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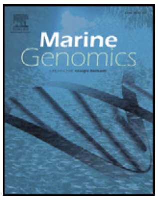
Cells to Shells: The genomics of mollusc exoskeletons



Biomimetic and bio-inspired uses of mollusc shells

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ABSTRACT

Climate change and ocean acidification are likely to have a profound effect on marine molluscs, which are of great ecological and economic importance. One process particularly sensitive to climate change is the formation of biominerals in mollusc shells. Fundamental research is broadening our understanding of the biomineralization process, as well as providing more informed predictions on the effects of climate change on marine molluscs. Such studies are important in their own right, but their value also extends to applied sciences. Biominerals, organic/inorganic hybrid materials with many remarkable physical and chemical properties, have been studied for decades, and the possibilities for future improved use of such materials for society are widely recognised. This article highlights the potential use of our understanding of the shell biomineralization process in novel bio-inspired and biomimetic applications. It also highlights the potential for the valorisation of shells produced as a by-product of the aquaculture industry. Studying shells and the formation of biominerals will inspire novel functional hybrid materials. It may also provide sustainable, ecologically- and economically-viable solutions to some of the problems created by current human resource exploitation.

General definitions

Bio-inspired materials synthesis Concepts derived from natural processes such as biomineralization using artificial materials (Lobmann, 2007)

Biomimicry (Biomimetic) Sustainably orientated methods mimicking living organisms and ecosystems in terms of shape, material, or organisation by using living organisms or materials of a biological origin (adapted from Lobmann, 2007).

Calcination Changing a substance's physical or chemical constitution by heating in oxygen or air, but below melting or fusion points. For instance; $CaCO_3 \rightarrow CaO + CO_2$ at ~850–~1200 °C

Circular economy As opposed to a linear economy (make, use, dispose), a circular economy aims to minimise waste and pollution through improving longevity, repair, reuse, remanufacture, and recycling.

Valorisation To assign or give value to something, where value can be economic, environmental, and/or social.

Mollusc shell microstructures

Composite prismatic A variety of prismatic structures with large horizontal prisms each composed of compound prisms radiating in three directions

Crossed-lamellar Lath-like crystals arranged in “plywood” structure. The most common structure in mollusc shells (90% of gastropods and 60% of bivalves)

Foliated structure An arrangement of thin folia or sheets of calcite which intersect growth surface at a low angle (4–7°), including regularly foliated, and crossed foliated, complex crossed foliated and calcitic crossed bladed structures.

Homogeneous Granular crystals with no typical crystal form

Nacreous Tablet-like crystals arranged into columns or in sheets. The toughest layer in mollusc shells

Simple prismatic Consists of column-shaped crystals. Individual prisms arranged perpendicular to the shell surface

Biomimetic and bio-inspired technologies. Materials inspired from mollusc shell composition/structure

Additive manufacturing Layers of diverse materials built up to form three-dimensional structures. A variety of materials from polymers to metals, to ceramics can be used.

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[1] Shell waste valorisation.

[2] Shell knowledge for material design inspiration.

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Freeze casting Templating of porous structures into a solidified phase by the solidification of a solvent. A large variety of materials can be processed by this method, independent of the materials property.

Langmuir mono-layers, self-assembled mono-layers Surface of well-defined chemistry used for patterning crystal location and examining the influence of organics on crystal orientation and crystal phase

Layer-by-layer assembly, electrophoretic deposition Both techniques are used for fabricating functional thin films with a layered structure, one by alternately immersing a clean substrate into several solutions, other under the influence of an electric field, where a coagulation of particles turns to a dense mass.

1. Introduction

The strength, hardness, and toughness of shells produced by molluscs are major characteristics of this group that have been recognised deep into human history. The mechanical attributes of their shells, alongside their beauty and intricacy, have made the molluscs that craft them a charismatic marine group. Shells have played an important role in many aspects of human culture: they have been used widely as cutting and weight bearing tools (Douka and Spinapolice, 2012), as well as being traded for goods globally until the 20th Century (Johnson, 1970). A myriad of other historical uses could be listed. The influence of molluscs on our society and economy is not purely historical. On the contrary, society has more to gain from the study and application of molluscs and their shells. For instance, despite concerted efforts, man-made ceramics and composites, usually produced at high temperatures and/or high pressure (Tam et al., 2009), remain inferior to mollusc shells in strength and toughness (Sellinger et al., 1998; Munch et al., 2008). The hierarchy of structural features and organic/mineral phase interactions observed in shells have yet to be recreated completely (Espinoza et al., 2009). There is a growing understanding of the need to improve the sustainability of all processes. This has led some to take another look at shells to determine whether established and novel biomimetic and bio-inspired applications can be implemented and/or commercialised. Further, as aquaculture continues to expand its share of global food production (FAO, 2014), the issue of shell waste from food production will become increasingly impactful unless shells can be revalued and repurposed.

Improving knowledge on the value of shells for novel applications, and their use as an alternative to existing resources requires a solid and fundamental scientific grounding. Mollusc shells are composed of >95–99.9% $CaCO_3$, the remainder being organic matrix (Currey, 1999; Harper, 2000). The organic matrix comprises mainly proteins, glycoproteins, chitin, and acidic polysaccharides. Important components of these organic molecules are hydrophobic, referred to as “frame-work macromolecules”, and provide a three-dimensional matrix for mineral deposition. Other soluble organic macromolecules, rich in negatively charged residues, are excellent candidates for interacting with the mineral ions (Weiner et al., 1983). These molecules are essential components in the morphological variation, spatial organisation, and the mechanical and biological properties of the biominerals produced (Addadi et al., 2006; Mann, 1988). In recent decades, the primary structure of more than 40 mollusc shell proteins has been elucidated (Marin et al., 2007), and some of the proteins that control the biomineralization process have been isolated and characterised (Arakaki et al., 2015; Weiner and Dove, 2003). However, the molecular mechanisms underlying shell formation processes remain poorly understood. Some of the research presented in this special issue of “Marine Genomics” aims at contributing to our understanding of the processes of shell production at molecular and cellular levels. For instance, several studies have probed the transcriptomes of bivalves, characterising the expression of many genes involved in the biomineralization process (Bjärnmark et al., 2016-in this issue; Vendrami et al., 2016-in this issue; Yarra et al., 2016-in this issue). Further, proteins not previously recognised as being related to the shell have been characterised in a proteomic study of the clam *Mya truncata*, suggesting that a shells function goes beyond a simple protective layer, and may also be actively involved in cell signalling processes and the immune response (Arivalagan et al., 2016-in this issue).

These studies are important not only because of the fundamental questions they pose and the novel insights they provide, but also because such insights can spark new avenues for applied sciences. An understanding of the role and differential spatial expression of genes involved in mollusc shell biomineralization may help materials scientists progress in the synthesis of shell-inspired nanostructures. Similarly, a better understanding of the proteins found locked inside the shell structure will help change our modern view of shells from aquaculture being considered a waste product. The following sections will give a brief and non-exhaustive overview of the uses for biomineralization in novel biotechnology applications, and the potential application of waste shells from the aquaculture industry.

2. Shell knowledge for bio-inspiration

Mollusc shells represent an important portion of the large family of biomaterials. With our oceans warming and acidifying at a rate that exceeds historical proxies, many calcifying organisms are being challenged for survival. By studying the process of biomineralization we gain a better understanding of how molluscs may react to contemporary climate change (Vendrami et al., 2016-in this issue), and the impact that human activity is having on these ecologically- and economically-important organisms. This knowledge is also likely to inspire novel biomimetic synthesis methods which may lead to more sustainable industrial and societal practices.

Shell producing mollusc classes have recognisable shell microstructures *e.g.* “prismatic”, “nacreous”, “foliated”, “crossed-lamellar”, “composite-prismatic”, and “homogeneous” (Carter, 1990). These different calcified layers are exquisitely controlled by macromolecules. Characterisation of the shell matrix macromolecules allows a better understanding of their functions, and further refines the biomineralization model. Applied sciences look to such research in the search for innovative sustainable solutions in the production of synthetic biomaterials. Specifically, new design strategies have been inspired from the molluscan nacreous layer, the most studied of all shell microstructures (Corni et al., 2012). Nacre, in which mineral platelets arranged in single layers are staged like brickwork with biopolymer “mortar”, has been shown to be several orders of magnitude stronger than the chemically precipitated counterpart: aragonite (Jackson et al., 1988). The complex hierarchical structure of nacre may hold the key to such strength, and may provide a model foundation for stronger future biomimetic materials. This hierarchical structure comprises ~32 nm nano-grains that create a tablet that is delimited by a fine three-dimensional network of organic material, forming 0.5–10 μm “bricks”, that ultimately form a meso-structure of layers, each approximately 0.3 mm thick (Fig. 1) (Luz and Mano, 2009; Meyers et al., 2011). Biomimetic design of materials and biomaterials inspired by the structure of nacre offers a perfect model for the development of new strong, tough, and light-weight structural materials. At laboratory scale, synthetic model matrices such as Langmuir monolayers (Donners et al., 2002) and self-assembled mono-layers (Aizenberg et al., 1999) have been successfully applied to mimic the biological control exerted by an organic matrix in creating $CaCO_3$ crystals with specific orientations that distinguish them from their inorganically produced counterparts. Organic/$CaCO_3$ hybrid materials have been developed by using molecules, such as proteins, as templates or additives (Nishimura, 2015). The principle of confinement using an organic scaffold during the mineralization process has been successfully used to control crystal formation and morphology (Kim et al., 2011). Even more sophisticated bio-inspired materials with tuneable morphologies and properties

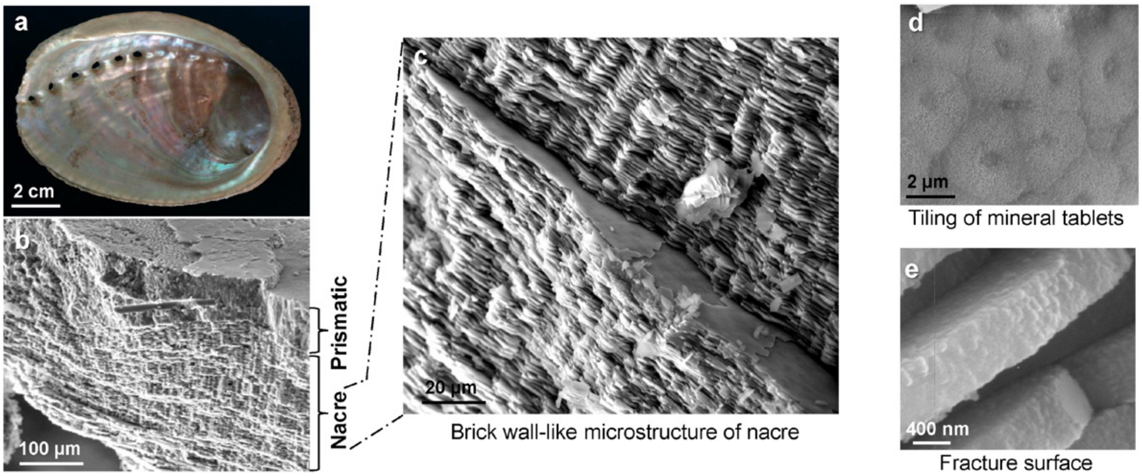

Fig. 1. The multi-scale structure of an abalone shell (*Haliotis* sp.): (a) Image of the interior view of a red abalone shell. Scanning electron microscope showing (b) cross section of shell, (c) brick wall-like microstructure of nacre, (d) tiling of tablets, (f) the tablets composed by the assembly of nano-grains.

have been synthesised using proteins capable of directing *in vitro* formation of minerals from an aqueous precursor solution (Singh et al., 2010). Inspired by the nacreous microstructure, bottom-up techniques such as layer-by-layer assembly (Tang et al., 2003), and electrophoretic deposition (Sarkar and Nicholson, 1996) have shown promise in being able to produce nanocomposites with well-defined structures, similar to that which is common place in shells.

In spite of a concerted effort in the identification of macromolecules in shells and in the field of biomimetic biomineralization, current avenues of research are based only on certain aspects of the biomineralization process, and as such lack the detail to match the intricacy of shells. Development of millimetre-scale materials inspired by the nacre of mollusc shells has proven another important approach in the field of bio-inspired materials (Barthelat and Zhu, 2011). Functional biomimetic and bio-inspired materials have only yet been produced in a laboratory, and their synthesis on an industrial scale remains out of reach (Nudelman and Sommerdijk, 2012). This is due in part to the technological limitations that currently prevent the scaling-up of such laboratory procedures, and also the prohibitive costs associated with it. To overcome some of the technical limitations, several original strategies have been employed to produce bio-inspired material with nacre-like architectures. Freeze casting (Deville, 2008) and additive-manufacturing techniques (Fu et al., 2011) offer the potential for industrial-scale manufacturing.

Currently, industrial applications of the biomineralization process are mainly of a bio-inspired nature, the direct use of biomimetic technology is still in its infancy. The cement company: *Calera* (U.S.A.), for example, applies bio-inspired processes that essentially mimic marine cementation by taking CO_2 from the atmosphere and locking it into a solid structure during cement production (Constantz et al., 2013). The efficacy of this carbon sequestration process remains controversial, however, *inter alia* regarding the calcium source. *CO_2 solutions* (Canada), however, demonstrates a perfect example of a biomimetic approach to sequester carbon, using carbonic anhydrase to convert CO_2 to limestone eventually turning it into materials by combining it with bauxite (Penders-van Elk et al., 2015). Further, the successful application of microbially-induced $CaCO_3$ precipitation as cementitious building materials sets an example for materials inspired from other biomineralization systems (Dhami et al., 2013).

Until recently, a major research tendency was to identify the influence of single genes and macromolecules over the entire biomineralization process. Biomineralization is now recognised to be the result of the synergy of all macromolecules present during mineral formation. As more genomic and proteomic information is gathered regarding biomineralization, the relevance of synthetic biology in this field will increase. Such avenues hold great promise, but as yet remain in their infancy (Dade-Robertson et al., 2015). If, as widely suggested, it is the shell matrix macromolecules and genes from which they derive that are key to understanding the biomineralization model, then it may be the case that *in vitro* synthesis of key biomineralization genes, proteins, and systems will provide major future advances in the production of synthetic bio-materials.

Our modern day society uses natural resources ~1.5 times faster than they can be renewed by the Earth's systems (Borucke et al., 2013). This puts a strong demand on the development of new materials whose production puts a lower strain on the Earth's rare raw materials and energy resources. The development of functional hybrid materials, through environmentally benign routes, with multiple combinations of outstanding properties including: light weight, high flexibility, mechanical strength, dynamic function, and structural hierarchy is likely to be an important outcome of the continued deciphering of shell matrix macromolecules and biomineralization genomics as long as intensive fundamental research continues.

3. Valorisation of waste shells

Molluscs account for ~23% of global aquaculture production by live weight, which equated to ~15 million tonnes of biomass in 2012 (FAO, 2014). Currently, the shells produced (up to 60% of the product by weight) are largely considered as waste, and end up in landfill. This is in opposition to a large body of research highlighting their impressive attributes and a long history of their recognition as a valuable resource. Further, $CaCO_3$ is one of the most highly exploited resources on the planet. As highlighted in Arivalagan et al. (2016-in this issue) mollusc shells are not simply a source of $CaCO_3$ but a complex composite containing a myriad of proteins. The organic shell matrix accounts for only a tiny fraction of the shell by weight but provides important characteristics that, as described in the following section, can provide shell-derived $CaCO_3$ with unique attributes that can be applied. Despite widespread discussion, the large scale valorisation of discarded shells has yet to be realised. Millions of tonnes of shell waste are an important consideration. It is clear, however, that despite projected increases in aquaculture reliance in the future, shell waste is still orders of magnitude less than the yearly global $CaCO_3$ demand. Further, although some mollusc aquaculture removes shells during processing for many food products, a significant proportion of molluscs are sold with their shells, making shell waste retrieval more complex. The following applications, if viable, will not have a large impact on the limestone mining industry. However, in terms of waste repurposing such applications could be extremely important in improving the sustainability of the food and aquaculture

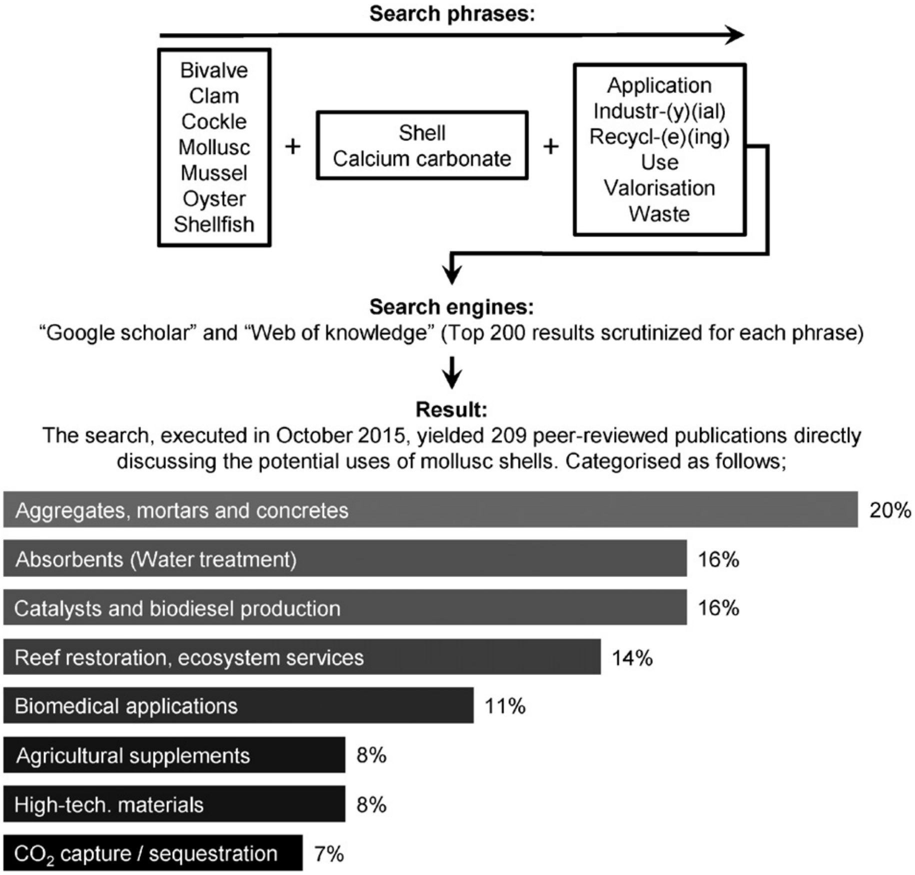

Fig. 2. A schematic detailing the method and results of a generalised abbreviated search elucidating the discussed potential uses of waste mollusc shells. The schematic shows the derivation of non-biased search terms and the search engines and result cutoffs used. Results were grouped into broad application categories, and the percentages represent the proportion of each group in the overall analysis of waste shell use.

industries. Further, the importance of waste valorisation has recently been highlighted by the European Commission's commitment to a ~€6 billion Circular Economy package (European Commission, 2015).

In order to provide an overview of the discussed potential uses of mollusc shells from aquaculture, a generalised abbreviated search was performed on "Google Scholar" and "Web of Knowledge". As highlighted in Fig. 2, search phrases were derived from sets of generalised keywords which were selected for their lack of bias to any particular application. The top 200 results of each search were scrutinised for peer-reviewed publications directly discussing the use of mollusc shells. Relevant articles were categorised according to the type of application (Fig. 2). The field would further benefit from a full-scale systematic review of this subject.

The most often cited prospective use of shells involves their incorporation in construction materials (Fig. 2). Lertwattanaruk et al. (2012), for example, tested mortars made with ground mollusc shells and found they could be a viable replacement for cement. Further, some properties such as water requirement and setting time showed improvements on conventional mixes (Lertwattanaruk et al., 2012). However, strict construction material regulations may prove limiting for large scale applications of this sort.

Molluscs shells have been advocated as absorbents in water treatment (Shariffuddin et al., 2013) and CO_2 capture techniques (Ma and Teng, 2010), as well as being touted as good catalysts in biodiesel production (Boro et al., 2012). Shells of the green-lipped mussel (*Perna canaliculus*) were processed to form hydroxyapatite and found to be good photocatalytic agents in waste water treatment, and a potential replacement to commonly used, but costly, Titanium dioxide (Shariffuddin et al., 2013). Similarly, calcined oyster shells in some cases outperformed reagent-grade $CaCO_3$ in CO_2 absorption experiments, possibly due to organic matrix-derived CaO impurities that buffered against catalyst activity decay (Ma and Teng, 2010). However, the calcination process, which, in this case, involves heating shells to 700–900 °C for several hours, must also be considered prior to advocating shells as a viable and sustainable source of CO_2 absorption and biodiesel catalysts.

The use of dead oyster shells to form reefs for shoreline protection through wave attenuation, natural water treatment, and live oyster population restoration has been discussed widely (Beck et al., 2011; Coen and Luckenbach, 2000; Piazza et al., 2005), and implemented on small-scales, predominantly in the U.S.A. Such an application not only provides environmental benefits because of its use of waste shells and lack of high-energy processing, but also because of the ecosystem services such reefs provide by creating a suitable habitat for oyster spat settlement and the development of new ecosystems (Coen and Luckenbach, 2000). Care, however, must be taken when considering ecosystem engineering: the intentional growth of the oyster *Crassostrea gigas* (an invasive species in North America, Europe, and Australasia, native to the Pacific coast of Asia) for instance, certainly has economic value, but also has many negative effects (as reviewed by Ruesink et al., 2005), particularly regarding native oyster populations.

The use of shells in bone tissue engineering is thought to be facilitated by organic matrix-derived impurities in the $CaCO_3$. Green et al. (2013) highlight that the residual organic matrix of mollusc shell-derived $CaCO_3$ makes the composite both bioactive and biocompatible, thus able to promote bone regeneration. This was shown in the landmark surgical procedure of Atlan et al. (1997), and has been intensely studied more recently (Brion et al., 2015; Green et al., 2015).

Mollusc shells have been suggested as a potential filler in high-tech polymer manufacture. Hamester et al. (2012) concluded that $CaCO_3$

derived from mollusc shells could be a viable replacement for commercial $CaCO_3$ as a filler in polypropylene composites. Once again, however, several hours of high temperature heat treatment was required to prepare the shells, bringing into question the sustainability of such an application.

Finally, shells have been tested as a liming agent for the treatment of acidic soils in agriculture (Lee et al., 2008). They have also been used on a small-scale as a calcium supplement in poultry feed (Scott et al., 1971). Both applications could reduce the reliance on mined limestone in the agriculture industry as well as providing a more economically beneficial source of $CaCO_3$ depending on the proximity of the farms to mollusc aquaculture regions.

The vast majority of potential uses of waste shells from the aquaculture industry, of which examples are given above, remain unrealised at a commercial level. However, as the idea of sustainable growth spreads in the public conscience there is an ever-growing desire to repurpose waste materials. Waste shell repurposing is a sustainable process in its own right. Some of the applications may also provide a more sustainable solution than established processes, whilst others may prove less sustainable on large scales. Once the pros, cons, and limiting steps of each application type have been established, applications with promising environmental credentials should be prioritised. Hence, the preceding rationale should urge a change of mind-set away from considering mollusc shells as a waste product towards considering them a valuable resource.

4. Conclusions

Fundamental research, including that by the CACHE network (presented in this special issue), is providing a better understanding of the mechanisms underlying mollusc shell biomineralization, and the effects of climate change and ocean acidification on molluscs. This article highlights how such research can have a wider impact by promoting new avenues of exploration in beneficial bio-inspired and biomimetic applications, and pushes us to reconsider shells as a precious resource rather than a waste product. Indeed, some of the sustainable applications mentioned in this article might contribute to the United Nations Framework Convention on Climate Change's two key strategies to address climate change: adaptation (more sustainable practices), and mitigation (carbon sequestration techniques).

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