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Exploring the drivers of early biomineralization

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Summary points:

- The first skeletons are known from protists, 810 Million years ago (Ma)
- Large, putative metazoan, calcareous skeletons first appear in the terminal Ediacaran, ~550 Ma.
- Calcification was an independent and derived feature that appeared in diverse groups.
- The presence of a pre-existing organic scaffold, which provided the framework for interactions between extracellular matrix and mineral ions, can be inferred in many skeletal taxa.
- Calcareous biomineralization may have been favoured in the highly saturated, high alkalinity carbonate settings of the Ediacaran, where carbonate polymorph was further controlled by seawater chemistry.
- By the Early Cambrian, there is a marked increase in the diversity of skeletons as an escalating defensive response to increasing predation pressure, and biomineralization may have come under stronger biological control.
- The initial triggers for widespread biomineralization in the Ediacaran remain unclear.

Abstract

The first biomineralised hard-parts are known from ~810 Million years ago (Ma), consisting of phosphatic plates of probable protists formed under active biological control. Large skeletons in diverse taxa, probably including total-group poriferans and total-group cnidarians, first appear in the terminal Ediacaran, ~550 Ma. This is followed by a substantial increase in abundance, diversity, and mineralogy during the early Cambrian. The biological relationship of Ediacaran to early Cambrian skeletal biota is unclear, but tubular skeletal fossils such as *Cloudina* and *Anabarites* straddle the transition. Many Ediacaran skeletal biota are found exclusively in carbonate settings, and present skeletons whose form infers an organic scaffold which provided the framework for interactions between extracellular matrix and mineral ions. Several taxa have close soft-bodied counterparts hosted in contemporary clastic rocks. This supports the assertion that the calcification was an independent and derived feature that appeared in diverse groups, that was initially acquired with minimal biological control in the highly saturated, high alkalinity carbonate settings of the Ediacaran, where carbonate polymorph was further controlled by seawater chemistry. The trigger for Ediacaran-Cambrian biomineralization is far from clear, but may have been either changing seawater Mg/Ca ratios that facilitated widespread aragonite and high-Mg calcite precipitation, and/or increasing or stabilising oxygen levels. By the Early Cambrian, the diversity of biomineralization styles may have been an escalating defensive response to increasing predation pressure, with skeletal hardparts first appearing in abundance in clastic settings by the Fortunian. This marks full independence from ambient seawater chemistry and significant biological control of biomineralization.

1. Introduction

Skeletal organisms form a major part of today's ecosystems, and so the origin of hardparts – that is the co-option of minerals to form biominerals – is one of the major events in the history of the Eucarya. The rise of calcareous and silica biomineralization changed sediment production from one of inorganic and microbially-mediated precipitation to a system under considerable biological control. **Today**, nearly all calcium carbonate and silica leaves the oceans as skeletons, produced by diverse taxa in a wide range of both marine and freshwater settings. Biomineralization then was not only a key biological evolutionary innovation that enhanced ecosystem engineering and complexity, but also marked a step change in the workings of the long-term carbon and silica cycles. The evolutionary origins and drivers of biomineralization remain, however, obscure.

The oldest skeletal hard parts documented are microfossils from the Neoproterozoic, ~ 810 Million years ago (Ma) (1). Calcareous skeletons, including those from putative metazoans, appeared rapidly and globally in the late Ediacaran, ca. 550 Ma (2). By the beginning of the Cambrian (541 Ma), diverse mineralized skeletons are thought to have evolved in protists, **algae** and animals, using calcite, aragonite, calcium hydroxyapatite (phosphate), as well as silica. Skeletal abundance and diversity then increased dramatically over the succeeding 25 million years (2).

Many modern metazoan groups with skeletal taxa have non-skeletal close relatives, and Ediacaran to early Cambrian skeletal taxa of varied mineralogy represent a diverse range of phyla (Figure 1). In addition, despite divergent skeletal morphologies (2), calcium carbonate skeletons may have appeared at least twenty times among metazoans and as many as eight times within both the Porifera and

Cnidaria alone (3). These observations support the hypothesis of convergent or parallel evolution of biomineralization at the phylum level (4).

The global onset of widespread biomineralization ~550 Ma suggests the operation of an extrinsic trigger in the Ediacaran-early Cambrian interval that in turn conferred selective advantage to the acquisition of a skeleton. The earliest known skeletal macrobiota appeared in redox stratified oceans often characterised by a shallow and fluctuating oxic chemocline (5), high levels of silica (6), and a high Mg/Ca ratio seawater chemistry (7). Possible triggers for this biomineralization event include the availability of oxygen, changes in seawater chemistry such as an increase in calcium, or the rise of predation (3, 8). Much uncertainty persists, however, as to the relative importance of these factors, and their potential inter-relationships, and how they might relate to the rise of biologically-controlled biomineralization.

2. Origin of biomineralization pathways

Orthologous genes and their encoded proteins involved in biomineralization are known to be co-opted and diversified among vertebrates, echinoderms, molluscs, and bilaterians in general (9,10). Multiple origins for biomineralization in animals is supported by the appearance of biomineralization after divergence of the major bilaterian clades, and also by the observation that some Cambrian skeletal taxa are interpreted **on the basis of morphology** as early members of extant phyla rather than stem representatives of larger groups such as Deuterostomia, Protostomia, Bilateria or even Metazoa (4).

Most skeletons combine minerals with structural organic matter, where the physiological cost of producing the mineral is usually small compared to the organic matrix (11). Calcareous organisms synthesize calcium-binding and extracellular

matrix proteins that provide templates for mineralization as well as macromolecules to act as anti-calcifying inhibitors, so essentially placing diagenetic crystal growth under biological regulation (2,12,13). This suggests that such biomineralization is a derived feature that probably originated in many groups from a calcium-regulated extracellular matrix system (12,13). Indeed, calcium signalling pathways underwent a dramatic and unparalleled diversification coincident with the radiation of animals in the early Cambrian (14).

3. **Dramatis personae: the early record of hard-parts**

Neoproterozoic-Ediacaran skeletal taxa

The first skeletons documented are phosphatic (calcium hydroxyapatite and organic carbon) microfossils from the Fifteenmile Group of Yukon, Canada, dated at $<810.7 \pm 6.3$ Ma (1). These are diverse scales (Figure 2A) probably derived from protists. High-resolution transmission electron microscopy shows these scales to be constructed of a hierarchically organized interwoven network of fibrous hydroxyapatite crystals, each elongated along the [001] direction, indicating that microstructural crystallization was under biological control (1).

Weakly mineralized curved, sheetlike, hardparts (up to ~5 mm) are described from the 700–600 Ma Pahrump Group of southeastern California (15). These forms may represent leafy algae. A notable gap in the record follows, as the next skeletal fossils known are sizable calcareous skeletons (1 mm to 1 m), which appeared rapidly and globally in the late Ediacaran, ca. 550 Ma (3). Over ten genera with biomineralized skeletons are described from the terminal Ediacaran (~550-541 Ma) of diverse affinity including unicellular eukaryotes (protists), possible red algae, possible total group cnidarian affinity (crown-eumetazoans), and problematica (2,16,17). All are known

only from carbonate rocks, and the vast majority had a sessile habit (18). Here below, putative metazoans are briefly described.

The globally-distributed taxon *Cloudina* (ca. 550-540 Ma) forms a tube of nested funnel-shaped and eccentrically arranged cones with flaring rims, up to 150 mm long and 7 mm in diameter (Figures 2C, 3B). The *Cloudina* skeleton is composed of extremely thin (8-12 μm) primary layers of elongated micritic crystals ($< 4 \mu\text{m}$) fusing to form secondary lamina (up to 60 μm thick), strengthened by early epitaxial cement crusts which infill the space between walls of successive cones (16).

Cloudina shows evidence for asexual reproduction including intercalar budding and longitudinal fission. These reproduction styles as well as rapid increase of the tube diameter, a closed apex, occasional tabulae and hexagonal symmetry of some species, are compatible with, but not conclusive of, a total group cnidarian and, therefore crown-eumetazoan affinity (19, 20). *Cloudina* can show elevated growth of cemented and mutually-attached individuals to form substantial reef frameworks (Figure 2C), and is also found re-worked to form concentrated 'shell' beds (22). Although the presence of *Cloudina* reefs has been disputed (23), in-situ reef growth is confirmed by the mutual attachment of *Cloudina* individuals by 'meniscus' skeletal structures in life position together to form frameworks, and the presence of decimeter-scale cement-filled, reef framework cavities (21). *Cloudina* skeletons also record the oldest possible evidence of predatory boring (24).

Sinotubulites (Figure 3C) has a widespread distribution (19,25,26), and bears a semi-circular to polygonal open thick tube up to 20 mm in length and 4-5 mm in diameter, with multiple, fine concentric slightly eccentric layers (40-50 μm thick) of micritic texture with transversely and unevenly corrugated ringlets along the tube length. The affinity of *Sinotubulites* remains problematic.

Namacalathus (Figure 2D) is a further widespread taxa with a stalked cup- or goblet-shaped form up to 35 mm in width and height, where the cup has a rounded central opening on the top and rounded lumens on lateral facets (27). *Namacalathus* displays an almost regular hexagonal radial symmetry in cross section, although 5- and 7-fold radial cups based on the number of lateral facets also occur. The wall of both the stem and the cup is continuous and up to 100 µm thick. *Namacalathus* is often associated with microbial mats or reef habitats. Some cups appear to show asexual reproduction by regular budding in a bilateral pattern (28). The skeleton of *Namacalathus* is composed of a calcareous foliated ultrastructure displaying regular concordant columnar inflections, with a possible inner organic-rich layer. These features point to an accretionary growth style of the skeleton and a possible affinity with the Lophotrochozoa, more specifically within the Lophophorata (Brachiopoda and Bryozoa) (28). It is not clear, however, how such an affinity is consistent with hexaradial symmetry (29).

Namapoikia rietoogensis, is an unusually large (20 mm to 1 m), robustly skeletal, and clonal Ediacaran metazoan which encrusted the walls of synsedimentary fissures within microbial-metazoan reefs (Figure 2E). *Namapoikia* formed laminar or domal morphologies with an internal structure of open tubules and transverse elements, and had a very plastic, non-deterministic growth form that could encrust both fully lithified surfaces as well as living microbial substrates, the latter via modified skeletal holdfasts (30). The skeletal growth appears to have propagated via the rapid formation of an organic scaffold via a basal pinacoderm prior to calcification (Figure 2F). The open tubular internal structure, highly flexible, non-deterministic skeletal organisation, and inferred style of biomineralization of *Namapoikia* places probable affinity within total-group poriferans.

Discoidal *Suvorovella* (Figure 3A) occurs in carbonates of the Aim Formation of the south-eastern Siberian Platform, ca 550-543 Ma (31,32). Whole *Suvorovella* skeletons and broken angular fragments form a thick and persistent 'shell' bed from 1.5 to 2.3 m in thickness, which extends to over 1 km in length. The evidence for breakage of *Suvorovella* supports the biomineralized form of this taxon.

Suvorovella ranges from 10 to 100 mm in diameter and consists of a hollow, flattened disc, with a low conical, slightly eccentrically positioned, an irregularly concentrically folded apex, and an outer flat zone bearing widely separated thin concentric ribs and radiating low relief ridges imparting a diamond-shaped pattern to the surface. These radiating ridges are probably casts of thin, densely anastomosing grooves running from the apex to the periphery, terminating in a distinct rim. The lower surface of the skeleton is smooth. *Suvorovella* specimens are preserved as replicas by an isopachous crust of early diagenetic marine radial fibrous dolomite cement that precipitated upon a micritic envelope, probably replacing an original skeleton was probably aragonitic (32).

A further partially-biomineralising Ediacaran skeletal taxon is *Coronacollina*, which occurs in the sandstones of the Ediacara Member (33). *Coronacollina* is described as possessing a central, presumed non-mineralised tri-radially symmetrical mound with radiating long (up to 370 mm), very straight and rigid, spiculate sclerites of either chitinous character or unresolved mineralogy (Figure 2B).

In sum, the oldest skeletons documented are notable for their small size and probably protistan affinity, and phosphatic mineralogy and microstructural crystallization under demonstrable biological control (2). By contrast, while terminal Ediacaran putative metazoan skeletal taxa are diverse, they share the inferred presence of a precursor organic skeleton. Some show evidence of flexibility suggesting the

presence of a very thin and relatively elastic organic skeleton impregnated with mineral granules (16, 26). Others, such as *Namapoikia*, may have propagated via the rapid formation of an organic scaffold prior to calcification (29). Many Ediacaran skeletal microstructures **where known** are either fibrous or microgranular (which may represent diagenetic recrystallization of a primary fibrous microstructure), with no documented retention of preferred crystallographic orientation and where individual crystallites are not composed of smaller units, i.e. they are non-hierarchical. These features of Ediacaran skeletal macrofossils suggest the operation of relatively simple biomineralization mechanisms from a pre-existing organic matrix such as chitin or collagen localized in epithelial cells. These likely represent ancient modes of biomineralization, which was not under demonstrably active biological control.

Contemporary skeletal and non-skeletal counterparts

Some skeletal putative metazoan taxa appear to have non-skeletal, organic-walled counterparts, including *Suvorovella-Eoporpita*, *Cloudina-Conotubus*, *Sinotubulites-Corumbella*, and (32) (Figure 3). **All these skeletal and non-skeletal ‘twins’ have a unique construction of fine-scale features not known in any other known Ediacaran or Cambrian taxa. Unlike skeletal taxa, these non-skeletal taxa are found in siliciclastic rocks.**

Suvorovella (Figure 3A) has a similar size range and close overall morphology to many discoidal, soft-bodied Ediacaran taxa (32). In particular, the soft-bodied taxa *Eoporpita medusa* (Figure 3D), *Hiemalora stellaris*, and *Palaeophragmodictya spinosa* show both a similar low conical, eccentrically positioned, folded apex, and a flatter outer zone with dense radiating branching structures similar to *Suvorovella*.

The non-skeletal *Conotubus* (Figure 3E) shows a very similar morphology and size range to *Cloudina* (Figure 3B), and the organic-walled *Corumbella* (Figure 3F) resembles *Sinotubulites* (Figure 3C) in all fine-scaled detail, including multiple concentric layers, the surface pattern of merging ringlets, and a polygonal cross section. Similar alternating ‘plates’ are present in both *Corumbella* and *Sinotubulites*, arranged in a slightly asymmetrical pattern along the mid-line of the fossils.

Whilst it is possible that these skeletal/non-skeletal pairs are taphonomic or diagenetic variants of the same taxa, or different taxa restricted to specific ecological niches or environmental settings, this is not supported by further observations of differences in preservational style. The existence of primary biomineralized shells in *Suvorovella* is confirmed by the presence of multiple broken, angular fragments forming a shell hash (32), and never present features of plastic deformation such as stretching, wrinkling, folding, contraction, or other post-mortem degradational features as noted in soft-bodied discoidal taxa, which are always preserved as casts and moulds. Likewise, *Corumbella*, when preserved in the carbonate Tagatia Guazu Formation of Paraguay shows no petrographic evidence for the presence of any original skeletal hardparts (34), and furthermore shows features of plastic deformations such as bending, twisting and axial-stretching without any loss of overall integrity (35). *Conotubus* also shows similar bending, folding, and transverse segment imbrication (36). Such preservation is in notable contrast to the tubes of *Cloudina* which, like *Suvorovella*, can show brittle breakage, form reefs and concentrated shell beds (22) and show possible evidence of predatory boring (24).

The rise of Cambrian biomineralization

Diverse and abundant skeletal assemblages assigned to multiple new phyla appeared later in the early Cambrian (**Fortunian** to ‘Stage 2’), including univalved and bivalved shells, tooth-like structures, arthropod-type exoskeletons, spicules, sclerites, tubes, cones, and ossicles (17). Of the more than 178 architectures recognized in skeletonised marine animals, 89 had evolved by the early Cambrian and 146 (80%) by the middle Cambrian (37).

New data show that the stratigraphic distribution of some so-called Ediacaran and earliest Cambrian skeletal biotas overlap, and tubular skeletal fossils such as *Cloudina* and *Anabarites* straddle the transition (38). Given that the affinity of many Ediacaran taxa is poorly constrained, however, the relationship between Ediacaran and early Cambrian skeletal taxa remains unclear.

The early Cambrian record shows a rapid increase in both diversity of mineralogy and complexity of skeletal microstructures which become conserved within lineages, Skeletal hard parts first appeared in clastic environments in the **Fortunian**, suggesting a **physiological** independence from ambient sea water chemistry (32).

4. Controls of the onset of biomineralization

Possible triggers for the onset of widespread biomineralization include reaching a threshold of marine oxygen levels or stability, changes in seawater chemistry that facilitated the formation of skeletons, or a rise of predation that selected for protective hardparts.

The evolution of Ediacaran-early Cambrian marine redox

Although modern soft-bodied sponge-grade animals may tolerate O₂ concentrations as low as 1.25–10 mM (approximately 0.05–0.35 ml/l; 39), skeletonization is hypothesized to require higher O₂ levels, > 13 mM (approximately 0.4 ml/l; 39), in part because it requires synthesis of amino acids for collagen formation (40). Many have therefore suggested that a rise in atmospheric, and hence marine oxygenation, triggered the rise of skeletal tax as part of the Cambrian Explosion (41).

Various studies have suggested oxygen concentrations ranging from >4% present atmospheric levels (PAL) as early as 1.4 Billion years ago (Ga) (42), to conservative estimates in the range 0.1–1% PAL between 1.1–0.8 Ga (43). Local marine palaeoredox reconstruction via iron speciation and rare earth element profiles indicate that Cryogenian to early Cambrian open marine conditions were highly heterogeneous at a basin scale, and were typified by either continued redox-stratification or highly dynamic Oxygen Minimum Zones (OMZs), overlying potentially oxic basinal waters. Putative metazoans were restricted to localised oxygenated habitats, but precise oxygen demands for early metazoans are not well constrained. In the Nama Group, Namibia (~550-541 Ma), however, the use of integrated Fe speciation and cerium anomaly data shows that in-situ Ediacaran skeletal metazoans did not occupy low oxygen settings (44).

The development towards more stable oxic conditions does not seem to have been a single, unidirectional event (45), and it is not clear when deep marine settings ceased to become permanently oxic. Individual marine basins continued to record transient redox conditions over short timescales, particularly in shelf and slope environments, well into the Cambrian (5, 46, 47). In some areas dominantly

ferruginous and even euxinic water column conditions are recorded into Cambrian Series 3 and beyond (41).

There are some data to suggest that a deepening of the oxycline occurred in the Yangtze Block, China, initiated in Cambrian Stage 2 and continuing into the mid-Cambrian (48). This is interpreted to have contributed to increase in biological diversity. Current data, however, suggests that there was continued habitat restriction and redox instability well after the first appearance of skeletal metazoans (see review 49).

The potential role of changing marine redox

Animals in past low-O₂ or dominantly anoxic settings would almost certainly have been limited to non-skeletal forms, small body sizes, low metabolic rates, low-energy feeding strategies and opportunistic lifestyles (50). This has led to suggestions that such ferruginous, low-O₂ environments may have been more habitable to animals than modern oceans” as ferruginous (rather than euxinic) oceans would have favoured the adoption of high-surface-area respiratory structures and body plans with reduced pressure from synergistic sulphide stress compared to modern metazoans (51). This has led to suggestions that such ferruginous, low-O₂ environments may have been more habitable to animals than modern oceans (51). Other models, however, show that even relatively modest levels of Fe²⁺ can significantly depress seasonal minima and maxima in dissolved O₂, thus creating metabolic effects that may have inhibited the emergence of metazoans for most of the Proterozoic (52).

But the role of low or dynamically fluctuating redox as a control of evolution is poorly understood. Indeed fluctuating, dysoxic habitats and oxygen minimum zones might in fact promote evolutionary novelty (53). Modern, low-oxygen regions are

heterogeneous and dynamic habitats that support low diversity, opportunistic and non-skeletal metazoans (54). Such habitats may have promoted morphological novelty in soft-bodied benthos, providing the ancestral stock for subsequently skeletonized lineages to appear as innovations once oxic conditions became widespread and stable, in turn promoting major evolutionary diversification (53).

The role of changing seawater chemistry

Organisms produce hard parts with whatever is physiologically cheap to precipitate in any given setting (17). For example, gastropods living at sulfide and metal-rich hydrothermal vents form highly unusual sclerotomes using the iron sulfides pyrite and greigite (55). It is therefore no surprise that most skeletons are composed of calcium carbonate, given the high saturation of CaCO₃ in modern tropical surface seawaters.

Calcium carbonate supersaturation

The observation that Ediacaran skeletal taxa (all except *Coronacollina*) occur only in carbonate rocks, but that non-skeletal, organic counterpart taxa are found in siliciclastic rocks, suggests the operation of local environmental conditions that promoted calcareous skeletonisation in pre-existing soft-bodied biota of diverse affinity but with relatively low metabolic demands. Ediacaran macrobiota biomineralization, including the first possible metazoan calcification, was probably facilitated by the high carbonate supersaturation and alkalinity **suggested to have been present in Ediacaran shallow marine carbonate settings (56). This has been inferred due to the presence of anomalously large carbonate skeletons, cements, and ooids (32,56, 57), as well as the global dominance of carbonate lithologies in terminal**

Ediacaran successions and high estimated carbonate sediment accumulation rates for this interval that exceed Cambrian equivalents by one to two orders of magnitude (32,56).

Experimentation confirms that modern carbonate skeleton formation is strongly dependent on carbonate supersaturation (58), and so calcification has a relatively low metabolic cost compared to organic matrix formation in the highly saturated surface seawaters of low latitudes. Earliest macroskeletal biotas were also sessile, where the physiological cost of calcification is even further minimised.

The exception of *Coronacollina* to this model suggests that if some Ediacaran biomineralizers bore either rigid chitinous, or only lightly or selectively biomineralized morphologies, their vulnerability to dissolution would be substantial, particularly in siliciclastic sediments which are deposited under lower seawater carbonate saturations. It is likely that the full inventory of Ediacaran lightly- or partially-biomineralizing taxa is yet to be documented.

Changing seawater Mg/Ca ratio

Early ferroan dolomite precipitates are described from the Cryogenian (59, 60) and Ediacaran (7, 59, 61, 62). Dolomite [$\text{CaMg}(\text{CO}_3)_2$] has a highly ordered crystal lattice with slow kinetic growth rates, does not readily form in modern oceans despite supersaturation, and has never been documented as a biomineral. Dolomite formation may have been facilitated by widespread anoxia and high seawater Mg/Ca ratios (51), which has been confirmed by fluid inclusion analysis (63). The palaeodepth distribution of early marine ferroan dolomite cement has been used to infer dominantly ferruginous anoxic “aragonite-dolomite seas”, with a very shallow oxic chemocline that supported only soft-bodied macrobiota in the late Ediacaran (7). But

the evolution of seawater chemistry to lower Mg/Ca ratios in the last few Myr of the terminal Ediacaran, **perhaps** as a result enhanced continental denudation that **potentially** increased the input of Ca into oceans (8), may have facilitated the rise of skeletal animals by the emergence of “aragonite seas” (7).

Analysis has shown that skeletal clades adopted the minerals as dictated by ambient ocean chemistry (Mg/Ca ratio and $p\text{CO}_2$), strongly suggesting that skeletal mineralogy was highly influenced by extrinsic physico-chemical rather than intrinsic (genetic) factors (3, 64). Seawater chemistry varied considerably through the Ediacaran to Cambrian (Figure 4D). High $m\text{Mg}:\text{Ca}$ and/or low $p\text{CO}_2$ favoured aragonite or high-Mg calcite (HMC) inorganic and skeletal precipitation from the Ediacaran until the Cambrian early ‘Stage 3’, but low $m\text{Mg}:\text{Ca}$ and/or high $p\text{CO}_2$ and the onset of greenhouse conditions favoured low-Mg calcite (LMC) formation thereafter (65).

Phosphate availability

Phosphate can be a limiting nutrient in many marine ecosystems, perhaps explaining why calcium phosphate biomineralization is relatively rare among modern biota. Dynamic global marine redox conditions, enhanced by local restriction, may have led to an increase in dissolved phosphate in pore and bottom waters (66). **This is thought to have increased markedly between 800-635 Ma (67).** This **in turn may** have facilitated the necessary geochemical conditions for the advent of calcium phosphate biomineralization in the Tonian (2) and in the early Cambrian (68).

Biotic drivers

Producing skeletal hard-parts requires energy and so imposes a metabolic cost. Greater size (and hence competitive superiority and reproductive enhancement), biomechanical strength, as well as increased elevation above the sea floor, are all conferred by acquisition of hardparts. But most notably, a skeleton confers protection from predation.

The cost-benefit ratio of biomineralization has changed over geological time, varying not only with the availability of precursor ions in seawater, but also with evolutionary innovations, as the energy required to produce a skeleton will change as a function of community ecology, particularly with increases in predation pressure (2).

The mineralogy of clades from the Ediacaran to Lower Ordovician as well as quantitative analysis of trends reveals a close interaction between changing seawater chemistry, ecological opportunity, and escalating response (65, 68). There is a notable shift from exclusively aragonite or HMC in the Ediacaran to Fortunian, to dominantly LMC mineralogies from the mid-Cambrian to Ordovician (Figure 4A). This trend coincides with the successive evolutionary importance of skeletal biota with increasingly energetic lifestyles, from sessile unattached in the late Ediacaran-Fortinian, to sessile attached from the Fortunian – Stage 4, benthic motile from the Terreneuvian, and finally nektonic from the late Early Cambrian onwards (Figure 4B).

Ecology is reflected in the choice of biomineral (68). Sessile, benthic stem-group poriferans or cnidarians appear in the Ediacaran with often massive skeletons of aragonite or HMC mineralogies coincident with high mMg:Ca and/or low $p\text{CO}_2$ (aragonite) seas (Figure 4C); new aragonitic sessile clades and additional motile

benthos of stem-group Eumetazoa appear in the Terreneuvian with often composite or articulated, protective skeletons. The first LMC skeletons of novel organic-rich composite materials did not appear until the late early Cambrian, coincident with the onset of $m\text{Mg}:\text{Ca}$ and/or high $p\text{CO}_2$ (calcite) seas. Phosphatic possible cnidarians and stem- and crown-group lophotrochozoans appeared during the earliest Cambrian coincident with elevated marine phosphate levels (Figure 4D). Active, benthic-pelagic predatory groups (vertebrates, chaetognaths, some arthropods) appearing mainly in the late early Cambrian preferentially possessed phosphatic skeletons and teeth, which were more stable at the low pH ranges of extracellular fluids associated with intense activity and high-energy ecologies (68).

The preference for phosphatic teeth in actively swimming predators, and for stiff and tough aragonitic shells in slow benthos despite the high energetic cost of these materials, is suggestive of an evolutionary response of prey to an escalation in predation pressure (68). The Ediacaran-middle Cambrian interval shows the successive evolution of skeletal biota with increasingly energetic lifestyles, suggesting that the increasing physiological cost of skeletonisation in more demanding metabolisms was offset by the increased chance of survival conferred by a protective skeleton: an arms race had surely begun.

Summary and the way forward

The onset of biomineralization was a complex and protracted event, involving changing oxygen availability and stability, a dynamically evolving seawater chemistry, and the changing cost-benefit of skeletonisation with the rise of predation in the early Cambrian. **The earliest known** biomineralization, although potentially under varying degrees of biological control, appears to have a close dependence upon the

availability of precursor ions in seawater. Only in the **Fortunian** did skeletal taxa gain any independence from such environmental constraints, as they diversified into clastic habits. We can then infer that by the early Cambrian, genetic and molecular mechanisms controlled **metazoan** biomineralization and mineralogy had become evolutionarily constrained (4).

Much remains to be understood about the patterns and processes of early biomineralization. In particular, the reasons for the apparent gap between the first protistan skeletal hard parts (810 Ma) and macroskeletal taxa (~550 Ma), and how biomineralization evolved from passive to more active-controlling mechanisms. The known record suggests that protists **may have** gained active control over biomineralization far earlier, and possibly with more ease, than more complex or metabolically-demanding groups such as metazoans. For example, did more active control over biomineralization allow expansion into clastic settings by the **Fortunian**, or was this driven by quite different controls such as genetic developments or changing cost-benefit due to rising predation pressure? Still unresolved are the relative roles of oxygen thresholds and/or stability and seawater chemistry, and whether these controls are related. Additionally, the demonstrable empirical relationship between biomineral and ecology in the early Cambrian taxa points to underlying molecular mechanisms that remain quite unknown and unexplored. While calcification may first have arisen as a non-selective response to environmental change, it was later co-opted for defence and subsequently evolved under tighter biological control.

Finally, the real impact of the rise of biologically-controlled skeletonisation on the carbon and silica cycles remains to be quantified. **Although** carbonate skeletal grains are locally common in the Ediacaran to **lower** Cambrian, some argue they did not

become **sufficiently** abundant to account for a significant proportion of total carbonate production until the middle Ordovician (69).

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Figure captions

Figure 1. The distribution of early metazoan skeletons. Showing mineralogy for each phylum, stratigraphic distribution of major clades, phylogenetic relationships and divergence time estimates for animals with a Cambrian fossil record. Modified from (4).

Figure 2. Neoproterozoic skeletal taxa. (A) Scanning electron micrograph (SEM) of a single *Characodictyon* plate (from 70). (B) External mold of holotype of *Coronacollina acula* (from 33). Arrow indicates main body. (C) Field photo of reef-building *Cloudina*, Nama Group, Namibia. (D) Field photo of *Namacalathus*, Nama Group, Namibia. (E) Field photo of *Namapoikia*, Nama Group, Namibia. (F) Polished slab of *Namapoikia*, showing attachment to actively-growing, microbial substrate. Skeletal elements (yellow arrows) initially attached to microbialite. Vertical skeletal elements form inflated conical structures. White arrows mark transverse elements, which are noted to thicken with age. Note pale grey colour and thicker width of older

vertical elements close to the substrate, in contrast to the darker grey and thinner width of younger elements.

Figure 3. Ediacaran skeletal (A-D) and non-skeletal (E-H) counterparts. (A) Skeletal *Suvorovella*; **(B)** Skeletal *Cloudina* (Photo: Shuhai Xiao). **(C)** Skeletal *Sinotubulites* (Photo: Shuhai Xiao/Yaoping Cai). **(D)** Organic *Eoporpita medusa*. **(E)** Organic *Conotubus* (photo: James Schiffbauer/Yaoping Cai). **(F)** Organic *Corumbella* (photo: Lucas Warren).

Figure 4. Schematic representation of changing seawater chemistry and skeletal mineralogy from the terminal Ediacaran to Ordovician (lower Tremadocian). Distribution of (A) skeletal carbonate mineralogies, (B) ecological guild, expressed as percentage of number of genera per zone. (C) Schematic changing carbonate mineralogy, (D) schematic changing phosphate concentrations. E = Ediacaran Period; Fort = Fortunian; ORD = Ordovician Period; LT = lower Tremadocian Series; Dru./Guz = Drumian and Guzhangian stages. Modified from (68).