Geochemical proxy systems in marine $CaCO_3$ biominerals record both environmental changes and biomineralisation processes

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Abstract

The isotopic and elemental composition of calcium carbonate formed by marine organisms underpins a substantial portion of our knowledge of past climates. These geochemical 'proxy' systems have revolutionised our understanding of palaeoenvironmental change but remain largely rooted in empiricism because of poorly understood biological 'vital effects'. Here, we outline how this is both a problem and an opportunity — while some proxies have their basis in biological processes, this is the root cause of uncertainty in others. Moreover, integrating geochemistry into biomineralisation models provides additional constraint on cellular processes; geochemical data have untapped potential in the field of biomineralisation and could be used to simultaneously understand the proxies in question and to determine why biomineralising organisms are sensitive to environmental change.

Keywords: biomineralisation, trace element, stable isotope, ion transport, shell chemistry, geochemical proxy, calcification

INTRODUCTION

How has Earth's surface environment changed since its formation? The vastness of geological time naturally leads us to this question, of central importance to understanding how we, and the world around us, came to be. Notwithstanding knowledge of relatively recent climatic change handed down through oral tradition, the tools to unravel the enormous changes we now know to have taken place were developed only in the mid-20th Century. Fast-forward to today and it seems incredible to imagine a world in which this information did not exist; we now understand that Earth's climate has oscillated on temporal scales spanning many orders of magnitude, from the hundred-million-year timescales of supercontinent cycles to the subtle changes in Earth's orbit around the Sun that paced geologically recent glacial-interglacial climate change. Together, this knowledge not only puts our present-day climate in context but also provides a valuable framing for the interpretation of anthropogenic climate change (Lear et al. 2021). Of central importance to this revolution in the natural sciences have been chemical analyses of biologically formed calcium carbonate shells. In particular, since the mid-20th Century, the chemical and isotopic composition of the shells and skeletons of a diverse range of marine organisms, from tropical corals and edible molluscs through to the tiny, single-celled foraminifera, have provided an enormous wealth of information of Earth's climatic evolution. Using these tools has, for example,

enabled us to reconstruct seasonality deep in the geological past, to determine how polar ice sheets have waxed and waned through time, and perhaps of most crucial societal importance, to benchmark climate model performance and constrain the sensitivity of the Earth and climate system to changes in the concentration of ~~atmospheric~~ CO_2 in the atmosphere~~concentration~~.

Prior to the development of quantitative geochemical approaches, palaeoclimate reconstructions were qualitative and based on comparisons to modern flora and fauna. For example, the occurrence of tropical forests in the Eocene at mid-latitudes was inferred from fossil vegetation assemblages. This changed with the discovery of (stable) isotopes in the 1910s, which led to the pioneering work of Harold Urey on the temperature-dependent fractionation of oxygen-18 relative to oxygen-16 between phases (Urey 1947) and resulted in the development of oxygen isotope thermometry (Urey et al. 1951). This provided the first quantitative tool at our disposal, which was soon followed by the characterisation of the relationship between temperature and the incorporation of elemental impurities such as magnesium into $CaCO_3$ (Chave 1954).

The intervening years have been characterised by the development of a wide range of geochemical (trace) element 'proxy' systems in an ever-increasing number of mineralising organisms across the phylogenetic tree. In large part, this has been driven by technological developments, with the advent of inductively-coupled-plasma optical emission spectroscopy in the 1950s followed by mass spectrometry in the 1980s (ICPMS). Coevally, developments in gas-source mass spectrometers mean that oxygen and carbon isotope measurements are now possible on samples as small as the individual shells of single-celled calcifying plankton, while multi-collector ICPMS instruments have opened up a suite of new stable isotope proxies.

These advances, together with experimental and theoretical evidence of the behaviour of geochemical systems in abiotic ('inorganic') calcium carbonates, soon led to the realisation that virtually all geochemical systems in biological-formed carbonate are out of chemical equilibrium with the ambient seawater environment in which these organisms live. For example, biogenic calcites are characterised by a large degree of variability in terms of their magnesium content, ranging from around 0-20 mol% $MgCO_3$, whereas inorganic calcite precipitated from seawater contains ~8 mol% (see e.g. Branson et al. 2024). Likewise, the existence of heterogeneity in $CaCO_3$ oxygen isotope data beyond that explicable by temperature was known since the inception of the proxy (Urey et al. 1951, see Chen and Watkins, this issue). This variability necessitates at the very least that some of these minerals formed out of equilibrium with seawater, hinting at substantial biological or disequilibrium imprints on shell chemistry. This phenomenon, often assigned the catch-all term 'vital effect', is now known to impart some control on virtually every biomineral based geochemical proxy system, and it is for this reason that the overwhelming majority of proxy systems remain empirical and require the assumption of uniformitarianism (the notion that Earth has always changed in uniform ways and the present is the key to the past).

While such effects may be a nuisance for palaeoclimatologists, vital effects also offer an opportunity: they tell us something about the biological process of calcification. Using the above example, we might infer that an organism such as a coccolithophore (single-celled photosynthesising algae), which produces trace metal pure calcite, either transports calcium into, or magnesium out of, the calcification site, effectively diluting the large amount of Mg present in seawater. Shell geochemistry therefore not only provides a key source of palaeoclimatic information but also offers important insight into how organisms build their shells, of key relevance to understanding their sensitivity to climate change.

GEOCHEMICAL WINDOWS INTO EARTH'S PAST ENVIRONMENTS

The vast wealth of proxies now available prevents us from providing a comprehensive overview here. We therefore focus on four examples that give a sense of the possibilities that await prospective palaeoclimatologists (Fig. 1). In each case we briefly introduce the proxy system and explore how the system differs from thermodynamic expectation.

~~Mg/Ca and~~ Temperature reconstruction using Mg/Ca

The dependency of the Mg/Ca ratio on temperature in the calcitic shells of foraminifera has been utilised in both benthic and planktonic species and applied in all ocean basins on Earth. Deep sea-dwelling species have notably been used to determine temperature change in the deep ocean throughout the late Pleistocene glacial cycles (Elderfield et al.~~,~~ 2012) and across the Cenozoic (Lear et al. 2000), in the former case demonstrating a striking coherence with an entirely independent record of Antarctic temperature change (Fig. 1B). The presence of foraminifera in ocean sediment cores spanning the last ~100 million years thus offers the potential to precisely reconstruct temperature change across geologic timescales. The proxy is rooted in the thermodynamically controlled substitution of Mg for Ca in the calcite crystal lattice, yet the enthalpy of the reaction predicts that this temperature dependency of Mg incorporation should be substantially less sensitive than is commonly observed in biogenic minerals. In addition, most species of foraminifera are characterised by shell Mg/Ca many times lower than inorganic calcite precipitated from seawater. Together, these comparisons (Fig. 1A) strongly suggest that Mg is removed or Ca concentrated at the calcification site, with both processes promoting calcification via the removal of a kinetic inhibitor or increasing saturation state, respectively. While this means that all Mg/Ca-temperature calibrations are empirical, this feature of shell chemistry has been enormously advantageous in that the steeper empirical slope reduces the uncertainty in the resulting palaeoenvironmental reconstructions. The corollary is that determining whether there was an evolving biological control on this aspect of the biomineralisation pathway is key to its accurate application across geologic time.

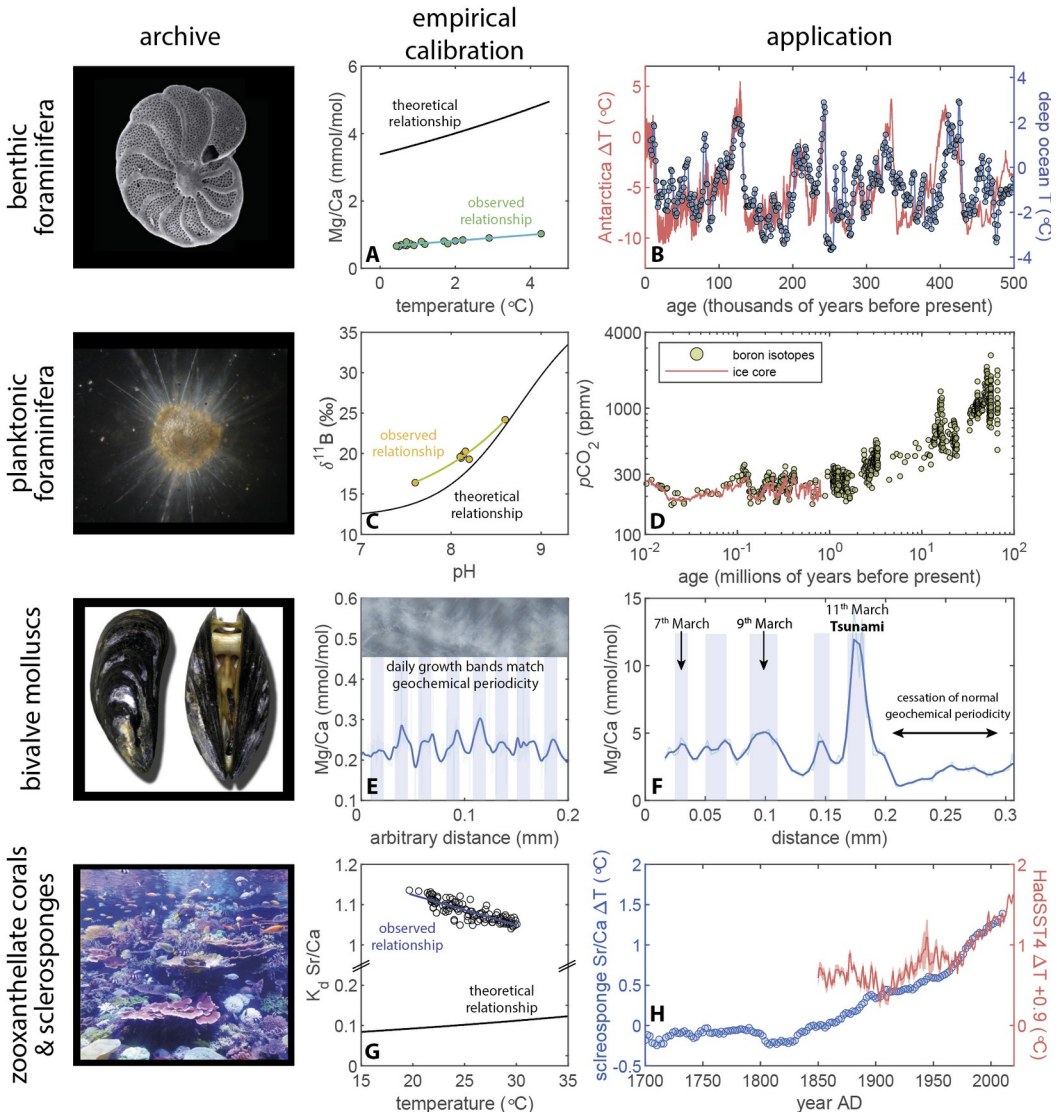

FIGURE 1 Examples of geochemical proxy systems and their application, highlighting the empirical nature of quantification or calibration (note the offsets between the theoretical and observed proxy relationships). (**A**) Mg/Ca-temperature relationship in the shells of benthic foraminifera, applied (**B**) to reconstruct late-Pleistocene deep ocean temperature at ODP Site 1123 (Elderfield et al. 2012), compared to the Antarctic ice core record. (**C**) The relationship between the boron isotopic composition of planktonic foraminifera and pH, applied (**D**) to reconstruct Cenozoic pCO_2 (pH and CO_2 are tightly coupled; Rae et al. 2021), compared to measurements from the composite Antarctic ice core record. (**E**) Daily growth bands visible in some mollusc shells (inset light microscope image) demonstrate daily geochemical periodicity in Mg/Ca (Arndt et al. 2023), applied (**F**) to identify the impact of the 2011 Tōhoku tsunami on mollusc calcification (Sano et al. 2021), note the atypical size of the Mg/Ca peak and subsequent interruption of normal biomineralisation processes as the daily bands disappear. (**G**) The relationship between Sr/Ca and temperature in biogenic aragonite, applied (**H**) to extend the record of anthropogenic climate change beyond the instrumental record (McCulloch et al. 2024); HadSST4 data set (+0.9°C to align the two)), indicating that – at least in the Caribbean – 1.5°C global warming may already have occurred.

Boron Isotopes, Ocean pH, and Atmospheric CO_2

The boron isotopic composition of $CaCO_3$ ($\delta^{11}B$ [defined as the per mil deviation of $^{11}B/^{10}B$ of a given sample from that of reference material NIST SRM 951]; see Chalk and Rollion-Bard, this issue) records the pH of the aqueous solution from which it formed with a well-understood mechanistic basis: two major species of boron are present in seawater (borate and boric acid), with~~and~~ their proportions dependant on pH. Because there is a large difference in the isotopic composition of the two species, and borate is dominantly incorporated into $CaCO_3$, $\delta^{11}B$ of boron trapped in the mineral broadly records pH at the site of mineralisation. The pH of seawater is closely tied to the concentration of CO_2 in the atmosphere (Rae et al. 2021), such that~~o~~ much of our knowledge of past atmospheric CO_2 is derived from $\delta^{11}B$ measured in the sub-millimetre-sized planktonic foraminifera (Fig. 1D; e.g. Rae et al. 2021). The consistency of the $\delta^{11}B$ atmospheric CO_2 reconstructions with direct ice core CO_2 measurements demonstrates the accuracy of the approach (de la Vega et al. 2023). Building on this confidence, the $\delta^{11}B$-CO_2 record now covers most of the geological interval since the extinction of the dinosaurs. Like Mg/Ca-derived palaeotemperatures, these reconstructions are based on empirical calibrations, as most species do not form shells with the $\delta^{11}B$ exactly the same as~~of~~ seawater borate (Fig. 1C). This suggests that foraminifera modify the pH of seawater from which they calcify. In the example shown in FIGURE 1C, this may suggest an elevated calcification site pH, which the organism may effect to aid calcite precipitation. Given that calcification site pH is likely to be sensitive to ambient seawater pH in many cases (this is one key reason that many calcifying organisms are sensitive to ocean acidification), this provides an example of how a proxy system simultaneously tells us something about the biomineralisation process of the organism as well as the environment in which it lived.

Daily Chemical Cyclicity in Growth-Banded Organisms

Daily-resolution geochemical bands are present in many bivalve molluscs, such as giant clams (*Tridacna*) and the edible mussel *Mytilus edulis* (Fig. 1E) which produce continuously secreted layered shells. Laser microsampling of this banding has revealed the presence of daily cyclicity in the concentrations of several trace elements, which are demonstrably physiologically driven given that they are also present in specimens grown under invariant laboratory conditions (Arndt et al. 2023 and references therein). The ability to count geochemical layering means that sub-daily-resolved records of environmental conditions are possible in samples millions of years old. The potential of this information is highlighted by the identification of a known tsunami event in the shell of a mussel (Fig. 1F; Sano et al. 2021), ~~possible because observed textural and geochemical bands can be counted backwards from the day the specimen was sampled~~visible as a stress-induced change in shell chemistry, enabling shell geochemistry to be placed on an absolute chronology. This case study highlights that mollusc shell geochemistry is controlled to a substantial degree by the organism and thus provides an example of a proxy that has its basis in circadian physiological processes which impact ion transport to the calcification site. In the example shown in FIGURE 1F, the tsunami first resulted in a high-Mg/Ca band, which is probably a stress-related response impacting the selectivity of calcium versus magnesium transport (Sano et al. 2021), followed by a cessation of banding as the circadian rhythm of the organism was interrupted.

Placing anthropogenic warming in context using Sr/Ca thermometry

The strontium/calcium ratio (Sr/Ca) of coral and sclerosponge aragonite has been widely applied as a palaeothermometer and has found particular utility in unravelling recent (anthropogenic) climate change because many species produce regular growth bands which can be used to generate an absolute timescale. An example of this is shown in FIGURE 1H (McCulloch et al. 2024), in which sclerosponge Sr/Ca was used to show that substantial global warming occurred prior to the early 20th Century instrumental baseline, such that, at least in the Caribbean, the 1.5°C global warming target may already have been exceeded. Reconstructions such as this are based on empirical Sr/Ca-temperature calibrations, which differ from thermodynamic prediction in both the direction of change and degree of Sr substitution into the lattice (Fig. 1G; Gaetani and Cohen 2006). However, given that inorganic aragonite Sr/Ca similarly does not fit thermodynamic expectation (Gaetani and Cohen 2006), this offset cannot be purely physiologically driven. These observations suggest that the formation of both inorganic and biologic aragonites take place a long way from equilibrium conditions, and are reconcilable with a model centred on the temperature-dependent entrapment and diffusion of ions in the poorly-ordered surface layer of a growing crystal (Watson 2004). This provides an example of an indirect biological control on a proxy system via the creation of conditions at the growing mineral surface which means that kinetic processes dominate, as opposed to the more direct control exerted via, for example, selective ion transport. Indeed, this may be the root cause of many other geochemical offsets that are ~~lumped~~ placed under the umbrella of vital effects.

VITAL EFFECTS

The above examples highlight the wealth of societally and scientifically important insights that geochemical proxies have provided, from CO_2 changes deep in Earth's geologic past to determining the magnitude and onset of anthropogenic warming. In each case, the desired information was derived from empirical calibrations, with the differences between these and thermodynamic predictions or abiotic $CaCO_3$ illuminating some biological processes that alter the chemical composition at the calcification site from that of ambient seawater. For example, preferential inward transport of Ca, or outward transport of Mg (Branson and de Nooijer, this issue) and an elevation of calcification site pH (increasing the $CaCO_3$ saturation state by shifting inorganic carbon speciation from HCO_3^- to CO_3^{2-}) both promote precipitation *and* alter the chemistry of the calcification site. A more comprehensive (albeit non-exhaustive) overview of the range of processes that may contribute to differences between biogenic and abiotic $CaCO_3$ chemistry are introduced in turn below within the context of a schematic model of biomineralisation (Fig. 2). This model and the overlain processes are not intended to represent a specific organism, but rather give an overview of the range of factors that cross disciplinary boundaries, and which could contribute to vital effects.

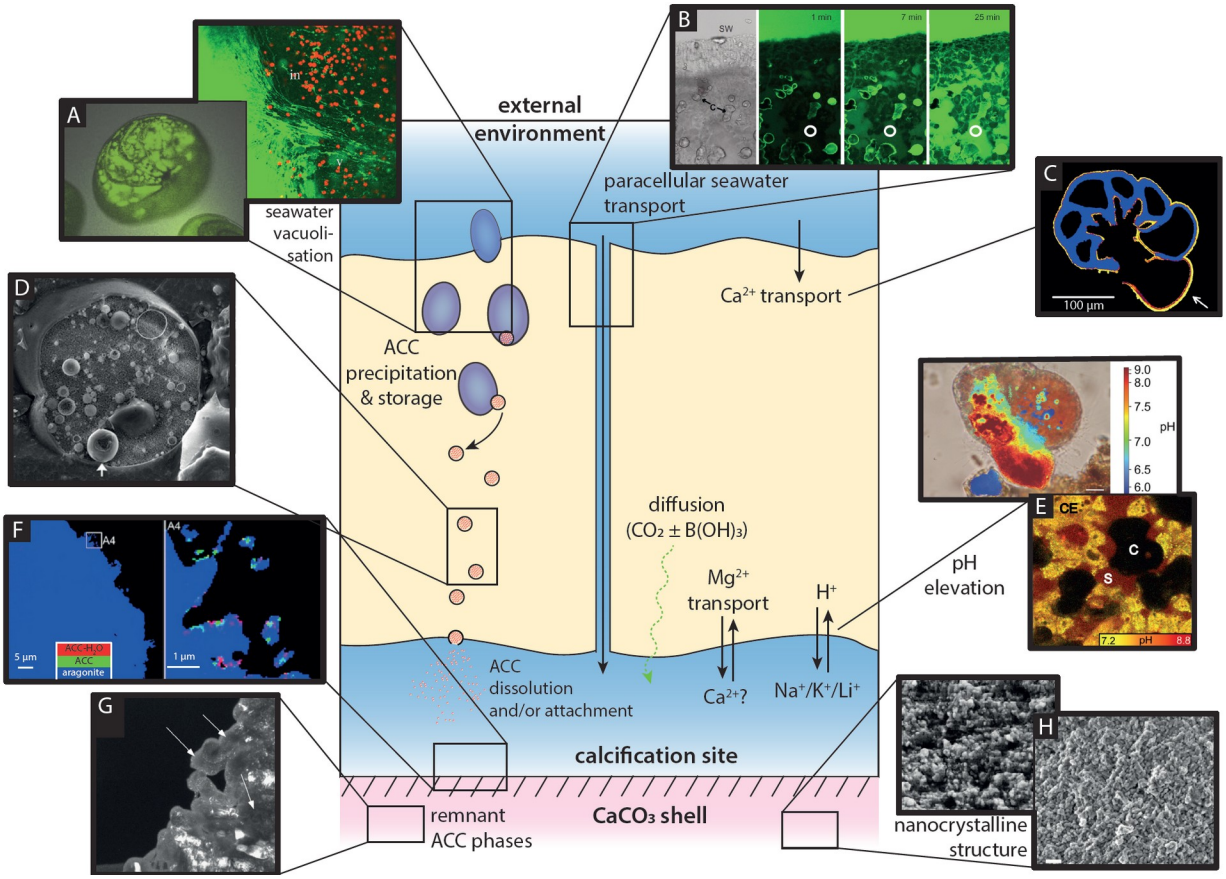

FIGURE 2 Schematic overview of biomineralisation processes that may fractionate the geochemistry of marine carbonate biominerals, with key supporting observations. No specific organism is represented; not all processes depicted here are applicable to all organisms. The ions for biomineralisation may be transported either as packages (vacuoles) of seawater (**A**~~: fluorescent confocal microscope image of calcein-labelled seawater (green colour) ingressing into a high-Mg foraminifera,~~ (Bentov et al. 2009; Evans et al. 2018~~; in = intracellular, v = vacuoles~~); ~~red fluorescence results from symbiont autofluorescence) which may also~~or 'leak' between cells (**B**~~,~~: ~~'paracellular' seawater transport in corals (~~Venn et al. 2020) timelapse fluorescent confocal images show labelled seawater permeating into the organism through time). Images in panels A and B track these processes using fluorescent membrane-impermeable labels placed into the seawater. Alternatively, the ions for calcification may be transported directly into the cell via membrane channels or pumps (**C**: isotope tracer evidence in a low-Mg foraminifer (Nehrke et al. 2013), in which it was shown that transfer of the organism to isotopically labelled seawater immediately before chamber formation resulted in an isotopically-labelled chamber, natural/spike Ca isotope ratio shown in blue and yellow respectively). Calcium (and carbon) may be stored intracellularly as amorphous calcium carbonate (ACC) before it is required (**D**: ACC spheres in sea urchin cells (Vidavsky et al. 2016) imaged using cryo-scanning electron microscopy). At the calcification site, pH may be raised (**E**: as evidenced by fluorescent confocal microscope imaging of pH-sensitive labels in foraminifera and corals (de Nooijer et al. 2009; Venn et al. 2011); CE = calicoblastic epithelium, C = crystal, S = fluid filled space) in order to promote calcification, while calcium may be pumped in and Mg pumped out to achieve the same goal (**D**). In some organisms, delivery or precipitation of ACC to/at the calcification site has been observed (**F**: applying synchrotron photoemission electron microscopy to corals (Sun et al. 2020)) and remnant amorphous phases have been observed in the shell (**G**: darkfield transmission

electron microscopy image of a bivalve (Jacob et al. 2011), with crystalline material shown in white while amorphous material that does not diffract appears dark, see arrows). Finally, the nanogranular shell texture of a diverse range of biogenic carbonates may indicate precipitation via an amorphous phase (**H**: scanning electron microscopy of fractured surfaces of a planktonic foraminifer chamber wall and coral skeleton (Arns et al. 2022; Mor Khalifa et al. 2021; images are ~2 µm in diameter)).

Vital effects exist because calcification in all organisms takes place in a (semi) enclosed space which has a composition that the organism modifies or controls. In many cases, such as in the foraminifera and corals (Erez 2003; Venn et al. 2020), the fluid's original composition in this space has been shown, or argued, to be predominantly that of seawater, although this is probably not always the case, for example in coccolithophores.

Seawater may be transported to the calcification site either via the process of endocytosis, in which vacuoles (packages) of seawater are enclosed by a membrane (Fig. 2A), or by leaking between cells (paracellular transport; Fig. 2B). Both processes have been demonstrated by observing the transport of membrane-impermeable fluorescent molecules to the calcification site (Erez 2003; Venn et al. 2020). In the former case the composition of the seawater may be modified and/or precipitation of $CaCO_3$ may already take place before delivery to the calcification site. This intracellular formation of $CaCO_3$, particularly in an amorphous form that readily facilitates its reuse (Fig. 2C; Jantschke and Scholz, this issue), may be a useful strategy as it enables the rates of ion accumulation and shell or skeleton formation to be decoupled, at which time some organisms might be particularly vulnerable. The formation of an amorphous calcium carbonate (ACC) precursor phase has potentially large ramifications for shell chemistry because ACC has a very different elemental composition compared to crystalline $CaCO_3$ (Evans et al. 2020).

Alternatively, some organisms, such as the coccolithophores and certain species of foraminifera, dominantly acquire the Ca^{2+} necessary for calcification via ion transport, which has been argued for on the basis that some organisms do not incorporate membrane-impermeable dyes, or rapidly acquire the composition of isotopically labelled seawater (Fig. 2D; Nehrke et al. 2013). In this endmember case, the composition of the calcification site will be determined by the selectivity of channels and pumps for Ca over other elements present in seawater and the cytosol (one of the liquids found inside cells).

The chemistry of the calcification site itself may be (further) modified. Outward transport of magnesium favours precipitation as it has a 'poisoning' effect on $CaCO_3$ growth (Stolarski et al., this issue), which may be charge-balanced via the inward delivery of calcium, acting to additionally increase saturation state. Simultaneously, pH elevation, which has been demonstrated in foraminifera and corals (Fig. 2E; de Nooijer et al. 2009; Venn et al. 2011), aids precipitation by increasing the CO_3^{2-}/HCO_3^- ratio and promoting inward CO_2 diffusion (Chen and Watkins, this issue), helping to provide carbon necessary for calcification. These processes influence

trace element thermometers, stable isotope compositions, and boron isotope systematics, as described above.

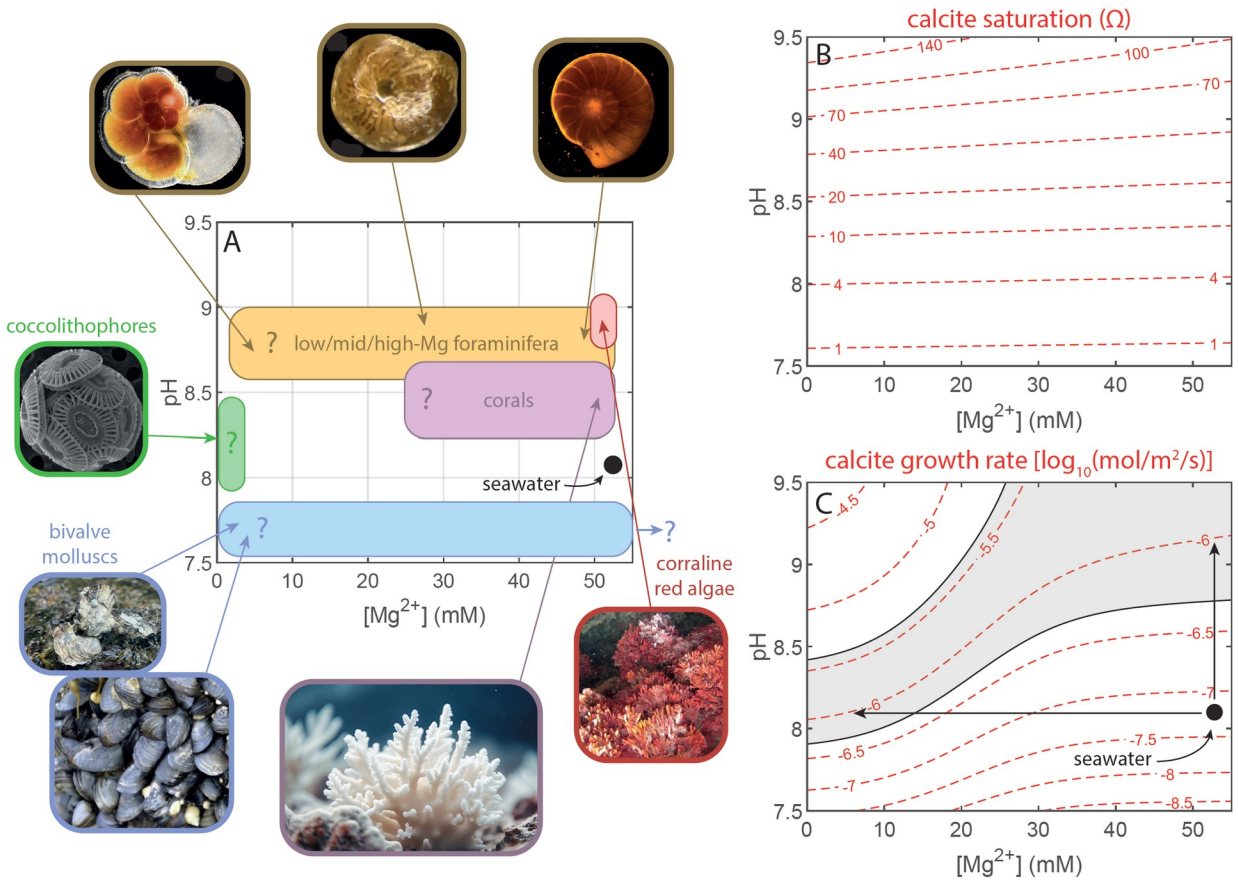

FIGURE 3. An example of two strategies to facilitate calcium carbonate precipitation from seawater: increasing pH (vertical axis) or removing Mg^{2+} (horizontal axis). The former increases the saturation state of seawater by shifting carbon speciation towards CO_3^{2-} and potentially increases the concentration of dissolved inorganic carbon (DIC) by promoting inwards diffusion of CO_2, while the latter reduces the inhibitory effect of Mg^{2+} on $CaCO_3$ crystal growth. (**A**) The possible calcification site conditions of diverse marine calcifying organisms. We stress that this is an indicative guide only, with the location of some fields highly uncertain and inferred in many cases from shell chemistry. (**B**) The impact of pH and $[Mg^{2+}]$ on seawater calcite saturation index (Ω), derived with the ~~PHREEQC~~ geochemical model PHREEQC. To model the effect of pH elevation on CO_2 diffusion, this example calculation covaries pH and DIC (see the supplementary materials for details). Contours of saturation index (dashed) are broadly horizontal because $[Mg^{2+}]$ has little effect on the activities of Ca^{2+} and CO_3^{2-} ~~activities~~. (**C**) The effect of pH/DIC and $[Mg^{2+}]$ on the rate of calcite crystal growth based on empirical growth rate equations (see the supplementary materials). Contours of growth rate (dashed) are sigmoidal in contrast to panel **B** because Mg^{2+} inhibits crystal growth. The shaded region shows estimated growth rates of foraminifera (see Branson et al. 2024 and references therein), ~~shown as an example~~ as ~~an~~ empirical estimate of surface area normalised precipitation rate are~~is~~ available for this organism. Starting from normal seawater, two strategies to increase precipitation rate are apparent (arrows).

Finally, the delivery of ACC in some biomineralising organisms may modify shell/skeletal chemistry either indirectly, by changing the composition of the calcification site if ~~i~~the ACC dissolves, or directly, via attachment to the growing crystal surface (Fig. 2F). Remnant amorphous phases observed in the shells of some organisms (Fig. 2G) and the nanocrystalline structure of many biominerals (Fig. 2H) provide evidence for this. The degree to which this process controls mineral chemistry depends on the transformation mechanism(s), specifically, whether ACC dissolves and reprecipitates as a carbonate mineral or if it reorders in the solid state. To our knowledge, this distinction (or the relative importance of the two paths) remains unknown for any system of interest and is thus a major source of uncertainty in terms of understanding the mechanistic basis of proxy systems.

The above description of biological processes that deliver ions to the calcification site and promote precipitation leads us to the question: *what are the evolutionary benefits of opting one process over another?* To provide one answer and to highlight the applicability of geochemical data to understanding biomineralisation processes, we use the case study of the impact that Mg^{2+} and pH have on $CaCO_3$ precipitation, following Zeebe and Sanyal (2002). Increasing pH shifts carbon speciation towards CO_3^{2-} and therefore increases the $CaCO_3$ saturation state ($\Omega = [Ca^{2+}][CO_3^{2-}]/K^*_{sp}$, where K^*_{sp} is the stochiometric solubility product and square brackets denote concentration), thus facilitating calcification and promoting inwards diffusion of CO_2. In contrast, changing $[Mg^{2+}]$ has a very minor impact on Ω. However, several marine calcifying phyla (e.g. molluscs, some foraminifera, and coccolithophores) produce calcite with Mg/Ca that is so much lower than inorganic calcite that it presumably must imply large degrees of ion transport to lower the calcification site Mg/Ca. The likely reason for this is that the presence of Mg^{2+} in solution inhibits $CaCO_3$ growth because the removal of the Mg^{2+} hydration sphere on attachment is a slow process relative to that of Ca^{2+} (seawater Mg/Ca = ~5). As such, while Mg has little impact on the degree of oversaturation (Fig. 3B), solutions with higher Mg/Ca kinetically favour the precipitation of the more soluble $CaCO_3$ polymorph aragonite, or they lower the rates of calcite precipitation where that polymorph can be engineered. To illustrate this, we show the empirical impact of pH and $[Mg^{2+}]$ on the growth rate of inorganic calcite (Fig. 3C), calculated using growth rate data sets (combining those of Nielsen et al. 2016, and Wolthers et al. 2012). Doing so results in sigmoidal growth rate isopleths (cf. Fig 3B), illustrating that raising the pH by ~1 unit, or removing almost all of the Mg from seawater, increases in calcite precipitation rate by around an order of magnitude in both cases.

This exercise demonstrates that both processes (pH increase and Mg^{2+} removal) greatly aid rapid shell or skeleton formation and are likely to be a key reason for selective ion transport and pH elevation. It is interesting to note that different marine organisms sit in very different regions of this $[Mg^{2+}]$-pH space (Fig. 3A), with some possibly opting exclusively to raise pH or decrease $[Mg^{2+}]$. Given that Mg transport is almost certainly more energetically costly than pH elevation (Zeebe and Sanyal 2002), that some organisms employ this pathway implies that shell precipitation rate is not the only factor ‘being optimised’; e.g. the structural

properties of the resulting biomineral, or modifying Mg/Ca in order to preferentially form calcite over aragonite, may be worth the energetic cost of ion transport.

CONCLUDING REMARKS - A PROBLEM AND AN OPPORTUNITY

Above, we briefly explore the variety of reasons that biological calcification yields a shell or skeleton that differs compositionally in chemical or (and) isotopic ~~composition~~ terms from thermodynamic expectations and (or) abiotic $CaCO_3$. While this complicates proxies, in that no system has a fully understood mechanistic basis, many systems would be far less useful for environmental reconstructions without their biological overprints. For example, Mg^{2+} incorporation in planktonic foraminifera is three times more sensitive to temperature than in inorganic calcite, diurnal geochemical banding would not exist if calcification were not tightly mediated in molluscs (Fig. 1E), and the boron isotopic composition of aragonitic skeletons may simultaneously record calcification site and seawater pH, given that the two are often tightly linked.

Moreover, vital effects afford us the opportunity of simultaneously understanding both biomineralisation processes and past environmental changes. The co-evolution of shell mineralogy and seawater major element chemistry provides insight into the effect that an organism's environment has on its calcification pathway (Stolarski et al., this issue). More broadly, shell geochemistry is a valuable tool to understand biomineralisation processes because the observations are noninvasive given that they can be made on the skeletal material left after the organism has died, although direct observations of biophysical processes are, of course, also essential. The measurement of multiple different chemical systems coupled with an ever-improved understanding of their behaviour in comparative abiotic experiments mean that we stand at a transformative time in the application of shell chemistry to the study of biomineralisation. Given that mechanistically understanding calcification processes is key to improving proxy-derived palaeoenviromental reconstructions by moving these beyond purely empirical approaches, this knowledge will greatly benefit both fields ~~greatly.~~ , which ~~in turn,~~ should be more closely integrated: the copious proxy data that were generated primarily or initially for the purposes of climate research remain largely untapped in constraining biomineralisation processes, for example.

In this issue, the subsequent articles give specific examples of how this may be achieved, while providing overviews and details of the key proxy systems and biomineralisation processes (Fig. 2). Our aim is that this contribution be used as a springboard towards ensuring that geochemical proxies are fully leveraged in informing biomineralisation models, and that direct observations of biomineralisation processes are used to mechanistically understand proxies. Ultimately, both fields will benefit from being more closely connected.

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