Escalation and ecological selectively of mineralogy in the Cambrian Radiation of skeletons

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ABSTRACT

Assembly of the necessary biochemical machinery for biomineralisation long-predated the appearance and rapid diversification of metazoan skeletons in the late Ediacaran to Middle Cambrian (~550–520 million years ago (Ma)), and the independent acquisition of skeletons of differing mineralogies suggests a trigger that conferred selective advantage to possession of a skeleton even though this involved physiological cost. The cost–benefit ratio of biomineralisation 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.

Here, we demonstrate that during the Cambrian Radiation the choice of biomineral was controlled by an interaction between changing seawater chemistry and evolving ecology. The record also reveals the successive skeletonisation of groups with increasing levels of activity from the Ediacaran to Middle Cambrian. The oldest (~550–540 Ma) biomineralised organisms were sessile, and preferentially formed low-cost, simple, skeletons of either high-Mg calcite coincident with high mMg:Ca and/or low pCO$_2$ (aragonite seas), or phosphate during with a well-documented phosphogenic event. More elaborate, but tough and protective, aragonitic skeletons appeared from ~540 Ma, dominantly in motile benthos (mostly stem- and crown-group Lophotrochozoa). The first low-Mg calcite skeletons of novel organic-rich composite materials (e.g. trilobites) did not appear until the late early Cambrian (~526 Ma), coincident with the first onset of low mMg:Ca and/or high pCO$_2$ (calcite seas). Active, bentho-pelagic predatory groups (vertebrates, chaetognaths, some arthropods) appearing mainly in the late early Cambrian preferentially possessed phosphatic skeletons, which were more stable at the low pH ranges of extracellular fluids associated with intense activity and high-energy ecologies.

These trends suggest that the increasing physiological cost of biomineralisation in successively more demanding metabolisms was offset by the increased chance of survival conferred by a protective skeleton, so indicating a driver of escalating community ecology, in particular an increase in predation pressure.

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1. Introduction

Biomineralised hard parts appeared in protists at ~750–812 Ma, metazoans at ~550 Ma, and macroalgae by ~515 Ma, but the major radiation of skeletons is restricted to the earliest Cambrian (~540–520 Ma) (Bengtson, 1994; Knoll, 2003; Cohen et al., 2011). Of the more than 64 different mineral phases known to form biominerals, by far the most common are those formed of calcium carbonate: indeed, more than 300 crystal forms are identified in calcite and these combine to produce a thousand variations (Lowenstam and Weiner, 1989).

The acquisition of calcareous and phosphatic skeletons reflects multiple, independent co-optations of molecular and physiological processes that are widely shared among eukaryotic organisms (Westbroek and Marin, 1998). Indeed the biochemical supply of ions and the assembly of the necessary genetic and biochemical machinery for biomineralisation may be an ancient feature of eukaryotes (Aizawa and Miyachi, 1986; MacLennan et al., 1997). These include genes such as α-carbonic anhydrases, the ability to form transient amorphous mineral phases in both carbonate and phosphate, anticalcification inhibitors, and gene duplication, domain shuffling, and other genomic re-modelling (Aizenberg et al., 2003; Boßelmann et al., 2007; Jackson et al., 2007; 2011). All biominerals are found in intimate association with proteins, polysaccharides, and other macromolecules, which allows for an extraordinary diversity of biomineral form and function. Macromolecules also modify the morphology and growth kinetics of calcite (Gayathri et al., 2007), so offering a highly flexible mechanism whereby minor changes in the interacting, primary structure of proteins can control calcite crystal shape to produce a diverse range of complex, high-fidelity, skeletal architectures over evolutionarily rapid timescales.

Eukaryotic lineages probably differentiated long before the acquisition of skeletons within them (Bengtson, 1994; Knoll, 2003). As a result, some have proposed that abiotic factors acted as either thresholds or triggers for this sudden biomineralisation phenomenon, such as the availability of oxygen, phosphate- and carbonate ions in sea water (e.g. Daly, 1907; Towe, 1970; Riding, 1982; Cook and Shergold, 1984). In particular, motile physiologies demand oxygen, and so it has been presumed that a rise in oxygen, perhaps incrementally, during the Ediacaran facilitated the evolution of metazoan complexity (Canfield et al., 2007). The necessary molecules for skeletal formation, as well as muscle system activity, may also have been inhibited by lack of oxygen (Runnegar, 1982). Much uncertainty persists, however, as to the global nature of these changes in redox, the magnitude of atmospheric oxygenation, and the relationship of atmospheric oxygen to that of oceanic ventilation (Butterfield, 2009).

Biological activity often leads to complex feedbacks and emergent properties within an ecosystem that modifies both the physical and chemical environment, as well as the availability of nutrients and energy (ecosystem engineering). For example, sponges when abundant remove considerable dissolved carbon and bacteria from seawater and transfer this to sediment, so altering the geochemistry of both settings (Sperling et al., 2011). Likewise, vertical burrowing enhances oxygenation of sediment and microbial primary productivity, so increasing the availability of food for benthic metazoans (Lohrer et al., 2004). This makes the untangling of cause and effect in the radiation of metazoans highly problematic.

The rise of predation of metazoans by metazoans (macrophagous predators), although impossible without sufficient oxygen and other prerequisite conditions, has also been invoked to explain the explosion of diverse skeletal forms over some 30 Myr from ~550 to 520 Ma (Bengtson, 1994; Knoll, 2003). Of the more than 178 architectures recognised in skeletonised marine animals, 89 had evolved by the early Cambrian and 146 (80%) by the middle Cambrian (Thomas et al., 2000). Clearly most potential 'skeletal morphospace' was exploited rapidly once hard parts had appeared. This is not surprising because skeletons are used for a variety of single or multiple functions including structural support, protection, locomotion, respiration, attachment, filtration, grinding and cutting, light-harvesting, gravity-sensing, magnetic guidance, and storage of useful metabolites.

Five principal biominerals were acquired rapidly and exploited during the terminal Neoproterozoic to early Cambrian: skeletons of silica, phosphate, aragonite, low-Mg calcite (LMC) and high-Mg calcite (HMC) all appeared within some 25 Myr (see reviews of Lowenstam and Weiner, 1989; Bengtson, 1994; Knoll, 2003). This diversity is not surprising as biominerals have differing mechanical (e.g. stiffness, strength, toughness) and chemical (such as solubility and ion kinetics) properties, and so organisms with varying ecologies will have very different selective requirements. As biomineral properties are optimised for each function and ecology, so diverse biominerals will be required to fulfil these variable demands.

It has been suggested that selection of mineralogy at the onset of skeletal acquisition within a clade is governed by ambient sea water chemistry depending on either mMg:Ca (Tucker, 1992; Porter, 2007) and/or pCO$_2$ pressure (Sandberg, 1983; Zhuravlev and Wood, 2008), where HMC and aragonite skeletons initiate in >2 mMg:Ca and/or low pCO$_2$ (aragonite seas) and LMC in <2 mMg:Ca and/or high pCO$_2$ (calcite seas). These observations do not, however, explain why during late Ediacaran to early Cambrian aragonite seas, some organisms deployed HMC, others aragonite, and a third group used phosphate to build skeletons, shells and teeth. Here, we demonstrate that skeletal mineralogy was determined not only by changing physiochemical conditions during the Ediacaran to Cambrian, but also by ecology. The formation of any biomineral is a balance between the properties of that mineral and the cost of production, which varies not only with the availability of ions in seawater but also with ecological demand.

2. The cost of biomineralisation

Producing skeletal hard-parts requires energy and so imposes a metabolic cost. But this cost is problematic to measure because it is represented only as energy spent in respiration which cannot be clearly separated from other metabolic expenditures. In studies on molluscs, however, it has been demonstrated that the cost of calcification is far less (5%) than that of associated protein production (Palmer, 1983; 1992). This is not surprising given the high saturation of CaCO$_3$ in modern tropical surface seawaters, as organisms will tend to produce hard parts with whatever is abundant in the local environment, i.e. physiologically cheap (Bengtson, 1994). Mineral solubility is therefore broadly inversely related to physiological cost: silica is the least soluble biomineral, calcium carbonate generally abundant, and calcium hydroxyapatite is energetically costly. LMC is thermodynamically more stable than aragonite, and aragonite is less soluble than HMC under the same ambient conditions (Mackenzie et al., 1983; Morse et al., 2006). Secreting aragonite is more costly than calcite: aragonite has a packing density of 2.95 gcm^{-3}, compared to 2.72 gcm^{-3} for calcite (Weiner and Addadi, 1997). Indeed, the greater energetic requirement of aragonite production (Allemand et al., 2011) might force organisms to precipitate a calcite polymorph if ecological requirements demand a relatively dense skeleton.

Some groups, such as benthic, sessile members of the Porifera and Cnidaria, appear to calcify with ease (Wood, 1987) and produce fabrics not unlike abiotic precipitates, so suggesting that skeletonization involves relatively low cost. Poriferan and Cnidarian-grade metazoans and others (e.g. brachiopods and crinoids) are sometimes known as 'hypercalcifiers', inferred to have limited capacity to pump ions across membranes and so buffer calcifying fluids (Rhodes and Thompson, 1993; Stanley and Hardie, 1998; Knoll et al., 2007). Porifera and Cnidaria show multiple, independent, acquisition of calcareous skeletons, often of differing mineralogy according to the ambient seawater

mMg:Ca and pCO2 (Cuif and Gautret, 1991; Stanley and Hardie, 1998). Indeed, some corals grown in experimental seawater of elevated CO_2 decalcify yet retain basic life functions, including reproductive ability: they resume skeletal growth when reintroduced to normal modern seawater conditions (Fine and Tchernov, 2007). These results also highlight the arbitrary current distinction between some scleractinian corals and Corallimorpharia anemones, which are more closely related to each other than to other clades of scleractinians (Medina et al., 2006).

The cost of skeletonisation is probably far higher in mobile than immobile organisms. Skeletal transportation costs as a fraction of the overall energy budget are not well known, but data for the marine gastropod *Nucella lamellose* suggests that the cost of locomotion roughly triples with a doubling of shell weight (Palmer, 1992), and in crustaceans, the mineral content in skeletons is highly variable, being higher in areas requiring robustness such as chelae, or in animals that hide rather than employ rapid escape behaviours (Boßelmann et al., 2007).

In modern biotas, calcium phosphate (usually, hydroxyapatite) biomineralisation is often associated with the intense activity and high-energy lifestyles of motile predators (Ruben and Bennett, 1987). Calcium hydroxiapatite builds a less soluble skeletal component than can be achieved by carbonate, which is particularly important in vertebrates (Ruben and Bennett, 1987) and the most reactive arthropods (Boßelmann et al., 2007) where low pH ranges of extracellular fluids develop due to lactic acid production for ATP generation. Among vertebrates with osseous skeletons, this acidosis generates slight skeletal dissolution and consequent vascular hypercalcemia (Ruben and Bennett, 1981). Phosphate is also known to be released into the exoskeleton of fast-moving carnivorous crabs (Boßelmann et al., 2007) which possess metabolisms resembling that of vertebrates.

3. Mechanical properties of biominerals

Notwithstanding similar lattice energies, calcite and aragonite have differing characteristics. Aragonite lacks cleavage planes, but has the disadvantage of small crystal size and needle-like morphology: aragonite also has a strong tendency to form spherulitic clusters of crystals with high porosity (Weiner and Addadi, 1997). By contrast, calcite tends to form larger crystals, but these are very brittle as calcite cleaves easily where a crack can propagate with minimum dispersion of energy. As a result even stacked calcite shell microstructures are less tough than similar aragonite microstructures (Vincent, 2001; Barthelat and Espinosa, 2007). HMC tends to produce loose, brittle, crystal packages due to limited control over crystal orientation (Zhang et al., 2011a).

Nacre is a polycrystalline aragonite with excellent mechanical properties despite being a brittle ceramic. Although nacre has a very low organic content (1%), it is superior to most other shell structures and composite ceramics in stiffness, strength, and toughness: nacre is 1000 times more resistant to fracture than a single crystal of pure aragonite and 10 times harder and so is highly suited to form impact-resistant armour (Vincent, 2001; Barthelat and Espinosa, 2007). Cross lamellar structure is likewise strong with little organic matrix (Furuhashi et al., 2009). The siliceous spicules of hexactinellid sponges possess mechanical properties similar to those of nacre: these consist of layered silica with a very small fraction (<1%) of proteinaceous material and are, similarly, highly resistant to fractures (Miserez et al., 2008).

Biomineralised crustacean cuticle possesses remarkable mechanical properties as the orientation of chitin and co-alignment of LMC axes create a hard, stiff shield, while the underlying more elastic layer can dissipate the acting impact energy: the outermost layer of crystalline calcite also increases resistance to wear (Al-Sawalmih et al., 2008). The more costly calcium hydroxyapatite has a greater chemical stability than calcium carbonate in the acidic conditions that prevail in most vertebrate systems, particularly after intense exercise (Ruben and Bennett, 1987).

The mechanical shortcomings of simple aragonite, calcite and phosphate microstructures are overcome by the organic composites developed in many metazoans above poriferan and cnidarian grades. Major structural innovations include the development of (1) heterogeneous, multilayered skeletal elements, (2) regular alternations of organic and inorganic lamellae, and (3) secondary composite structures at the nanoscale. Such anisotropic structures decrease the yield stress between layers from the outer surface inwards by up to a factor of 10, whilst increasing the energy dissipation during predatory penetration up to a factor of 4 (Weiner and Addadi, 1997; Li et al., 2006; Bruet et al., 2008; Connors et al., 2012).

4. Rise of metazoan predation

Many theories on the major transitions in evolution invoke predation as a key factor, in particular an increase in individual size, the shift from sessile to motile ecologies, invasion of the water column, and the appearance of increasingly complex forms of external skeletal structures (e.g. Stanley, 1973; Vermeij, 1990; Signor and Vermeij, 1994). Coevolution between predators and their prey has long been suggested to have led to an intensification of selective pressure and increased complexity of individual metazoan form, defensive structures, and ecology, during the Cambrian Radiation.

The metazoan last common ancestor was likely to have been a microphagous suspension feeder, and as modern Cnidaria use stinging cells to prey on pelagic animals, predation is often argued to have appeared with this group. However, predation upon other animals appears to be a derived ecology for all the three major clades of eumetazoans: indeed, there is no evidence for a carnivorous lifestyle before the mid-Ediacaran for any eumetazoan lineage (Erwin et al., 2011).

Borings or drill-holes in the Ediacaran *Cloudina* have been attributed to predators (Bengtson and Yue, 1992). Other predatory borings (Conway Morris and Bengtson, 1994; Zhang and Pratt, 2008), whole-organism ingestion based on gut contents and coprolites (Conway Morris, 1977; Zhu et al., 2004; Ivantsov et al., 2005; Vannier and Chen, 2005; Han et al., 2007), insertion and extraction of flesh from smashed shells (Robson and Pratt, 2007), repaired predatory attacks (Babcock, 2003; Zamora et al., 2011; Zhang et al., 2011b), and sophisticated visual, captive, and masticatory systems in the largest metazoans (Purnell, 1995; Fortey and Owens, 1999; Nedin, 1999; Szaniawski, 2002; Chen et al., 2007a; Vannier et al., 2007; García-Bellido et al., 2009; Paterson et al., 2011), have all been reported from early–middle Cambrian skeletal fossils. Priapulids and other cephalorynch worms, xenusians, anomalocaridids, large trilobites and other arthropods, chaetognaths (protoconodonts), and conodonts were among durophagous Cambrian predators (Burzin et al., 2001).

5. Materials and methods

We here consider the relationship between skeletal mineralogy and ecology, and their quantitative trends, in order to understand the role of ambient physicochemical conditions and ecology in the changing cost-benefit ratio of skeletonisation through the Ediacaran to Cambrian.

Inferred primary mineralogy of major skeletal taxa from the Upper Ediacaran to Middle Cambrian was assessed, together with first appearance datum (FAD), and skeletal type: cone or external tube; massive skeleton; teeth; bivalved shell; single shell; plates/sclerites/scales/spicules (Table 1). Data are collected from all principal basins and derived from stratigraphically well-constrained units only.

Table 1

Inferred primary mineralogy of taxa, and inferred ecological guild, as listed on Fig. 1 (Distribution of major skeletal taxa from the upper Ediacaran to middle Cambrian). FAD—first appearance datum; E—upper Ediacaran; lND—lower Nemakit-Daldynian; uND—upper Nemakit-Daldynian, lT—lower Tommotian; mT—middle Tommotian; uT—upper Tommotian (Terreneuvian); lA—lower Atdabanian; uA—upper Atdabanian; B—Botoman (Cambrian Series 2); MC—middle Cambrian (Cambrian Series 3); UC—upper Cambrian (Furongian); LO—Lower Ordovician. Skeleton type and composition: C—cone or external tube; M—massive skeleton; T—teeth; V—bivalved shell; S—single shell; P—plates/sclerites/scales/spicules; a—aragonite; c—low-Mg calcite; m—high-Mg calcite; p—phosphate; s—silica, including agglutinated forms. See text for primary mineralogy criteria.

Taxon	FAD	Ecology	Skeletal type and composition	Comments and references
Cloudina-group	E	Benthic, sessile, ?attached	C m	Grant (1990), Wood (2011), Zhuravlev et al. (2012)
Namapoikia	E	Benthic, sessile, attached	M a	Wood et al. (2002)
Namacalathus-group	E	Benthic, sessile, attached	S? m	Grotzinger et al. (2000), Wood (2011), Zhuravlev et al. (2012)
Sinotubilites	E	Benthic, sessile, unattached	C a	Chen et al. (2007b)
Chaetognatha including Protoconodonta	lND	Nektic, motile, fast	T p	Bengtson (1983), Szaniawski (2002); Vannier et al. (2007); FAD—Khomentovsky and Karlova (2005)
Anabaritida	lND	Benthic, sessile, unattached	C a	Kouchinsky & Bengtson (2002); Burzin et al. (2001); FAD—Khomentovsky and Karlova (2005)
Orthothecimorpha	uND	Benthic, sessile unattached/motile slow	C a	Kouchinsky (2000b), Feng et al. (2001); Burzin et al. (2001); FAD—Khomentovsky and Karlova (2005)
Helcionelliformes	uND	Benthic, motile, slow	S a	Runnegar (1985, 1989), Bengtson et al. (1990), Kouchinsky (2000a), Feng and Sun (2003); Kouchinsky (2001); FAD—Khomentovsky and Karlova (2005)
Paragastropoda	uND	Benthic, motile, slow	S a	Runnegar (1985, 1989), Bengtson et al. (1990), Kouchinsky (2000a); Kouchinsky (2001); FAD—Khomentovsky and Karlova (2005)
Coelosclerotophora including Chancelloriida	uND	Benthic, sessile, attached/motile, slow	P a	Bengtson et al. (1990), Mehl (1996), Kouchinsky (2000a), Porter (2004); Conway Morris and Peel (1995), Vinther (2009); FAD—Khomentovsky and Karlova (2005)
Renalcida	lND	Benthic, sessile, attached	M m	James and Klappa (1983), Zhuravlev and Wood (2008); Riding (2001).
Cambroclavida	lT	Benthic, motile, slow?	P a	Bengtson et al. (1990); Conway Morris et al. (1997); FAD—Steiner et al. (2007)
Tommotiida including Tannuolinidae	lT	Benthic, sessile, attached	P p	Holmer et al. (2002); Skovsted et al. (2011); FAD—Khomentovsky and Karlova (2005)
Linguliformea	lT	Benthic, sessile, attached/unattached	V p	Ushatinskaya (1995), Skovsted and Holmer (2003); Dornbos et al. (2005), Ivantsov et al. (2005); FAD—Khomentovsky and Karlova (2005)
Hyolithelmintida	lT	Benthic, sessile, unattached	C p	Grigorieva (1980), Vinn (2006); Skovsted and Peel (2011); FAD—Khomentovsky and Karlova (2005)
Paracarinachitidae	lT	Benthic, motile, slow	P a	Conway Morris and Chen (1991)
Conulariida including Hexangulaconulariida	lT	Benthic, sessile, attached	M p	Conway Morris and Chen (1992), Hughes et al. (2000)
Rostroconchia	lT	Benthic, motile, slow	S a	Pojeta and Runnegar (1976), Kouchinsky (2000a); FAD—Khomentovsky and Karlova (2005)
Bivalvia	lT	Benthic, sessile, unattached	V a	Runnegar and Bentley (1983), Runnegar (1985), Berg-Madsen (1987), Kouchinsky (1999)
Archaeocyatha	lT	Benthic, sessile, attached	M m (rare—a)	James and Klappa (1983), Brasier et al. (1994), Kruse et al. (1995), Zhuravlev and Wood (2008); FAD—Rozanov and Zhuravlev (1992)
Cribricyatha	mT	Benthic, sessile, attached	M m	Zhuravlev and Wood (2008); Wood et al. (1993); FAD—Rozanov and Zhuravlev (1992)
Hyolithomorpha	lT	Benthic, motile, slow	V ?m	Marti Mus and Bergstrom (2007); Burzin et al. (2001); FAD—Rozanov and Zhuravlev (1992)
Coleoloida	lT	Benthic, sessile, unattached	C a	Landing et al. (2002); FAD—Rozanov and Zhuravlev (1992)
Obolellata	mT	Benthic, sessile, attached	V m	Ushatinskaya and Zhuravlev (1994); Ushatinskaya (2001); Williams et al. (2000)
Calcarea	mT	Benthic, sessile, attached	M + P m	Jones (1979), James and Klappa (1983); FAD—Kruse et al. (1995)
Khasaktiidae	mT	Benthic, sessile, attached	M m	Zhuravlev et al. (1993), Brasier et al. (1994), Zhuravlev and Wood (2008)
Radiocyatha	mT	Benthic, sessile, attached	M a	Wood et al. (1993); FAD—Rozanov and Zhuravlev (1992)
Tabulaconida	B	Benthic, sessile, attached	M a, m	modular species only Zhuravlev et al. (1993), Fuller and Jenkins (2007)
Mobergellidae	uT	Benthic, motile?	P p	Skovsted (2003); FAD—Rozanov and Zhuravlev (1992)
Hydroconozoa	uT	Benthic, sessile, attached	M c	Zhuravlev et al. (1993), Brasier et al. (1994), Wood et al. (1993)
Stenothecoida	lA	Benthic, sessile, unattached	V c	Ushatinskaya and Zhuravlev (1994); FAD—Rozanov and Zhuravlev (1992)
Trilobita	lA	Benthic, motile, fast, and nektic	P c (rare—p)	Dalingwater (1973), James and Klappa (1983), Wilmot and Fallick (1989), Dalingwater et al. (1991), Lee et al. (2007); Hughes (2001); FAD - Rozanov and Zhuravlev (1992)

Table 1 (continued)

Taxon	FAD	Ecology	Skeletal type and composition	Comments and references
Other biomineralised arthropods (Bradoriida, Phosphatocopida, Aglaspidida, *Phytophilaspis*)	uA	Nektic, fast?	P p	Briggs and Fortey (1982), Siveter and Williams (1997), Skovsted and Peel (2001), Zhang (2007), Lin et al. (2011); Vannier and Chen (2000), Ivantsov et al. (2005)
Agmata	B	Benthic, sessile, unattached	C s	James and Klappa (1983); Fritz and Yochelson (1987).
Rhynchonellata	lA	Benthic, sessile, attached	V c	Ushatinskaya and Zhuravlev (1994); Ushatinskaya and Malakhovskaya (2006)
Kutorginata	uT	Benthic, sessile, attached	V c	Not shown on Fig. 1, Ushatinskaya and Malakhovskaya (2006)
Echinodermata	uA	Benthic, sessile, attached/ unattached/motile, slow	P m	James and Klappa (1983), Dickson (2004); Guensburg and Sprinkle (2001), Zamora and Smith (2008); FAD—Rozanov and Zhuravlev (1992)
Palaeoscolecida and other skeletal vermiform Ecdysozoa	uA	Benthic, motile, slow/fast	P p	Müller and Miller (1976), Wrona (1982); FAD—Rozanov and Zhuravlev (1992)
Byroniida	uA	Benthic, sessile	C p	Bischoff (1989); FAD—Bengtson et al. (1990)
Tardypolipoda or Xenusia	uA	Benthic, motile, slow	P p	Bengtson et al. (1986); Gámez Vintaned et al. (2011); FAD—Rozanov and Zhuravlev (1992)
Conodonta	MC	Nektic, fast	T p	Bengtson (1983); Purnell, 1995)
Polyplacophora	UC	Benthic, motile, slow	P m?	Haas (1972), Carter and Hall (1990); FAD—Stinchcomb and Darrough (1995)
Cephalopoda	UC	Nectic?, slow?	S m?	Crick (1981), Chen and Teichert (1983); FAD—Landing and Kröger (2009)
Bryozoa	UC	Benthic, sessile, attached	M c?	Taylor and Weedon (2000), Smith et al. (2006); FAD—Landing et al. (2010)
Hexactinellida	lND	Benthic, sessile, attached	P s	Rigby (1986), Dornbos et al. (2005), Ivantsov et al. (2005).
Demospongia	uA	Benthic, sessile, attached/ unattached	P s	Rigby (1986), Dornbos et al. (2005), Ivantsov et al. (2005); FAD—Bengtson et al. (1990)
Foraminifera	lND	Benthic, sessile, unattached	C s	Felitsyn (1992); McIlroy et al. (2001); FAD—Kontorovich et al. (2008)
Radiolaria	MC	Nectic?, passive	S s	Alez (2011)

Skeletal organisms with carbonate skeletons are now preserved as either LMC or dolomite, replacing primary LMC, HMC or aragonite. Skeletal calcium hydroxyapatite is now usually preserved as either dahllite, francolite, or monazite. Primary skeletal composition cannot always be inferred through reference to Recent descendants or relatives (Wood, 1991), and in vitro experiments show that some skeletal biota are able to change their skeletal mineralogy depending on changing sea water chemistry (e.g. Ries, 2010, 2011).

The following criteria are used to infer the primary mineralogy of skeletal taxa, based on James and Klappa (1983), Sandberg (1983), and Zhuravlev and Wood, (2008) (Table 1):

(1) Detection of original element concentrations either from fluid inclusions in precipitates or from skeletal material (Mg—for HMC; Sr—for aragonite).
(2) Preservation of specific skeletal fabrics either in calcite or in phosphate minerals and silica replicas (e.g. foliated and prismatic microstructure—LMC; microgranular microstructure—HMC; nacreous and lamello-fibrillar microstructures—aragonite).
(3) Relative quality of preservation of different precipitates within the same sample: fabric preserved—LMC; fabric preserved and spar-filled moulds with microdolomite—HMC; coarse spar mosaic-filled moulds, generally irregularly cross-cutting original structure—aragonite.
(4) Epitaxial synsedimentary marine cements developing in optical continuity with skeletal elements: bladed equant calcite—LMC; fibrous calcite—HMC; botryoids of acicular crystals—aragonite.
(5) Phylogenetic application of skeletal mineralogies in extant groups to their probable fossil relatives.
(6) Relative stable isotope composition ($\delta^{13}C$, $\delta^{18}O$) of different precipitates in the same sample with less altered signatures characterizing LMC fabrics.

Primary calcium hydroxyapatite is inferred by comparison with Recent lingulate brachiopods (Ushatinskaya, 1995; Streng and Holmer,

2005) and chordates (Donoghue and Sansom, 2002), or by unusual microstructures which do not match any known primary carbonate fabrics (Müller and Miller, 1976; Bengtson, 1983, 1994; Holmer et al., 2002; Porter, 2004). Only phosphatic botryoids are considered to be secondary fabrics which may or may not reflect primary skeletal composition (Bengtson et al., 1990). Some trace elements, such as Neodymium and other Rare Earth Elements can be used for recognition of primary phosphatic composition if the skeleton is replaced with clay minerals (Wrona, 1982; Sturesson et al., 2005).

Silica is inferred for specific spicule types indicative of hexactinellids and demosponges (Ivantsov et al., 2005), radiolarian tests (Maletz, 2011), and for some Ediacaran-early Cambrian agglutinating foraminifera, including tubicolous *Platysolenites* (McIlroy et al., 2001).

Quantitative data on the stratigraphic distribution of ~3500 genera through the late Ediacaran–early Tremadocian is gathered from Zhuravlev (2001). The bulk distribution of biogenic phosphate, LMC, HMC, and aragonite is calibrated to the number of genera per zone per mineralogy.

Skeletal taxa were also assigned to one or more of seven ecological guilds: sessile, unattached; sessile, attached; benthic, motile slow; benthic, motile fast; nektic, passive; nektic, motile slow, and nektic, motile fast, based on field observations and wide literature analysis (Table 1), and likewise calibrated to the number of genera per zone per guild. As the majority of these genera are monotypic, this analysis provides a reasonable quantification of biomineralisation trends through the late Ediacaran to early Tremadocian.

6. Trends in mineralogy and ecology

Seawater chemistry varied through the Ediacaran to Cambrian (Fig. 1A): high mMg:Ca and/or low pCO$_2$ favoured aragonite and HMC precipitation from the Ediacaran until the early Atdabanian, but low mMg:Ca and/or high pCO$_2$ and the onset of greenhouse conditions favoured LMC formation thereafter (Zhuravlev and Wood,
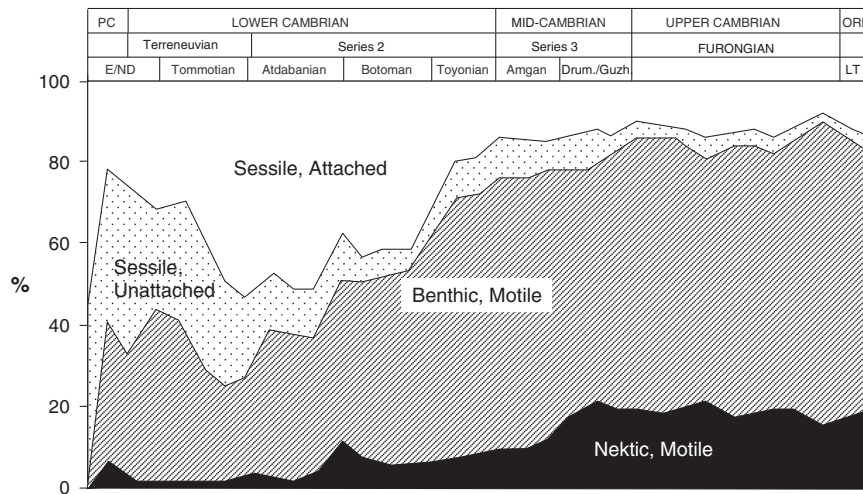
A   Seawater Chemistry
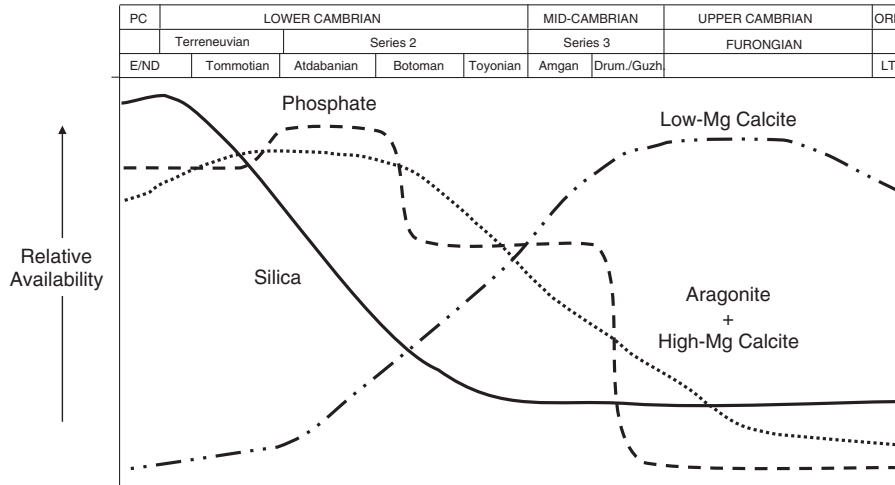
B   Mineralogy
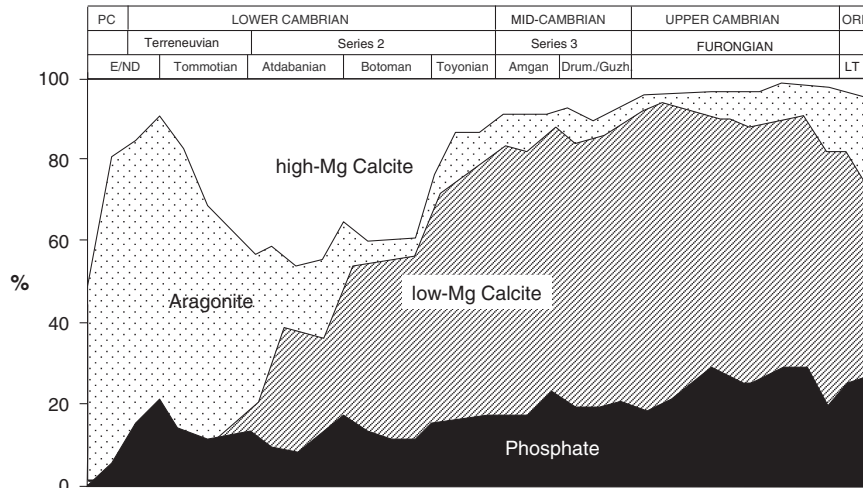
C   Ecology

Fig. 1. A, Schematic representation of changing seawater chemistry from the upper Ediacaran to lower Tremadocian. Distribution of B, skeletal carbonate mineralogies, and C, ecological guild, expressed as percentage of number of genera per zone, PC, Precambrian; E, Ediacaran Period; ND, Nemakit-Daldynian Stage, ORD., Ordovician Period, LT, lower Tremadocian Series, Drum./Guzh., Drumian and Guzhangian stages.

2008). A well-documented phosphogenic event occurred during the early Cambrian (Cook and Shergold, 1984), and although silica is the least soluble biomineral it was available in large qualities in Neoproterozoic seas but declined thereafter (Maliva et al., 1990).

Quantitative analysis of genera reveals a notable shift from exclusively aragonite or HMC in the Ediacaran to Terreneuvian, to dominantly LMC mineralogies from the mid-Cambrian to Ordovician (Zhuravlev and Wood, 2008) (Fig. 1B). These trends coincide with a significant increase of both benthic, motile and nektic, motile biota over sessile forms

from 30 to 40% of total skeletal biota at the beginning of the Cambrian to 80% by the middle Cambrian onwards (Fig. 1C). Of the sessile biota, unattached forms peak during the Ediacaran to Tommotian declining rapidly thereafter; attached forms reach 50% of the total skeletal biota by the late Tommotian to Atdabanian, but decrease to some 20% from the end of the Early Cambrian.

Carbonate biominerals show a correspondence between inferred sea water chemistry and the first adopted mineralogy in skeletal clades originating in the Ediacaran to middle Cambrian (Fig. 2A) (Porter, 2007;
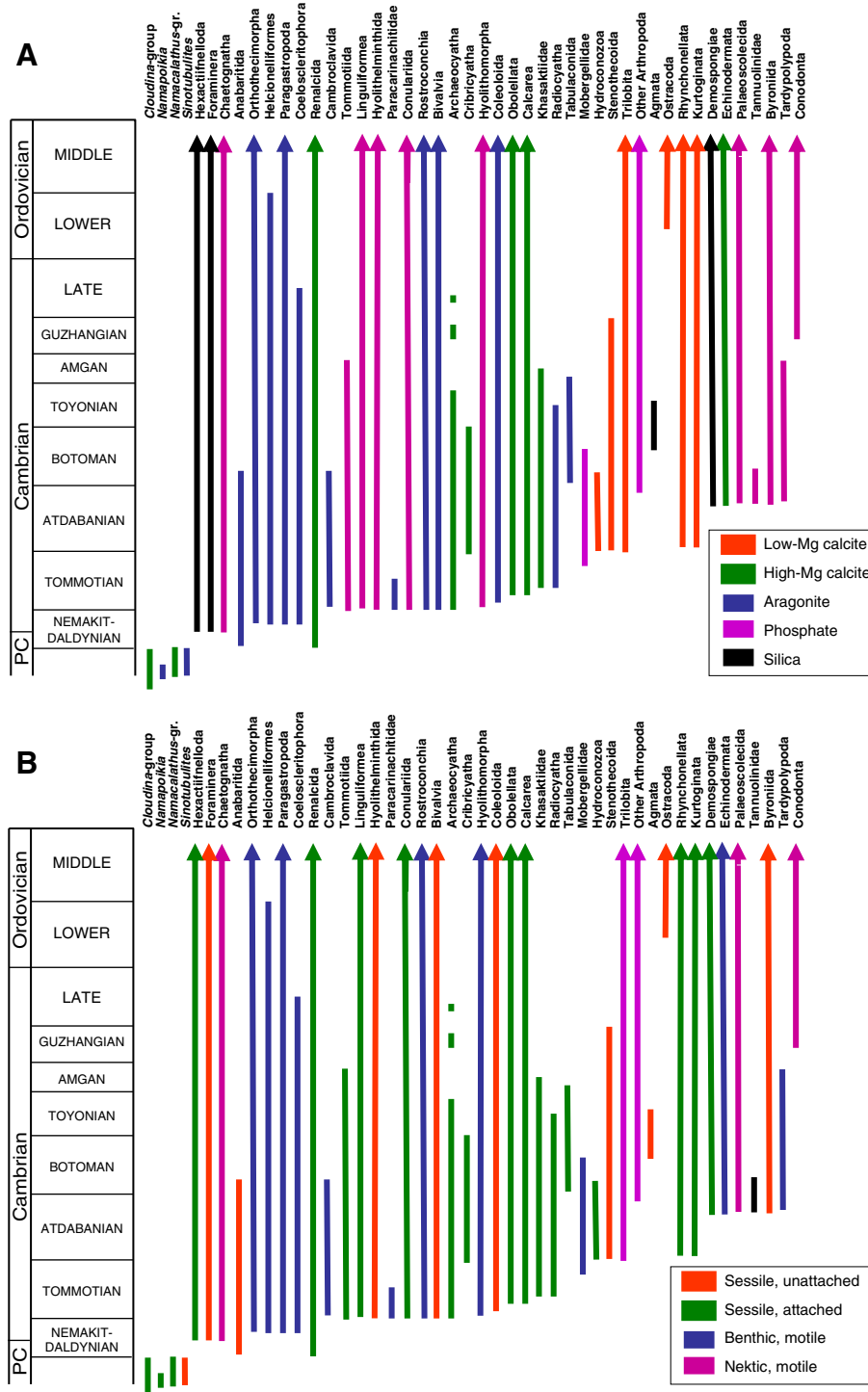

Fig. 2. Distribution of inferred A) mineralogy (modified from Zhuravlev and Wood, 2008) and, B) ecological guild of major skeletal taxa from the upper Ediacaran to Middle Ordovician in order of clade origination. Phylogenetic relationships are not shown and independent acquisition of skeletons in all clades is not implied.

Zhuravlev and Wood, 2008). Biominerals also, however, broadly follow the dynamics of ecology (Fig. 2B), where sessile, attached clades are often siliceous, phosphatic or HMC, sessile, unattached clades are either aragonitic or LMC, motile clades are often aragonitic, phosphatic or LMC, and nektic clades are often LMC or phosphatic. These relationships are expressed in the coupled decline of taxa with both HMC skeletons and those belonging to the sessile, attached guild, together with an increase of taxa with phosphatic hard parts and the rise of the motile and nektic guilds (Fig. 1B and C).

Ediacaran skeletal taxa were all sessile with both calcareous and siliceous skeletons. Cambrian sessile, attached forms possessed mainly heavily-calcified massive HMC skeletons (renalcids, archaeocyaths, cribricyaths, tabulaconids) or LMC shells (kutorginate and rhynchonellate brachiopods). A large variety of primary phosphatic tubes and cones probably representing cnidarian-grade organisms (hexaconulariids, paiutiids) and stem- and crown-group lophotrochozoans (hyolithelminths, tommotiids, mobergellans, lingulates) appeared during the early Cambrian phosphogenic event. Free-swimming nekton or bentho-pelagic swimmers (chaetognaths and conodonts) bore phosphatic teeth, while bivalved and some other arthropods possessed either phosphate (bradoriids, phosphatocopids, aglaspidids) or LMC (agnostids) cuticles. Sessile, unattached groups preferred protective aragonitic skeletons (anabaritids, coleolids, hyoliths), and motile benthos comprised dominantly either aragonite (molluscs, halkieriids, cambroclaves) or LMC carapaces (trilobites) depending on seawater chemistry state.

The first motile skeletal and non-skeletal eumetazoans appeared at the base of the Cambrian, together with new sessile benthic calcareous skeletal metazoans. Motile skeletal benthos bore exoskeletons of either valved shells or a scleritome (molluscs and halkieriids) as well as mineralised teeth (protoconodonts), together with new sessile calcareous skeletal metazoans. Many of the motile forms represent a diverse fauna thought to be dominantly of lophotrochozoan affinity, including halkieriids with protective, composite exoskeletons (scleritomes) (Conway Morris and Peel, 1995; Porter, 2008; Vinther, 2009). Further new benthic skeletal metazoans appeared in the late Terreneuvian (~535 to ~526 Ma), as well as diverse spiculate and hypercalcified sponges (Debrenne and Reitner, 2001).

Later in the early Cambrian, numerous multi-element, broadly metameric exoskeletons originated, reflecting the abundance of arthropod or arthropod-like taxa (biomineralised ecdysozoans) as well as new brachiopod and other lophotrochozoan groups (Ushatinskaya and Zhuravlev, 1994; Hollingsworth, 2011). Trilobites appear at the base of the Atdabanian (~526 Ma) coincident with the appearance of calcite seas (Zhuravlev and Wood, 2008). Skeletal deuterostomes (echinoderms) did not evolve until the late Atdabanian (~515 Ma) (Rozanov and Zhuravlev, 1992; Zamora et al., 2009), as did sclerites of vermiform ecdysozoans (Gámez Vintaned et al., 2011). The end of the middle Cambrian saw the first appearance of skeletal vertebrates in the form of conodonts (Bengtson, 1983), which were probably nektic active predators belonging to stem-group vertebrates (Purnell, 1995; Donoghue et al., 2006).

Fig. 3 quantifies the distribution of ecological guilds within each major biomineral through the Ediacaran to early Tremadocian. HMC skeletons are only represented by sessile biota, dominated by attached forms, but restricted mainly to the early Cambrian (Fig. 3A). Phosphatic hard parts are known successively in early sessile, attached biota, then in benthic, motile forms, and finally in nektic, motile clades which become important from the late early Cambrian onwards (Fig. 3B). Aragonite hard-parts are dominated by either sessile-unattached groups, but these decline through the Cambrian, or by motile benthos, which increase in number (Fig. 3C). LMC skeletons are represented by sessile, unattached benthos and nekton, but dominantly by motile benthos from the mid-early Cambrian onwards (Fig. 3D).

7. Discussion

There are uncertainties and lack of consensus concerning some assignments of ecological guild and original mineralogy, but these are minor and the trends described here are robust. Although new taxa continue to be described from Ediacaran to Cambrian strata, this interval is extensively studied and comparatively well-known and taphonomic effects are unlikely to be greater than for any other interval in the Phanerozoic.
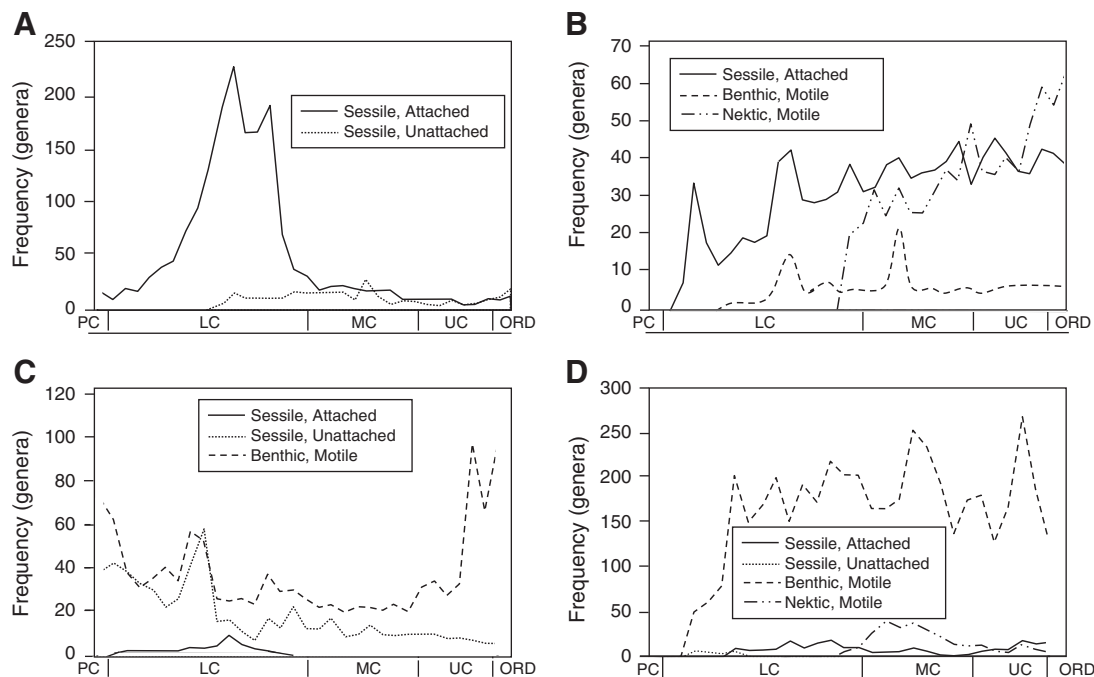

Fig. 3. Distribution of ecological guilds within individual biominerals expressed as total numbers of genera per zone from the upper Ediacaran to lower Tremadocian. A, High-Mg calcite; B, Phosphate; C, Aragonite; D, Low-Mg calcite. PC, Precambrian; E, Ediacaran Period; LC, lower Cambrian; MC, middle Cambrian; LC, upper Cambrian; ORD, Ordovician (lower Tremadocian).

During aragonite-facilitating seas, Ediacaran and Cambrian organisms belonging to the sessile, attached guild used mostly HMC, those of the sessile, unattached guild utilised aragonite, and the nektic, motile guild was represented by animals with phosphatic skeletons. With outset of calcite seas, the sessile biota possessed mainly LMC hard parts (Figs. 1 and 3). A minority of Ediacaran–Cambrian benthic groups bore a skeleton of either amorphous silica spicules (hexatinellids and demosponges) or agglutinating silica tubes (foraminiferans).

The only exception to these trends are the diverse benthic, unattached biota of possible cnidarians and stem- and crown-group lophotrochozoans which appeared with phosphatic external skeletons during the earliest Cambrian phosphogenic event indicative of elevated marine phosphate levels (Cook and Shergold, 1984). Such skeletons are assumed to be defensive, confirmed by the preservation of abundant boreholes in tubes and sclerites (Conway Morris and Bengtson, 1994; Zhang and Pratt, 2008). By contrast, the diversification of conodonts, protoconodonts, and arthropods possessing phosphatised skeletal elements only appeared after the decline of marine phosphate levels (Fig. 3B).

In modern biotas, calcium hydroxyapatite is associated with intense activity and high-energy lifestyles (Ruben and Bennett, 1987) and in the Cambrian, this mineral is also preferentially found in protoconodonts and arthropods where the teeth are biomineralised and clearly have an active predatory function (Fig. 3B). The early evolution of skeletal vertebrates coincides with the biomineralisation of feeding elements in actively swimming predators (conodonts) and microphagous suspension feeders (heterostracans), which represent basal stem-gnathostome groups whose life strategies were plesiomorphic to herbivory, while macrophagous predation was plesiomorphic to suspension feeding (Purnell, 1995, 2001). Conodont teeth were covered with enamel-type hypermineralised crown tissue crystallites which were arranged perpendicular to the functional surface enabling greater resistantance to wear (Donoghue, 2001). Additionally, the earliest Cambrian supposed chordates possess mineralised branchial denticles (Shu et al., 1999), with an inferred relationship to the intense activity and high-energy lifestyles of this group.

In planktic chaetognaths, thought to be the most primitive within this enigmatic phylum, the mitochondria-rich contractile locomotor muscles that sustain muscular activity during swimming require a high extracellular Ca^{2+} supply (Casanova and Duvert, 2002). This physiological requirement implies hypercalcemia and skeletal dissolution similar to that found in those in vertebrates, and may explain the phosphatic composition of the grasping elements (protoconodonts) in the first evolved chaetognaths that occupied a nektic predator niche (Vannier et al., 2007).

Arthropods comprise a significant part of Cambrian diversity and those which were swimming micro- and macrophagous predators possessed phosphatised cuticles (Williams et al., 2007; Lin et al., 2011). Even if these Cambrian arthropods did not possess phosphatised exoskeletons, their cuticles were probably impregnated with ACP as co-occurring 'soft-bodied' arthropods lack phosphatic preservation.

Variations in the mineral properties of LMC, HMC and aragonite are expressed by their selective use in organisms employing different ecological strategies. The bulk of Cambrian sessile, attached organisms belonged to algal-like forms and low-grade metazoans (renalcids, archaeocyaths, cribricyaths, coralomorphs). These groups produced massive, but simple, skeletons where the low cost of HMC was preferentially utilised (Fig. 3A) as the physical properties of this mineral—loose, brittle, crystal packages—did not present a disadvantage as these organisms also often strengthened skeletons by abundant secondary deposits. Morphological and palaeoecological characteristics of the earliest skeletal metazoans are all consistent with more efficient feeding and competitive substrate strategies, as well as anti-predation traits. In addition to a sessile habit, often involving attachment to a reef substrate, these include: the occupation of progressively younger skeletal parts (Cloudina, Sinotubulites, archaeocyaths) providing

increased feeding efficiency; thick organic walls (Sinotubulites) and apertural-defences (Cloudina, archaeocyaths) which offered protection from predation; and aggregating behaviour and possession of a stalk or holdfast (Namacalathus, archaeocyaths, cribricyaths, coralomorphs), and the ability to encrust, a modular habit, and large size (Namapoikia, archaeocyaths), providing competitive superiority on hard substrates as well as reducing susceptibility to predation (Wood, 2011).

A further type of HMC skeleton is observed in Cambrian sessile attached calcarean sponges and unattached echinoderms whose modern descendants form skeletons of highly sophisticated composite monocrystals (Aizenberg et al., 2003; Killian et al., 2009), primarily for biomechanical strength.

Cambrian sessile, unattached and motile animals appear to have been unable to sustain the cost of thick skeletal secretion. Accordingly, gaining nacre might have provided the best mechanical protection, and nacre and crossed-lamellar structures were exploited by a high variety of Cambrian molluscs which represent the second most diverse benthic motile group after arthropods (Runnegar, 1985; Bengtson et al., 1990; Kouchinsky, 1999, 2000a,b; Feng and Sun, 2003; Fig. 3C herein). Less sophisticated aragonitic structures are observed in anabaritids, hyoliths, obolellats, and other Cambrian sessile unattached and slow motile animals which could also satisfy the requirements of building both relatively resistant and energetically efficient skeletons.

LMC structures, although of inferior mechanical properties, appear to become advantageous over HMC and aragonite in the middle Cambrian (Zhuravlev and Wood, 2008) (Figs. 1A, B and, 3D). Trilobites appear about ~526 Ma coincident with the onset of calcite seas (Zhuravlev and Wood, 2008), and the rapid exploitation of such skeletal types may have been facilitated by the parallel evolution of complex, organic-rich mineral composites: the simplest strategy for increasing body size when protected by an exoskeleton (Thomas et al., 2000). It is interesting to speculate that the innovation of the remarkable compound eyes of trilobites, in large part a result of the optical properties of calcite (Clarkson, 1997), may not have been possible until this time.

An orientation of c-axes perpendicular to the outer functional surface similar to biomineralised crustacean cuticle is common in trilobites (Dalingwater, 1973; Wilmot and Fallick, 1989) as well as the kutorginate and rhynchonellate brachiopods (Ushatinskaya and Malakhovskaya, 2006) also inhabiting calcite seas. Prismatic and foliated LMC structures in molluscs, although of reduced mechanical strength (Hou et al., 2004; Furuhashi et al., 2009) might have played a significant role as isolating outer shell veneers in later calcitic seas. Such structures appeared in some middle Cambrian molluscs (Runnegar, 1985). This trend of increased LMC hard-parts was paralleled by multiple appearances of heterogeneous, organic-rich, multi-layered skeletal structures among new groups of arthropods, molluscs, brachiopods, bryozoans, and vertebrates. These imparted much greater resistance against dynamic penetrating loads that could result from predatory attacks.

In summary, while selection of mineralogy at the onset of skeletal acquisition within a clade appears to have been governed by ambient sea water chemistry (Porter, 2007; Zhuravlev and Wood, 2008), mineralogy was also selected according to ecology. Here we see a close interaction between environmental change and ecological opportunity. Sessile, benthic stem-group poriferans or cnidarians appear in the Ediacaran with often massive skeletons of aragonite or HMC mineralogies; new aragonitic sessile clades and additional motile benthos of stem-group Eumetazoa appear in the Terreneuvian with often composite or articulated, skeletons. The first LMC skeletons of novel organic-rich composite materials did not appear until the late early Cambrian, coincident with calcite seas. Phosphatic possible cnidarians and stem- and crown-group lophotrochozoans appeared during the earliest Cambrian coincident with elevated marine phosphate levels, but calcium hydroxyapatite is also preferentially found in protoconodonts, conodonts, and arthropods appearing mainly in the late early Cambrian, inferred to have intense activity and high-energy lifestyles.

Skeletons were also acquired in groups with successively higher energetic demands and motility during the Ediacaran to middle Cambrian: sessile, unattached; sessile, attached; benthic, motile; and nektic, motile. This suggests an attendant increase in the physiological cost of skeletonisation. We can infer that the cost-benefit ratio of biomineralisation escalated during this interval, such that the increasing cost of producing a protective skeleton, in part with increasingly costly minerals, was offset by the increased chance of survival.

8. Conclusions

The mineralogy of clades from the Ediacaran to Lower Ordovician as well as quantitative analysis of trends reveals a close interaction between changing sea water chemistry, ecological opportunity, and escalating response. There is notable shift from exclusively aragonite or HMC in the Ediacaran to Terreneuvian, to dominantly LMC mineralogies from the mid-Cambrian to Ordovician (Fig. 1B). This trend coincides with the successive evolutionary importance of skeletal biota with increasingly energetic lifestyles, from sessile unattached in the late Ediacaran- Terreneuvian, sessile attached from the Terreneuvian - Botomian, benthic motile from the Terreneuvian, and nektic from the late Early Cambrian onwards (Fig. 1C).

Ecology is reflected in the choice of biomineral. 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 pCO$_2$ (aragonite) seas; 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 mMg:Ca and/or high pCO$_2$ (calcite) seas. Phosphatic possible cnidarians and stem- and crown-group lophotrochozoans appeared during the earliest Cambrian coincident with elevated marine phosphate levels. Active, bentho-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.

Although greater size (and so competitive superiority and reproductive enhancement), increased elevation above the sea floor, and biomechanical strength are conferred by a skeleton as noted in the early to middle Cambrian sessile skeletal biota, it is difficult to offer a convincing alternative explanation for the rise of scleritome skeletons (including chancelloriids), mollusc and brachiopod shells, and biomineralised arthropod cutitcle, other than protection from predation.

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. 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.

Acknowledgements

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