

Editorial

The Effect of Ocean Acidification on Skeletal Structures

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It is well known that the increasing partial pressure of atmospheric CO₂ (*p*CO₂) is reducing surface ocean pH, a process known as ocean acidification (OA). This results in a reduced saturation of the seawater with respect to the CaCO₃ polymorphs aragonite, high-Mg calcite, and low-Mg calcite that are involved in the biological formation of calcareous skeletons and shells. The effect of OA on calcium carbonate precipitation and subsequent dissolution in carbonate depositional systems, such as coral reefs, is a hotly debated topic. While early studies suggested that certain carbonate-secreting organism groups may be strongly affected by OA or even become extinct [1,2], others observed highly variable, species-specific responses to OA, whereby some taxa are negatively affected, some are positively affected, and others are unaffected [3–5].

Ries et al. (2009) [5] provided a systematic baseline study on the effect of OA on biological calcification by quantifying rates of calcification for 18 species of marine calcifiers cultured under controlled laboratory conditions that ranged from present-day to predicted year 2500 *p*CO₂ conditions, thus spanning seawater conditions that were highly supersaturated to undersaturated with respect to aragonite and calcite. These results illustrated that the biological calcification response to OA is variable and complex, depending on the species' ability to utilize elevated CO₂ directly via photosynthesis or indirectly via photosymbiosis, on the ability to regulate pH (and thus carbonate chemistry) at the physiological site of calcification [6], on the extent to which the shell or skeleton is protected from dissolution by external organic layers, and on the solubility of the calcium carbonate polymorph incorporated into the shell or skeleton (with aragonite and high-Mg calcite being more soluble than low-Mg calcite).

The relative tolerance of certain photosynthesizing calcifiers to increased CO₂ conditions was also demonstrated, for example, by the work of Vogel et al. (2015) [7] on the bryopsidalean calcareous green algae *Halimeda* growing on a volcanic CO₂ seep in Papua New Guinea at pH conditions down to <7. These *Halimeda* showed increased calcification in the light that compensated for severely reduced calcification in the dark, resulting in the same net calcification rate as specimens outside the influence of the seeps. At the same study site, interspecific differences in coral reef communities were observed in response to natural gradients in CO₂-induced acidification as one moves away from the seeps. Yet, despite the spatial variations in species composition of these coral reef communities, the extent of coral cover remained the same [3]. Similarly, Guillermic et al. (2021) [8] showed that increased CO₂ can lead to increased growth of some species of zooxanthellate corals when those corals are able to continue regulating pH and, thus, carbonate chemistry at their internal site of calcification. This underscores the variability of calcifiers' response to CO₂-induced OA, as well as the complexity of factors controlling these responses.

Although organismal responses to OA are well documented, community- and ecosystem-level impacts of have been less studied. Meta-analyses of organismal physiological responses



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to OA reveal large variability in how intra-organismal interactions (e.g., symbioses) may modulate responses to OA [9]. A growing body of research has also documented that OA alters competitive interactions [10] and favors the expansion of fleshy algae [11], which collectively can simplify ecosystems, reduce functional diversity, and impair ecosystem function.

The combined effects of OA and other environmental factors, such as ocean warming (OW) and food availability, on the capacity of marine calcifiers to precipitate and maintain shell or skeleton have also attracted increased attention over the past decade. Synergistic effects of acidification and warming range from amplifying negative effects to mitigating them [8,12,13]. These studies demonstrate that biomineralization is a process that is not merely controlled by external seawater conditions, but is also strongly influenced by the organism precipitating the skeleton or shell. These studies also emphasize the importance of incorporating other stressors in the marine environment that are likely to accompany OA over the coming centuries, including warming, pollution, eutrophication, and changes in salinity.

This Special Issue builds on this knowledge by presenting some current developments in research on the effects of OA on calcium carbonate producing organisms. The papers assembled here highlight novel methodologies and previously undescribed impacts of OA on calcifying organisms at functional scales ranging from the mineral, to the calcifying fluid, to the whole organism, and from temporal scales spanning the deep geological past to the future.

Although extensive laboratory- and field-based studies have shown that marine calcifiers exhibit highly variable and complex responses to OA, few controlled laboratory experiments have been conducted to evaluate the impacts of CO₂-induced acidification on freshwater calcifiers. Ninokawa and Ries (this issue) [14] address this knowledge gap with a freshwater acidification experiment showing that various common species of freshwater calcifiers, including a species of crayfish, mussel, and two species of clam, exhibit nearly as diverse a range of calcification responses to acidification as observed for marine calcifiers, with response patterns ranging from negative to parabolic. Their experiment also shows that freshwater acidification impairs the feeding rates of crayfish, which likely contributes to their negative calcification response to freshwater acidification by reducing the amount of energy available for their molt-mediated process of shell formation. Notably, similar trends have been observed for marine species of decapod crustacea, including for mud crabs whose rates of feeding [15] and calcification [16] were both impaired under acidified conditions.

Ries and co-authors (this issue) [17] report on a combined acidification and warming experiment on three Indo-Pacific species of scleractinian zooxanthellate corals and one species of asymbiotic cold-water coral. They found that under normal temperatures, calcification rates of all three species of tropical corals increased with increasing $p\text{CO}_2$. However, when exposed to thermal stress that induced partial bleaching of the corals' symbionts, the tropical corals lost their ability to calcify more quickly under elevated $p\text{CO}_2$. Consistent with these observations, the cold-water species that lacks photosymbionts exhibited calcification rates that declined with increasing $p\text{CO}_2$. Notably, all four species of corals exhibited elevated pH at their site of calcification relative to seawater pH, with the offset increasing with $p\text{CO}_2$. However, for the one tropical species whose calcifying fluid pH was measured under both the control and elevated temperature treatments, thermal stress was shown to reduce the extent to which that coral species could elevate its calcifying fluid pH relative to seawater pH, a trend that was accompanied by both reduced symbiont abundance and decreased calcification rate. These results support the growing body of evidence that the temperature-induced loss of photosymbionts (i.e., bleaching) impairs the resilience of scleractinian zooxanthellate corals to the effects of CO₂-induced OA.

Eagle and coauthors (this issue) [18] report on controlled laboratory experiments investigating the complex physiological and calcification responses of four common Caribbean species of scleractinian zooxanthellate corals exposed to acidification and warming. They utilized the carbon and boron isotope composition of the skeletons of these corals to illustrate that dissolved inorganic carbon and coral energy reserves were lower in corals ex-

posed to elevated temperature. They also report that these coral species' ability to regulate calcifying fluid pH in response to acidification was not impacted by thermal stress [8]—which contrasts the responses of Indo-Pacific pocilloporid corals reported in this issue. Collectively, these results suggest that the biological regulation of pH and other carbonate system parameters within the calcifying fluid of corals is energetically more expensive under pH and temperature stress. Although Eagle et al. [18] found that physicochemical control over coral calcifying fluid chemistry is linked to the physiological responses of both the coral host and its photosymbionts, they show that the extent and even direction of these relationships can vary amongst species.

Khalil and coauthors (this issue) [19] investigated the impact of acidification and warming on a species of starfish—an organism that, unlike zooxanthellate corals, cannot directly benefit from increased CO₂ via enhanced photosynthesis or photosymbiosis. They report that the Mg/Ca ratio of the calcite produced by the starfish increased with temperature, but showed no relationship to pCO₂. However, elevated pCO₂ led to potentially negative changes in test structure, with these effects exacerbated under elevated temperature.

Ocean acidification can not only slow the rate of calcium carbonate shell/skeletal formation, but also impair an organism's ability to maintain and repair their shell/skeleton after its initial formation. Bivalves, in particular, engage in extensive shell repair in order to mitigate the effects of boring parasites and predators, such as boring sponges and gastropods, respectively. Although the impact of ocean acidification on bivalve shell production has been extensively explored, the potential impacts of OA on mechanisms of bivalve shell repair are largely unknown. In this issue, George and coauthors [20] show that mussels are able to repair shell damage imposed by boring predators even under acidified conditions, underscoring the high priority that bivalves place on the repair of sublethal shell damage.

Scucchia and coauthors (this issue) [21] present a new artificial-intelligence-based method for assessing the effects of OA on the internal three-dimensional structure of coral skeletons. Numerous prior studies have shown that acidification can impact coral skeletal structure across a range of spatial scales [22–24]. Scucchia and coauthors build upon this work by using synchrotron phase contrast-enhanced microCT (PCE-CT) data combined with artificial intelligence methods (deep learning neural networks) to quantify how ocean acidification impacts the internal skeletal structure of coral recruits. They show, for example, that coral recruits exposed to ambient (i.e., non-acidified) pH conditions have less variability in internal skeletal structure amongst individuals than when they are exposed to acidified conditions.

Over geological timescales, OA has been shown to have impacted marine calcifiers in as wide a range of ways [25] as has been reported for modern-day calcifiers exposed to acidification in controlled laboratory experiments [5]. Pomar and coauthors (this issue) [26] reflect on calcareous biomineralization throughout the last 3.7 Ga of Earth history under highly variable atmospheric and seawater chemistry conditions. They critically evaluate the various hypotheses that have been proposed for the evolution of calcareous biomineralization, including for protection from predation, for structural support, for the regulation of Ca²⁺ concentration, and for the release of protons (via HCO₃[−] → CO₃^{2−} + H⁺) to liberate aqueous CO₂ in support of photosynthesis. They also propose the “Phosphate Extraction Mechanism” as a potential reason for the advent of biocalcification, which addresses the potential role that calcification plays in increasing the efficiency by which photosynthetic prokaryotes and eukaryotes can acquire phosphate in nutrient depleted environments.

The collection of articles presented in this Special Issue reveals the diversity of ongoing research into the effects of CO₂-induced acidification on calcareous biomineralization, while introducing some new questions and provocative hypotheses. Continued investigation of these concepts should advance understanding of the mechanisms of biocalcification and improve predictions of how future CO₂-induced changes in marine and freshwater systems will impact calcifying organisms, as well as the ecosystems they comprise, in the decades and centuries ahead. Although many questions remain unanswered, this

collection of work supports the expanding body of evidence that the biological response to CO₂-induced acidification is more variable and complex than originally thought, requiring a more nuanced approach to exploring this important and fascinating process.

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