used to remediate groundwater contaminated with uranium.<sup>[45]</sup> The biomineralization of uranium primarily involves the precipitation of uranium phosphate minerals associated with the release of phosphate by microorganisms. Negatively charged ligands at the surface of the cells attract the positively charged uranyl ion ( $\text{UO}_2^{2+}$ ). If the concentrations of phosphate and  $\text{UO}_2^{2+}$  are sufficiently high, minerals such as autunite ( $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}$ ) or polycrystalline  $\text{HUO}_2\text{PO}_4$  may form thus reducing the mobility of  $\text{UO}_2^{2+}$ . Compared to the direct addition of inorganic phosphate to contaminated groundwater, biomineralization has the advantage that the ligands produced by microbes will target uranium compounds more specifically rather than react actively with all aqueous metals. Stimulating bacterial phosphatase activity to liberate phosphate under controlled conditions limits the rate of bacterial hydrolysis of organophosphate and the release of phosphate to the system, thus avoiding clogging of the injection location with metal phosphate minerals.<sup>[45]</sup> The high concentration of ligands near the cell surface also provides nucleation foci for precipitation, which leads to higher efficiency than chemical precipitation.<sup>[46]</sup>

## See also

- Biocrystallization
- Biointerface
- Biomineralising polychaetes
- Bone mineral
- Diatomaceous earth
- Magnetotactic bacteria
- Mineralized tissues

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### Footnotes

- a. Biomineralization is a process generally concomitant to *biodegradation*.<sup>[1]</sup>

### Notes

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## External links

- An overview of the bacteria involved in biomineralization from the Science Creative Quarterly (<http://www.scq.ubc.ca/?p=342>)
- ‘Data and literature on modern and fossil Biominerals’: <http://biomineralisation.blogspot.fr> (<http://biomineralisation.blogspot.fr>)
- Minerals and the Origins of Life (<https://webcast.stsci.edu/webcast/detail.xhtml?talkid=4006>) (Robert Hazen, NASA) (video, 60m, April 2014).
- Biomineralization web-book: [bio-mineral.org](http://bio-mineral.org/) (<http://bio-mineral.org/>)
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