Biominerals — Source and Inspiration for Novel Advanced Materials

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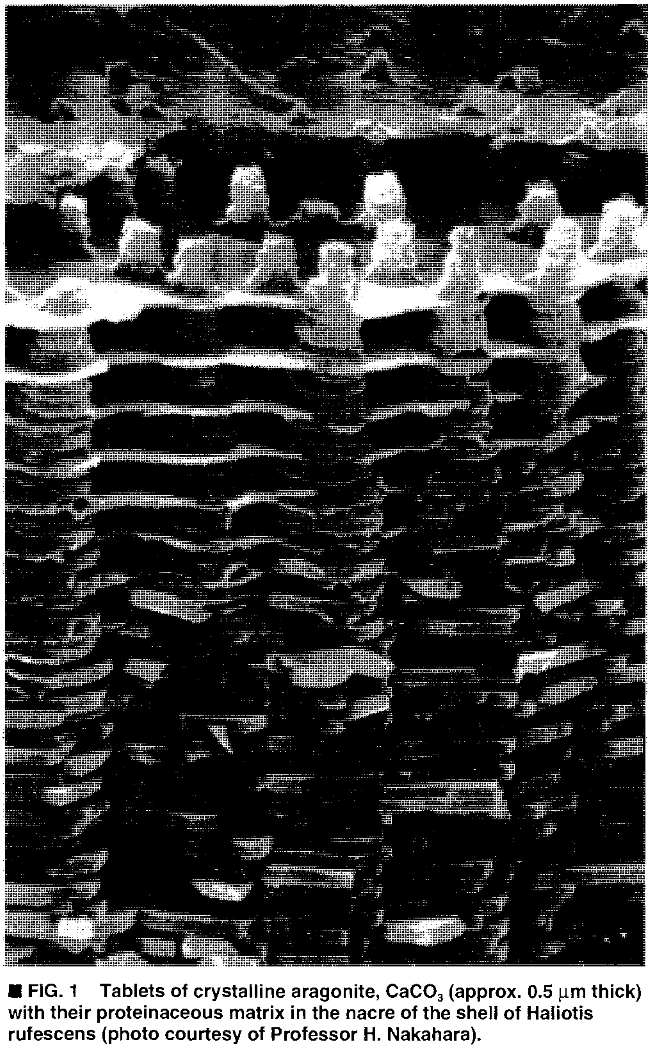
iomineralization seems an odd sort of word. How can you combine biology and minerals? However, a quick look around brings to light many familiar objects that are examples of biominerals. Most dramatic are the coral reefs and sea shells of the marine environment (calcium carbonate) and human bone and teeth (calcium hydroxyapatite) but there are many other examples. In the past 10 years, an increasing number of biominerals has been reported (Table 1). Interest in the biological and chemical processes that lead to biomineralization, however, has only developed rather recently. Early observations were made by paleontologists who were interested in the preservation, through geological time, of the hard parts of organisms such as shells and skeletons but only in 1989 did the field really come of age with the almost simultaneous publication of three monographs covering current knowledge of the biological, biochemical, chemical and taxonomic aspects of biomineralization (Mann *et al.* 1989; Lowenstam & Weiner 1989; Simkiss & Wilbur 1989).

But there is much more to biomineralization than just the interest in the biological materials 'because they are there'. Biominerals exhibit a wide variety of functions and understanding how biominerals perform these functions is a major new frontier in interdisciplinary scientific research. Much of the current interest derives from the inspiration to be found in biominerals for the design of novel materials. Biomineral phases can be crystalline, amorphous or partly crystalline/partly amorphous. They contain individual biomineral deposits that are generally less than 1 μ and may be as small as 10 nm. Such nanospace materials are of interest to emerging technologies (Birchall 1989). Furthermore, in many biological systems, the biominerals are present as components of composite materials, where the inorganic components are organized together with organic components such as proteins or polysaccharides to form the final biological structure. Two established instances will serve to illustrate the link between the structure of biominerals and the design of novel materials. A third example relates to our own studies of the biological mineralization of iron in some marine molluscs.

Biocoral

The natural coral skeleton is a porous structure with many channels and spaces, whose dimensions in certain coral species match those of human bone. This similarity to, and compatibility with, bone has been exploited in that coral can be used as an implant in bone tissue. In France, such a material, known as Biocoral® has been prepared by selective treatment of natural coral and used for some years as a substitute for bone grafts and in plastic surgery (Inoteb 1989). The Australian distributors (3M Company) indicate that Biocoral has been approved for use in Australia and already several surgical procedures have been carried out in Sydney and Melbourne. The mechanical properties of Biocoral can be controlled by changing its porosity, giving materials that match or exceed bone in compressive strength and elasticity. It is the chemistry of the coral preparation that is particularly appropriate for this surgical use. As noted above, bone is made of a phosphate salt of calcium, while coral is a carbonate salt. The particular form of $CaCO_3$ is aragonite, a metastable form of $CaCO_3$. This metastable nature means that, when implanted, the $CaCO_3$ gradually dissolves (i.e. is resorbed) and is replaced

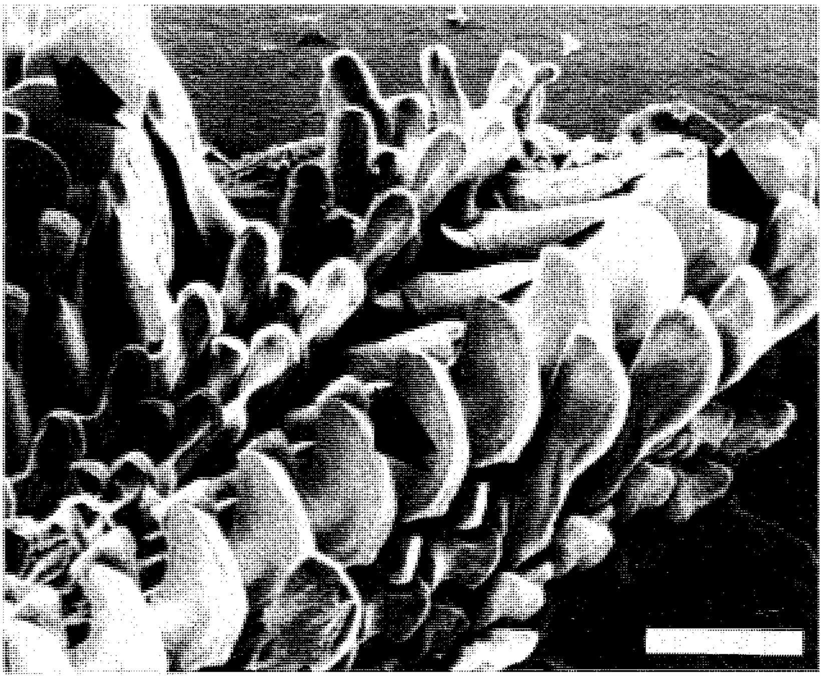


■ **FIG. 1 Tablets of crystalline aragonite, $CaCO_3$ (approx. 0.5 μm thick) with their proteinaceous matrix in the nacre of the shell of Haliotis rufescens (photo courtesy of Professor H. Nakahara).**

TABLE 1 The types and functions of the main inorganic solids found in biological systems

Mineral	Formula	Organism/Function
Calcium carbonate:		
Calcite	$CaCO_3$*	Algae/exoskeletons Trilobites/eye lens
Aragonite	$CaCO_3$	Fish/gravity device Molluscs/exoskeleton
Vaterite	$CaCO_3$	Ascidans/spicules
Amorphous	$CaCo_3.nH_2O$	Plants/Ca store
Ca phosphate:		
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	Vertebrates/endoskeletons teeth Ca Store
Octa–calcium phosphate	$Ca_8H_2(PO_4)_6$	Vertebrates/precursor phase in bone?
Amorphous	?	Mussels/Ca store Vertebrates/precursor phases in bone?
Calcium oxalate:		
Whewellite	$CaC_2O_4.H_2O$	Plants/Ca Store
Weddellite	$CaC2O4.2H_2O$	Plants Ca store
Group IIA metal sulphates		
Gypsum	$CaSO_4$	Jellyfish larvae gravity device
Barite	$BaSO_4$	Algae/gravity device
Celestite	$SrSO_4$	Acantharia/cellular support
Silicon dioxide:		
Silica	$SiO_2.nH_2O$	Algae/exoskeletons
Iron oxides:		
Magnetite	Fe_3O_4	Bacteria/magnetotaxis Chitons/teeth
Geothite	α–FeOOH	Limpets/teeth
Lepidocrocite	γ–FeOOH	Chitons (Mollusca) teeth
Ferrihydrite	5 $Fe_2O_3.9H_2O$	Animals and plants/ Fe storage proteins

* A range of magnesium–substituted calcites are also formed.



■ **FIG. 2 Scanning electron micrograph of the radula of the chiton A. hirtosa. Scale bar = 100 μm. The major lateral teeth are indicated by arrows.**

by newly formed bone, synthesized by cells that migrate into the porous structure from adjacent bone. The other common form of $CaCO_3$, calcite, does not dissolve under these conditions. The implant material contains some amino acids but no protein and thus differs from natural bone. The absence of foreign protein however is particularly attractive in an implant since this avoids any adverse immunological reaction and hence rejection. In this instance, the structure and composition of the natural biomineral, coral, can be used to prepare a highly useful biomaterial for surgery.

Flexible Concrete

The microarchitecture of the composite material that is the molluscan shell has been used to inspire the preparation of what at first glance appears to be a contradiction in terms: flexible concrete, or, more accurately, macrodefect-free concrete (Birchall 1989). Molluscan shells are composed of microcrystals of $CaCO_3$ organized within a protein-rich organic matrix (Fig. 1). Such shells have strengths in tension that are an order of magnitude greater than that of concrete. The innovative inclusion of a water-soluble polymer in the concrete formulation was derived directly from the analogy of the structural architecture within the shells and proved to be critical in obtaining a plastic rheology for the concrete. This novel concrete material has been used to fabricate building materials and automobile components, including car springs, although not yet on an industrial mass production scale.

Chitons and Limpets

The biological structure that has engaged our interest is the radula, a tongue-like organ, of two kinds of marine molluscs namely, chitons and limpets, that are widely distributed in intertidal environments (Webb *et al.* 1989, 1990). Chitons and limpets have highly mineralized teeth on the radula to scrape from rocky substrates the crustose coralline algae on which they feed. The organic matrix of teeth and mineralizing elements for subsequent hardening are secreted by epithelial cells as the teeth migrate slowly along the radula membrane. This migration results from the continual wearing away of the teeth during feeding. The radula is thus 'conveyor belt' of teeth, with the early teeth being soft and unmineralized and the fully mature teeth being hardened as functional composite structures (Fig.

The availability of teeth at varying stages of mineralization allows us to study the process of mineralization and the mechanisms involved, as well as the products, i.e. the biominerals together with associated organic material.

Both chitons and limpets use iron to harden their teeth, depositing within them a variety of iron oxides. These, together with other inorganic solids, reinforce and harden the organic matrix. In the limpet, silicon is also deposited, as amorphous silica SiO_2, while in the chiton, calcium is deposited as crystalline forms of hydroxyapatite. A distinct mineralized layer of magnetite (M in Fig. 3) and as many as four other oxides cover the surface of the chiton tooth that strikes the rocky substrate during feeding and the molecular mechanisms that lead to their formation have been clarified only recently (Kim *et al.* 1989; Webb *et al.* 1991). Behind the magnetite layer are densely packed fibres that are rope-like strands of chitin (Evans *et al.* 1990), their density determining whether magnetite is formed or calcium is mineralized. Most of the protein of the tooth is present in the calcified region, suggesting that proteins play a key role in initiating and controlling mineralization (Evans *et al.* 1991). For iron mineralization, this matrix-mediated control is less evident and mineralization and its products appear to be under kinetic control of the flux of iron into the tooth from the superior epithelial cells (Kim *et al.* 1989; Webb *et al.* 1991).

The microarchitecture of the chiton tooth can be related directly to its biological function as a feeding implement. Magnetite, with a hardness of 6–6.5 on the Mohs scale (i.e. harder than apatite but not as hard as quartz) is densely packed as a surface layer of the tooth cusp that impacts on the substrate during feeding. Behind this layer are chitin fibres, reinforced with hydroxyapatite, that act as 'shock absorbers' supporting the tooth during the physical stress of feeding. In summary, a matrix-poor but biomineral-rich region serves as the cutting edge that is complemented by a matrix-rich calcified region that gives it support.

Insights about the biological manipulation of materials and structures to perform a function can be used to develop new technologies. At the University of Groningen in The Netherlands, the chiton radula is being used to develop new designs for dredging machinery. In addition, the control of crystallization in biology is relevant to the problems faced by such emerging industries as those developing advanced ceramics as well as established mineral processing plants. Size and shape of crystals affects how readily the crystals can be filtered, washed and processed. Indeed a specific size range of the particle may be necessary for its role, such as is the case for the iron oxide particles on magnetic recording tape.

FIG. 3 Scanning electron micrograph of the posterior surface of a fractured fully mature tooth of the chiton A. hirtosa. Scale bar = 100 µm.

There are many options and challenges derived from the study of biominerals. As Derek Birchall of ICI (UK)'s Advanced Materials Group has put it (Birchall, 1989):

> Biology does not waste energy manipulating materials and structures that have no function and it eliminates those that do not function adequately and economically. The structures that we observe 'work' and their form and microstructure have been developed and refined over millions of years. The task of the modern materials technologist is to develop, within a very short timescale, materials the microstructure of which is such that they perform a function efficiently. It is as well, then, to look for fresh insights to biology at the wisdom encapsulated in the materials it uses.

Acknowledgements

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