

Unanswered Questions in the Evolution of Biomineralisation

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Introduction

Organisms have been building hard parts since the Late Precambrian. In fact representatives of all Kingdoms are able to biomineralise in the form of granules, plates, tubes, shells, bones or teeth. Biomineralised structures are mainly composites consisting of a mineralised component dispersed in an organic matrix and show an extraordinary diversity of microstructural arrangements and combinations. This wealth of diversity has stimulated a huge amount of interest and research, attracting the attention of biologists, materials scientists, archaeologists and palaeontologists and is increasingly using highly sophisticated techniques and interdisciplinary research to delve into the intricacies (e.g. DiMasi and Gower 2014).

Research on patterns of biomineralisation has been used in unravelling relationships between organisms (Bieler et al. 2014) or understanding functional morphology (e.g. Carter and Schneider 1997) and also for gaining an understanding for more applied uses, such as using bones or shells as geochemical proxies for assessing environmental parameters on both geological (Branson et al. 2013; Bell et al. 2014) and archaeological (Richards and Hedges 1999; Privat et al. 2002) timescales. The ability of organisms to produce low-density materials with a range of superior mechanical properties (toughness, high resistance to brittle failure) has implications in the synthesis of novel materials (Kaplan 1998; De Paula et al. 2010) and medical applications (Liao et al. 2000; Berland et al. 2005). Finally, our increasing concern about increased acidity in ocean waters has focused attention on the high dependency of many invertebrate taxa on building and maintaining their shells (Ries et al. 2009; Kroeker et al. 2013; Hyun et al. 2014).

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In such a field of active multidisciplinary research, it is difficult to provide an overall synthesis of the state of knowledge or to give an exhaustive sense of questions which need answers. However, this contribution attempts to highlight areas of research that are interesting in the context of understanding the very evolution of hard parts. It is a personal rather than definitive account and, as such, dwells on molluscan matters.

Are We Seeing the First Biomineralisers?

The beginnings of biomineralised hard parts, as recognised by the appearance of skeletal body fossils, are famously abrupt, heralding the start of the credible fossil record at the start of the Phanerozoic. If we want to tackle questions as to when, where and how biomineralisation started and to tease apart evidence for what selection pressures and enabling conditions were, we need an accurate fossil record.

Much has been done in the last decade to synthesise data on the fossil record of the first biomineralisers (Zhuravlev and Wood 2008; Wood 2011; Wood and Zhuravlev 2012). But such compilations are critically dependent on the quality of the fossil record itself. Here, more than perhaps elsewhere in the fossil record, the vagaries of taphonomic loss of original mineralogy, microstructure and detail are of great importance. It is notable that ‘small shelly fossils’ are relatively robust, complex objects. It seems unlikely that hard parts evolved in quite such an ‘advanced’ form and suggests perhaps that by their first appearance in the fossil record both the biochemical machinery and selection pressures necessary for the evolution of hard parts were already in place. Even earlier hard parts may have been made of very small units or have been very weakly mineralised, perhaps made of unstable mineral phases, or perhaps just from binding together abiotic grains supplied by the local sediments. The circumstances in which we might be able to recognise early products of biomineralisation are heavily dependent on lagerstätten (e.g. Zhang et al. 2014), and either lack of opportunity or failure to recognise these may impede our recognition of the earliest biomineralised structures.

We might perhaps expect early hard parts to rely on agglutination of raw materials from the abiotic environment. Bengtson (1994) and Lipps (1992) point out that agglutinated skeletons have been widespread amongst a wide range of protists and metazoans (molluscs, phoronids, polychaetes and insects) since the Cambrian, and McIlroy et al. (2001) describe agglutinated tubes from the Ediacaran that are interpreted by them as foraminifera. These agglutinated hard parts rely on producing sticky surfaces on to which grains can be ‘planted’. For example in bivalves, many modern and fossil anomalodesmatans attach sediment grains to the outsides of their shells by arenophilic threads, secreted by glands in the mantle (Sartori and Harper 2009). Such agglutinated structures are easy and, presumably, metabolically cheap ways to make skeletons. The potential for building really substantial hard parts by agglutination is highlighted by the modern bivalves *Granitorium* and *Samarangia*. These animals have smooth, relatively thin

aragonite shells but build themselves extraordinary ‘concrete overcoats’ complete with radial ornament fashioned by what is effectively early diagenesis, perhaps mediated by bacteria, of mucus-bound sediment particles (Taylor et al. 1999; Braithwaite et al. 2000). These extraordinary shells had been previously overlooked; indeed overzealous preparators had routinely ‘scraped them clean’. How capable are we of recognising such biomineralisation in the fossil record?

Many taxa biomineralise by means of laying down crystals onto a thin flexible organic sheet, for example the periostracum of molluscs and brachiopods. The periostracum functions both to separate the site of shell formation from the ambient fluid and also to form the template onto which the shell is then secreted, as well as other secondary functions such as retarding shell dissolution (Taylor and Kennedy 1969; Harper 1997). It is, however, becoming increasingly clear, in bivalves at least, that this sheet forms not just the template *onto* which calcium carbonate is deposited but also that calcification occurs within the sheet itself (Checa and Harper 2010; Checa et al. 2014). Early calcification occurs in the form of isolated spikes, but subsequently the inner layer of the periostracum becomes fully mineralised as the outermost layer of the bivalve shell. In the case of the palaeoheterodont *Neotrigonia*, ‘spike’ formation occurs deep within the periostracal groove at the very early stages of periostracum formation long before it reaches the shell margin (Checa et al. 2014). It is plausible to suggest this also as a model for early shell formation, but again this form of very basic biomineralisation would be difficult to recognise in fossil material.

Aside from the problems of recognising biomineralised structures as such, taphonomic problems also make identification of original mineralogies and microstructures less certain. Nevertheless, original microstructure may be determined from the surface topography of phosphatic internal moulds (Runnegar 1985), although the interpretation of these has not always been straightforward; see Vendrasco et al. (2011) for discussion. Such mouldic preservation requires original mineralogy to be inferred, in the case of early molluscs as aragonite. In other instances, where replaced shell material is present, suggestion of original mineralogy may be made using elemental analysis, ghost fabrics, isotopic evidence or from relying on phylogenetic inference (see Wood and Zhuravlev 2012).

The above points notwithstanding, the record of the evolution of well-recognised hard parts shows that biomineralisation evolved in a wide range of taxa, employing a number of different biominerals over a, geological speaking, rather narrow time interval. Zhuravlev and Wood (2008) recognise a window of time from the late Ediacaran to the Middle Ordovician when the majority of biomineralising groups are recognised in the fossil record with hard parts. Earlier instances are known, for example the Neoproterozoic modular *Namapoikia* (Wood et al. 2002) and scales of the earliest known mineralising protist (Cohen et al. 2011) from the mid-Neoproterozoic of Canada. During that time interval mineralised skeletal parts appear in taxa as disparate as single-celled organisms, sponges, corals, trilobites, annelids and chordates. The mineral phase of these hard parts is commonly calcium carbonate, silica or calcium phosphate, with the ability to secrete each evolved a number of times. Knoll (2003) estimates, for example, that calcium

carbonate hard parts have evolved at least 20 times in the Metazoa alone. It is also interesting that most major mineralisers arise at this time; there are few major mineralising clades which have evolved since the early Palaeozoic, although scleractinians which evolved from naked corals started to secrete aragonite in the Triassic (Stanley and Fautin 2001) and calcifying coccoliths in the Triassic (Siesser 1993) are obvious exceptions. Thomas and Reif (1993) document the myriad of different ways in which skeletons are achieved by organisms, and Thomas et al. (2000) show that 80 % of these are exploited by the Middle Cambrian.

Why Did Biomineralisation Evolve?

Clearly biomineralisation is polyphyletic, but this sudden explosion into a wealth of taxonomic and mineralogical diversity suggests strongly that the ‘time was right’ in the particular narrow window of geological time at the end of the Precambrian and the beginning of the Phanerozoic. But it is far from clear why this was the case. Was it because there was a sudden urgent selection pressure towards biomineralisation or might there have long been an ongoing advantage for organisms to possess hard parts, but that environmental conditions prevented or impeded their evolution until some ‘trigger’ event?

What Were the Selection Pressures Which Favoured Biomineralisation?

It seems intuitively obvious that many instances of biomineralisation produce structures whose primary functions are support (e.g. the vertebrate skeleton), crushing offensive weapons (e.g. jaws in worms and vertebrates, claws in many arthropod groups) or protection (shells of molluscs, brachiopods and the mineralised carapaces of some arthropods). Biominerals, however, may have other functions, such as the highly sophisticated double calcite lenses of trilobite eyes (Gál et al. 2000) or the ‘love darts’ in pulmonate snails (Hasse 2002). Although these two examples are almost certainly a derived, secondary use of biomineralisation, it may be less easy in other instances what functionality has been co-opted.

A common explanation for the evolution of hard parts is to appeal to a common selection pressure and the evolution of early predators (Vermeij 1990; Bengtson 1994; Knoll 2003; Porter 2011). The suggestion, therefore, is that they were primarily defensive. Alternative suggestions have been linked to the need to expel toxic calcium ions (Simkiss 1977) or that increase in body size allowed by increasing oxygen levels required support (Nicol 1966; Vermeij 1990). There is good evidence that Cambrian seas hosted a range of predators, as evidenced by the recognition of preserved gut contents (Conway Morris 1977), functional

morphology (Daley et al. 2013), coprolite contents (Shen et al. 2014) and healed injuries (Conway Morris and Jenkins 1985) or borings (Bengtson and Yue 1992). At least some of the hard parts produced at this time appear defensive, for example shells that contain and protect soft tissues, although again it is not easy to determine that this was their initial function. However, I am not wholly convinced of the view of Knoll (2003, p. 339) that ‘The diverse skeletons of Cambrian organisms share only one principal feature in common—they would have protected their owners against the bilaterian animal predators that took shape during the Cambrian explosion’. It is not obvious that all Cambrian hard parts are defensive. Some, for example chaetognath jaws, may even have been offensive, and whereas exoskeletons might offer either a place to hide or at least deflect blows, it is difficult to envisage most endoskeletons in this way. In much the same way as the explanation for lack of healed injuries in bivalve organism (Vermeij 1983), predators repelled by an internal skeleton will already have caused substantial soft tissue damage, with the result that even if the initial predation attempt is unsuccessful leakage of body fluids and metabolites will attract secondary predators or scavengers. In these instances perhaps it is more probable that support was the primary function. The only exception to this might be for more modular organisms, such as sponges and cnidarians, where predation is more akin to grazing (Rotjan and Lewis 2009) and small spicules embedded in the soft parts may deter or limit such attacks, though here again the arrangement of the megascleres, even in Cambrian forms, for example *Eiffelia* (Botting and Butterfield 2005), provides a rigid framework for support.

What Were the Environmental Facilitators Which Allowed Biomineralisation?

If there are advantages in possessing hard parts, did some environmental change in the Late Precambrian/early Phanerozoic facilitate their multiple acquisition? Various authors have suggested links with ocean chemistry changes. Widely cited events are phosphate spikes (e.g. Cook and Shergold 1984), increasing calcium levels (Brennan et al. 2004) and carbonate shifts (Riding 1982; Zhuravlev and Wood 2008), but it is difficult to reconcile these with the broad array of mineral types being used (Knoll 2003). Perhaps a more overarching solution comes with the idea of increasing levels of increasing atmospheric oxygen (e.g. Canfield et al. 2007) or at least increasing ventilation of oxygen through seawater (Butterfield 2009), necessary to fuel the metabolic costs of biomineralising or perhaps the recognition of major perturbations to the carbon cycle at the Pre-Cambrian/Cambrian transition (Knoll 2003).

What Influences the Mineralogy Exploited?

Lowenstam and Weiner (1989) list over 60 different minerals which have been recognised as being used by organisms and the list is growing, for example the addition of greigite (Fe_3S_4) from the foot scales of an extraordinary hydrothermal vent gastropod (Warén et al. 2003). However, the vast majority of hard parts are composed of a number of polymorphs of calcium carbonate, calcium phosphate or hydrated silica. Neontological and palaeontological evidence suggests that the mineralogy used by particular clades is usually fixed, implying a strict genetic control. There are, however, reports of 'unexpected' mineralogies in fossil material, e.g. aragonite in early brachiopods (Balthasar et al. 2011) and apparent primary calcite in a Cretaceous scleractinian coral (Stolarski et al. 2007), and there is also evidence that in particular rather extreme experimental conditions of altered seawater composition animals may be induced to secrete skeletal material of a different mineralogy (Checa et al. 2007).

It has often been suggested that for calcium carbonate secreters, taxa first utilise and then retain the mineralogy which is compatible with the seawater chemistry in which they evolve (Wilkinson 1979; Stanley and Hardie 1998; Porter 2007). In a detailed survey, Wood and Zhuravlev (2012) show that there are clear patterns in the mineralogy developed in late Precambrian and Cambrian biomineralisers. The aragonite-facilitating seas of the Ediacaran/early Cambrian were populated either by aragonitic or high magnesium calcite secreters, whereas in the subsequent 'calcite' sea these calcareous organisms were joined only by those secreting low magnesium calcite. These authors go on further to dissect the utilisation of aragonite and high magnesium calcite, discovering that there is some degree of ecological separation: aragonite (and later low magnesium calcite) was used by sessile unattached taxa (including some motile) whilst those which were sessile and attached tended to use high magnesium calcite. It is perhaps implicit here that there must have been particular benefits for these ecological associations, but exactly what these were is not clear. Wood and Zhuravlev (2012) also note that early Cambrian small shelly fossils utilised calcium phosphate, at a time coincident with the seawater phosphate spike noted by Cook and Shergold (1984). These early phosphatisers are interpreted as sessile cnidarians or lophotrochozoans, but later calcium phosphate became prevalent in highly energetic motile forms, i.e. amongst the chordates, some arthropods and the chaetognaths. Wood and Zhuravlev (2012) interpret this preference for calcium phosphate in active groups to be associated with the lower solubility of this mineral (compared to carbonates) in lower pH extracellular fluids which accompany such activity.

The Calcite Versus Aragonite Problem

Aside from the deep time aspects of polymorph choice, another aspect of some interest is understanding clades in which both low magnesium calcite and aragonite secretions are possible and that shells are produced with distinct layers of each. On occasion, bivalves also may produce the metastable carbonate Vaterite, for example in the shells of the freshwater *Corbicula fluminea*, but this is clearly pathogenic (Spann et al. 2010). Understanding the distribution of calcite and aragonite question has long been pondered by mollusc workers (reviewed in Harper 2000) but is also an issue for bryozoologists (Taylor et al. 2014).

Within molluscs it seems clear the primitive mineralogy was wholly aragonitic (Taylor 1973; Vendrasco et al. 2011) and there is good biochemical evidence to show that the choice of polymorph is strictly controlled by the organism by the presence of specific proteins within the organic matrix (Falini et al. 1996). However, a range of modern and fossil gastropods and bivalves also secrete both aragonite and calcite. This is clearly a polyphyletic trait—both in terms of the classes but also within. For example, in the bivalves there are at least four clades which secrete continuous layers of calcite (Carter 1980). The patterns of this expression are interesting. Although some infaunal bivalves do lay down calcite, it is a peculiarity of some individuals and in the form of patches rather than continuous shell layers (Carter et al. 1998). Continuous shell layers of calcite are restricted to epifaunal taxa, and, interestingly, the first appearance of calcite within these clades was always in the outer shell layer and no bivalve has ever entirely lost aragonite from the shell. The pattern observed in gastropods is very similar (Taylor and Reid 1990).

Explanations for the evolution of calcitic microstructures in molluscs fall into two types: (1) physiological and (2) adaptive. Lowenstam (1954) and Carter et al. (1998) suggested a physiological control suggesting that cold water taxa have higher calcite:aragonite ratios. However, this has been demonstrated unambiguously in relatively few cases (Taylor and Reid 1990) and it is difficult to explain the persistence of wholly aragonitic taxa (including all those which are infaunal) in either high latitude or deep sea faunas or why the temperature effect should only influence the outer shell layers, although Carter et al. (1998) suggest that it is the temperature that initially facilitates the deposition of calcite but go on to suggest that this may then be the basis for selection where it is advantageous. The idea that calcitic shell layers are in some way adaptive is tantalising. Taylor and Reid (1990) provide a very elegant hypothesis that explains the development in outer shell layers as an anti-dissolution trait based on the lower solubility of calcite compared to aragonite. They go on to show that calcitic shell layers are particularly prevalent and well developed in molluscs that live intertidally, an environment where there are marked diurnal changes in solubility of calcium carbonate driven by the changes in photosynthetic activities of marine algae (Daniel and Boyden 1975). It is, however, puzzling that freshwater and deep sea molluscs, which inhabit environments with more aggressive dissolution, do not appear to have evolved this

adaptation, and experimental dissolution work by Harper (2000) has shown that merely comparing inorganic properties of minerals is not a reliable guide to their physical properties: crystal size and organic matrix content all also influence solubility with the result that some aragonitic microstructures, such as nacre, are actually relatively insoluble.

What Are the Metabolic Costs of Biomineralisation?

Many of our questions about why particular mineralogies and microstructures were or are used by particular taxa might be better answered if we know more about the relative costs of biomineralisation. These are not easy questions to tackle experimentally, and, as in all of these instances, even if we know the metabolic costs for say coccoliths, it does not automatically follow that we would be able to apply those to such disparate organisms as molluscs or corals. It is also relevant to consider other aspects of the organism's biology and the relative importance of biomineralisation in their overall energy budgets. Although the metabolic rate of brachiopods is very low (Peck et al. 1997) and they make relatively thin shells, these, along with calcareous spicules within the tissue, make up >90 % of the dry weight of the animal (Peck 2008), and, therefore, the energy budget allocated to biomineralisation must be proportionately high, particularly compared with bivalves which physiologically are much more active.

Despite our general lack of knowledge on the topic, metabolic costs are often cited as explanations as to why certain shell microstructures are utilised and not others. For example it has been suggested that even though molluscan nacre is famously, tough and crack resistant, it has been lost in certain lineages because it is metabolically expensive to produce (Palmer 1983). There is a persistent suggestion that the major physiological cost of 'shell' secretion is making the organic matrix and that the cost of the mineral phase is negligible (Palmer 1983, 1992; Bengtson 1994, 2004; Wood 2011), but it is not clear that this is necessarily so, or if it is universal. Perhaps again, most work has been done on molluscs where it is known that there is very wide range variation in organic matrix content between different microstructures (from 0.1 % to over 8 % dry weight of shell). Palmer's work on gastropods showed that those taxa with more organic-rich microstructures grew and repaired faster than those with less.

The assumption that the mineral phase is easy to produce has not been tested. Wood and Zhuravlev (2012) go further and suggest that low magnesium calcite is cheaper to produce than either high magnesium calcite or aragonite based on their lattice energies (Mackenzie et al. 1983), but again it is not clear that this is necessarily true, nor the same for all biomineralising groups. Although biomineralisation pathways are, as yet, incompletely understood, it is clear that not all pathways are the same and that biominerals are not identical to their inorganic counterparts, for example in the inclusion of macromolecules within the crystals. The three crystallisation pathways discussed by Weiner and Addadi (2011) all

require movement of ions from an external or body fluid (which may often be by active transport, pumping against concentration gradients). Weiner and Addadi show that of three considered pathways, biomineralisation involves transport of material in a transient disordered state, sometimes in membrane-bound vesicles, to the site of the final crystallisation. These processes are likely to involve active transport.

Final Remarks

Scientists have been researching biomineralised structures for many decades, but some groups, such as bivalve molluscs, because of their economic or ecological importance have been extensively studied in this respect (Boggild 1930; Taylor et al. 1969, 1973; Carter 1990), other groups less well so. Even in taxa that are historically well studied, research is very active. New analytical techniques are opening new avenues for research (DiMasi and Gower 2014) and the prospect of reaching a much deeper understanding of the genetic controls involved in shell manufacture (Sleight et al. 2015).

It is important that we recognise that processes or patterns are likely to differ to some greater or lesser extent between groups of biomineralisers and apply information learnt about one group uncritically to another. The answers to many of the questions posed in this contributions are interwoven with one another, and their solutions will be found by collaborations between different disciplines.

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‘Biomineralization—Lessons from the past and for the future’ which proved a stimulating and thought-provoking session, really showing us how much more there is to learn.

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