



Inorganic carbon fluxes and perturbations by ocean acidification estimated using a data-constrained, process-based model of coral physiology

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Abstract

Recognition that ocean acidification (OA) alters calcification rates in many tropical corals and photosynthetic processes in some has motivated research into coral's carbon processing systems. Here, a multi-compartment coral model is used to assess inorganic carbon fluxes, accounting for carbon uptake, photosynthesis, transport across and between coral tissue and calcification. The increased complexity of this model is enabled by incorporating recent measurements of carbonic anhydrase activity and dissolved inorganic carbon (DIC) related photosynthetic parameters, allowing the model to respond to changes in external inorganic carbon chemistry. The model reproduced measured gross photosynthesis, calcification rates and calcifying fluid pH from *Orbicella faveolata* at current oceanic conditions. Model simulations representing OA conditions showed an increase in net photosynthesis and modest decreases in calcification which fall within trends seen in experimental data. Photosynthesis increased due to higher diffusive influx of CO₂ into the oral tissue layers, increasing DIC where symbiotic algae reside. The model suggests that decreases in calcification result from increased fluxes of CO₂ into the calcifying fluid from the aboral tissue layer and the bulk seawater, lowering its pH and reducing the aragonite saturation state. However, modeled pH drops in the calcifying fluid exceed those observed, pointing to the need for additional empirical constraints on DIC fluxes associated with calcification and coelenteron transport.

Introduction

One of the main impacts of anthropogenic climate change on the ocean is associated with the equilibration of atmospheric CO₂ into surface waters. Adding more of the mild acid CO₂ to the system lowers the pH of surface waters and the concentration of CO₃²⁻, in a process known as ocean acidification (OA) (Feely et al. 2004). These chemical changes are a consequence of the fact that dissolved inorganic carbon (DIC) exists in a pH-dependent equilibrium between CO₂, HCO₃⁻ and CO₃²⁻, in which the addition of

CO₂ leads to a decrease in CO₃²⁻ according to the net reaction $\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^-$.

Organisms that depend on DIC for major biological processes are relatively more affected by the impacts of OA (Riebesell et al. 2000, Cohen and Holcomb 2009). Photosynthesis requires CO₂ as a substrate for carbon fixation. It is common for marine autotrophs to concentrate CO₂ near the site of the enzyme RubisCO to ensure that it is fixed efficiently (Rost et al. 2003, Hopkinson et al. 2011, Reinfelder 2011). These carbon concentrating mechanisms are energetically costly and siphon energy from other internal processes, such as growth (Wu et al. 2010, Mackey et al. 2015). With more CO₂ in the water, there is the potential for a positive benefit to those organisms, less energy must be spent concentrating carbon for photosynthesis and more CO₂ is available to fix, leaving more energy for growth or reproduction (Wu et al. 2010, Mackey et al. 2015, Shi et al. 2017). In contrast to photosynthesis, calcification can be inhibited by OA (Cohen and Holcomb 2009, Hendriks et al. 2010, Kroeker et al. 2013). Calcium carbonate (CaCO₃) is supersaturated in the surface ocean, and the precipitation of calcium carbonate minerals, including calcite and

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aragonite, is energetically favored, facilitating the construction of CaCO_3 shells and skeletons and other hard parts. The addition of CO_2 to the water causes a decline in the saturation state of calcium carbonate minerals. This can lead to malformed shells or skeletons, or their dissolution (Feely et al. 2004, Cohen and Holcomb 2009, Kelly and Hofmann 2013), or require additional energy to maintain calcification (Furla et al. 2000b, Cohen and Holcomb 2009).

Scleractinian corals experience OA impacts to both photosynthesis and calcification. They host dinoflagellates of the family Symbiodiniaceae to provide photosynthetically fixed carbon (Falkowski et al. 1984, Lajeunesse et al. 2018) while secreting aragonite (CaCO_3) skeletons, forming colony structures and in most cases reefs (Cohen and Holcomb 2009, de Putron et al. 2010). Given the importance of coral reefs to marine biodiversity as well as to humans (Woodhead et al. 2019), understanding how corals will be affected by OA is imperative (Langdon and Atkinson 2005). Numerous studies have examined the impact of OA on calcification (de Putron et al. 2010, Hendricks et al. 2010, Chan and Connolly 2013, Kornder et al. 2018, Bove et al. 2020), revealing OA-induced declines in calcification rate, though species-specific responses in magnitude and direction are common (de Putron et al. 2010, Huang et al. 2014, Kornder et al. 2018). The regulation of the calcifying fluid, where mineralization takes place, appears to be critical to the ability of corals to respond to OA (Comeau et al. 2013, 2018, Comeau 2017a, DeCarlo et al. 2018). Long-term studies suggest that the calcifying fluid is under tight, internal biological control by the coral, despite being influenced by seawater pH levels (see below Krief et al. 2010; Comeau et al. 2018, DeCarlo et al. 2018). The mechanisms by which OA reduces calcification rates and calcifying fluid pH are still subject to debate. DIC for calcification may be obtained from respiration or biologically modified transcellular fluxes (Furla et al. 2000b, Tambutte et al. 2011, Allison et al. 2014, Sevilgen et al. 2019). Others have proposed that bulk seawater is transported and merged with existing calcifying fluid without being altered by the holobiont during the transport process. This is done using paracellular pathways or vesicles and employed directly for calcification (Cohen and Holcomb 2009, Tambutte et al. 2011, Gagnon et al. 2012). In both mechanisms, the OA-induced changes to seawater DIC chemistry will cause parallel changes in the calcifying fluid, reducing the pH and hence calcification.

Other studies have examined the effect OA has on photosynthesis of scleractinian corals, with widely varying findings (Langdon and Atkinson 2005, Anthony et al. 2008, Hoadley et al. 2015, Kornder et al. 2018). Langdon and Atkinson (2005) and Comeau et al. (2018) found increases in photosynthetic production under OA conditions, while Anthony et al. (2008) observed declines in production, and Takahashi and Kurihara (2013) and Hoadley et al. (2015)

found no effects of OA on photosynthetic parameters. None of these studies, however, quantified DIC uptake and fluxes associated with photosynthesis, leaving open the question of what is happening internally to cause these observations. Additionally, few studies have assessed the effects of OA on both photosynthesis and calcification in corals simultaneously (Langdon and Atkinson 2005, Takahashi and Kurihara 2013, Comeau et al. 2018), despite the fact that energy generated by the fixed carbon of photosynthesis, in conjunction with heterotrophic feeding, is used to power calcification (Goreau 1959, Furla et al. 2000b, Galli and Solidoro 2018).

In order to maintain both photosynthesis and calcification simultaneously, corals must regulate pH levels and DIC supply within different tissue layers and the calcifying space (Furla et al. 2000b, Tambutte et al. 2011, Bertucci et al. 2013). CO_2 and HCO_3^- fluxes and transport from the surrounding water and coelenteron to the oral endoderm supply the symbionts with the carbon needed for photosynthetic production (Furla et al. 2000a, Tansik et al. 2017). In close spatial proximity, the animal must maintain a high pH in the calcifying fluid so that CO_3^{2-} and HCO_3^- will be available for secretion of the skeleton. DIC can be transported from the seawater or the coelenteron through the tissues via paracellular pathways (Furla et al. 2000b, Tambutte et al. 2011, Venn et al. 2020). High rates of respiration in the aboral tissue layers provide energy for calcification and also produce respiratory DIC, which flows into the calcifying space from the aboral calicoderm, driven by the concentration gradients of CO_2 and HCO_3^- (Goreau 1959, Furla et al. 2000b, Tambutte et al. 2011). The excess protons produced by the conversion to HCO_3^- and CO_3^{2-} are transported out of the calcifying fluid by proton pumps and $\text{Ca}^{2+}/\text{H}^+$ exchange in order for the fluid to remain at a high pH, which increases the CO_3^{2-} concentration (Furla et al. 2000b, Jokiel 2011, Tambutte et al. 2011, Comeau et al. 2017a, Comeau 2017b). The demands from the different tissue layers weave an intricate web of fluxes and active transport throughout the holobiont, which may change depending on external and internal DIC environments (Comeau et al. 2017b). Understanding these interactions and fluxes not only clarifies the physiology of corals in general, but can also be applied to tease apart responses to multiple stressors and generate energy budgets.

One way to examine inorganic carbon fluxes within corals is through process-based models of DIC transport and reactions. Hohn and Merico (2012), for instance, brought together the chemical reactions in the fluid layers and a single tissue compartment to examine the impact of OA on coral calcification. Nakamura et al. (2013) considered the influence of biological activities in the coral polyp's fluid layers, and examined the effect of OA on both calcification and photosynthesis. Galli and Solidoro (2018) focused on biological costs, making energy a central part of their model. Here, we expand on these efforts and present a process-based

model of DIC flows through a coral that synthesizes novel and existing insights on DIC processing (Comeau et al. 2017a, b, Comeau et al. 2018, Tansik et al. 2015, 2017). Accounting for photosynthesis, respiration and calcification, acid–base chemistry and both the active transport and passive diffusion of different chemical DIC species through coral tissue layers, the model also tracks the carbon isotopes ^{12}C and ^{13}C , and considers isotopic fractionation in photosynthesis and calcification. Photosynthesis preferentially fixes ^{12}C , drawing it down in the oral tissues and leaving the remaining DIC isotopically heavy (Swart 1983). In calcification, the balance of ^{13}C -enriched DIC left behind by photosynthesis and the ^{12}C -enriched CO_2 from respiration impacts the incorporation of the isotopes into the skeleton (Swart 1983, McConnaughey 1989), providing information on DIC sources for calcification. Thus, the model results can be compared to observed isotopic signatures of both tissue and biogenic carbonate minerals, using them as a constraint on DIC fluxes.

The detailed process-focused nature of our model creates opportunities for the examination of changes to DIC flux between the different compartments as well as proposed drivers behind OA's effects on production, skeletal deposition and calcifying fluid pH. Essential to this effort is the incorporation of new data on carbonic anhydrase (CA) activity within the coral tissue, which catalyzes the hydration–dehydration interchange reaction between CO_2 and HCO_3^- . While it has been known for many years that corals have CA within their tissues and in the calcifying fluid (Weis et al. 1989, al-Moghrabi et al. 1996, Bertucci et al. 2013), only recently have stable isotope exchange techniques been applied to quantitatively determine CA activity in corals (Hopkinson et al. 2015, Tansik et al. 2015, 2017), improving our understanding of DIC movement within and through a coral by constraining fluxes through the tissues and from the seawater. This model captures processes relevant across a wide range of corals, however, we employ a Caribbean coral, *Orbicella faveolata*, as an example of how it can further our understanding of the potential effects of OA on a coral's physiology.

Materials and methods

Model description

The flux and processing of inorganic carbon and calcium of a scleractinian coral was examined using a box model that represents a vertical transect from seawater through the coenosarc tissues of the coral and into the calcifying space. The five boxes of the model represent the diffusive boundary layer, oral tissue, coelenteron, aboral tissue and the calcifying space (Supplemental Fig. S1). In each

compartment, mass balance for $^{12}\text{CO}_2$, $^{13}\text{CO}_2$, $\text{H}^{12}\text{CO}_3^-$, $\text{H}^{13}\text{CO}_3^-$, $^{12}\text{CO}_3^{2-}$, $^{13}\text{CO}_3^{2-}$, Ca^{2+} , and total alkalinity was expressed as:

$$\frac{dc}{dt} = \frac{(F_{\text{in}} - F_{\text{out}})}{V_j} + \sum R + \sum B$$

where F is the mass exchange of the chemical concentration (c) of each chemical constituent per unit time, V_j is the volume of the compartment j , $\sum R$ represents the net reaction rate due to acid–base reactions and carbonic anhydrase (CA) mediated exchange, and $\sum B$ indicates the net increase or decrease due to biological processes, including photosynthesis, respiration and calcification. Parameters and equations used in the model are detailed in Supplemental Tables 1 and 2. In brief, acid–base reactions were implemented following Zeebe and Wolf-Gladrow (2001). CA activity is incorporated as an independent rate constant that accelerates CO_2 hydration and HCO_3^- dehydration and the magnitude of this rate constant is set based on previous measurements (Hopkinson et al. 2015, Tansik et al. 2017). Photosynthesis by the symbionts was considered in the oral tissue layer and was modeled using Michaelis–Menten kinetics (Tansik et al. 2017). This allows the photosynthetic rate to respond in real time to changes in DIC chemistry. Respiration by the coral animal and the symbionts occurred in the oral tissue layer (Supplemental Fig. S1). The symbionts were, to the greatest extent possible, parameterized as their own unit within the coral, with their own photosynthetic and respiration rates. As the symbiosis is more completely explored, it will be possible to turn the symbionts themselves into another box. Respiration by the animal was accounted for in the aboral tissue layer and was elevated due to the high density of mitochondria relative to the volume (Johnston 1980, Allemand et al. 2004, Tambutte et al. 2007). Calcification occurs in the calcifying fluid (Supplemental Fig. S1). While the importance of the organic matrix in controlling calcification has been noted previously (Clode and Marshall 2003, Tambutte et al. 2011, Von Euw et al. 2017), there is not yet a way to properly parameterize this effect. As a result, calcification in the bottom layer of the model depended only on the aragonite saturation state in the current model (Supplemental Fig. S1). Fluxes between compartments were driven by the concentration gradients between compartments but constrained by membrane permeability. There were additional fluxes of all solutes from the bulk seawater to the calcifying fluid, reflecting the transport of chemicals through the paracellular pathways of the coral, controlled by the permeability of the tissues to bicarbonate (Furla et al. 2000b, Tambutte et al. 2011, Gagnon et al. 2012). An alkalinity pump was included based on the proposed $\text{Ca}^{2+}/\text{H}^+$ exchange transporter (Tambutte et al. 1996, Zoccola et al. 2004) as a way to maintain high alkalinity in the calcifying fluid (Supplemental Fig.

S1). Biologically modified seawater was imported to the coelenteron from surrounding polyps to account for the connectivity of coral colonies (Taylor 1977).

Model parameters were obtained from experimental photosynthetic and DIC processing data, supplemented by literature studies on coral calcification and DIC physiology, using data for *Orbicella faveolata* where available (see Supplemental Table 1 for details). *O. faveolata* is an important Caribbean boulder coral, the physiology of which has been studied extensively. The purpose of focusing on one species was to present an integrated representation of the physiology of a functioning organism, recognizing that there are often necessary functional dependencies between traits that would be missed if ‘average’ coral traits were employed.

Eight parameters were regarded as less well constrained than the others due to a scarcity of data in the literature (1) the alkalinity pump coefficient, (2) CA activity in the calcifying fluid, (3) tissue permeability to HCO_3^- , (4) the gastrovascular-coelenteron exchange coefficient, (5) the HCO_3^- transport coefficient, (6) the partition factor between respiratory DIC and other sources for calcification, (7) the volumetric rate of respiration in the aboral tissue layers, (8) the aboral/calcifying fluid interface tissue permeability to HCO_3^- (see Supplemental Text 1). Values were set based on what little literature was available or estimated and tuned using a parameter sweep as described below.

The model was implemented in MATLAB (MathWorks) and run to steady state. Initial conditions reflected equilibrium concentrations for given external seawater conditions (pH, DIC and Ca^{2+} concentration and temperature). pH values for all internal layers of the coral except the calcifying fluid were imposed based on microelectrode measurements (Cai et al. 2016). To further constrain the description and parameterization of photosynthesis and calcification, the isotopic compositions of the DIC were considered by representing natural ^{12}C and ^{13}C concentrations in all compartments. Tracking carbon isotopes provided a framework to assess ^{13}C incorporation into the skeletal material and therefore fluxes into this compartment.

For the eight most uncertain parameters, model simulations were run for best, high and low parameter estimates employing a factorial design to fully explore the parameter space (see Supplemental Text 1, Supplemental Table S3, and Supplemental Figures S2, S3). Parameter values from the results were compared and those that most closely matched gross photosynthesis, calcification, calcifying fluid pH and $\delta^{13}\text{C}$ isotopes found in the literature were then used for the baseline model run and ocean acidification scenarios (see Supplemental Text 1).

In order to evaluate the impact of ocean acidification on the DIC flow in a coral, external pH and DIC concentration were set to preindustrial values (pH 8.2, 2000 μM DIC), mid-century conditions (pH 8.0, 2100 μM DIC), and end-century

conditions (pH 7.8, 2225 μM DIC) in accordance with the IPCC’s RCP 8.5 scenario (IPCC 2014). No changes were made to the biological parameters of the system.

Results and discussion

The novel model of coral carbon fluxes integrates biological and chemical processes that affect DIC species within coral tissue compartments, providing a comprehensive, quantitative description of carbon flows that support photosynthesis and calcification. It provides a framework for exploring how changes to the external carbonate system affect calcification and photosynthesis and identifying gaps in our understanding of carbon processing in corals.

Major fluxes and metabolic processes

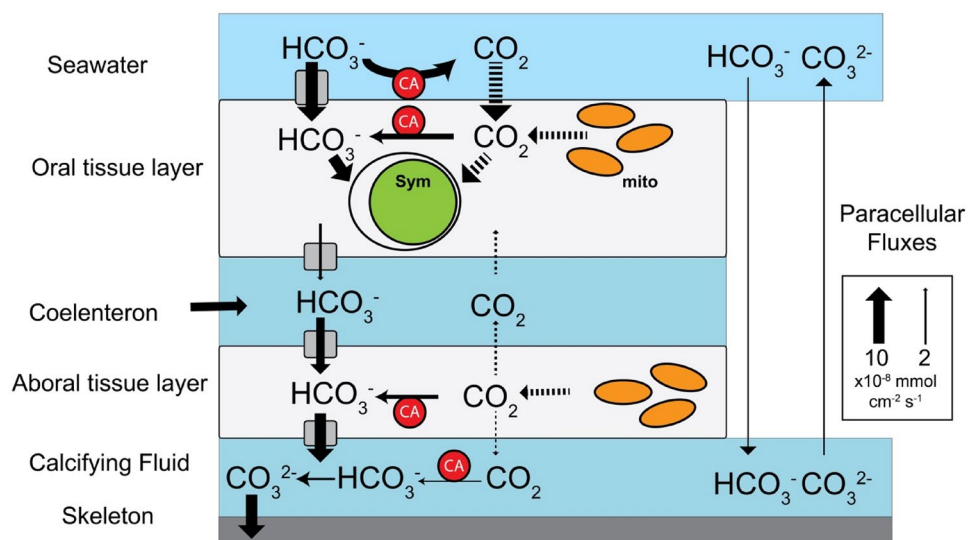
Using quantified CA activity rates and photosynthetic kinetic parameters for *O. faveolata* and parameter constraints from literature where available, our model accurately reproduces several important DIC fluxes, including the observed rates of photosynthesis, calcification, and the C isotope composition of photosynthate ($\delta^{13}\text{C}_\text{P}$) and aragonite ($\delta^{13}\text{C}_\text{G}$, Table 1). In our model, the fluxes of inorganic carbon supporting photosynthesis and calcification are largely decoupled due to exchange with the seawater-like fluid in the gastrovascular cavity through the coelenteron (Fig. 1). Inorganic carbon for photosynthesis is obtained from bulk seawater via active transport of HCO_3^- into the oral tissue layer and diffusive influx of CO_2 . Symbiodiniacea have the capacity to take up both CO_2 and HCO_3^- (Leggat et al. 1999), though the relative proportions vary depending on conditions. In our model, the coelenteron serves as a source of HCO_3^- for calcification but is not important for photosynthetic DIC supply (Fig. 1). Exchange between the oral tissue layer and coelenteron is limited in the model, with the coelenteron serving as a minor CO_2 source for the oral tissue layer and the oral tissue layer supplying a small flux of HCO_3^- to the coelenteron.

In contrast to photosynthesis, the simulations suggest that calcification is primarily utilizing DIC from the gastrovascular cavity and respired CO_2 (Fig. 1). The coelenteron supplies HCO_3^- to the aboral tissue layers, which ultimately supports ~70% of DIC for calcification with the remainder derived from CO_2 produced by respiration in the aboral tissue layer. The coelenteron is replenished through mixing with the gastrovascular cavity, which is assumed to have a fixed chemical composition based on previous measurements (Cai et al. 2016). Radioisotope studies indicate that DIC used in calcification is predominantly of metabolic origin (~70%, Erez 1978, Furla et al. 2000b) rather than seawater derived. Our model was not able to match this high contribution of respiratory DIC to calcification unless

Table 1 Comparison of modeled results to reference literature

	Modeled value	Measured value	Units	Species (location)	Source		
Photosynthesis	3.3×10^{-7}	3.1×10^{-7}	$\text{mmol cm}^{-2} \text{s}^{-1}$	<i>Orbicella faveolata</i> (Florida keys)	Tansik et al. 2017		
		$\sim 5.8 \times 10^{-8}$		<i>Acropora intermedia</i> (GBR Australia)	Anthony et al. 2008		
		$\sim 1.3 \times 10^{-7}$		<i>Porites lobata</i> (GBR Australia)	Anthony et al. 2008		
		5.2×10^{-7}		<i>Siderastrea radians</i> (Florida keys)	Okazaki et al. 2013		
		2.5×10^{-7}		<i>Solenastrea hyades</i> (Florida keys)	Okazaki et al. 2013		
		$\sim 1.4 \times 10^{-7}$		<i>Stylophora pistillata</i> (Israel)	Krueger et al. 2017		
		Calcification		1.0×10^{-7}	1.1×10^{-7}	<i>Orbicella faveolata</i> (Florida keys)	Tansik et al. 2017
2.2×10^{-6}	<i>Orbicella faveolata</i> (Mexico)		Colombo-Pallotta et al. 2010				
1.5×10^{-7}	<i>Siderastrea radians</i> (Florida keys)		Okazaki et al. 2013				
8.5×10^{-8}	<i>Solenastrea hyades</i> (Florida keys)		Okazaki et al. 2013				
2.2×10^{-7}	<i>Porites lutea 1</i> (Fiji/UK)		Allison et al. 2018				
1.1×10^{-7}	<i>Porites lutea 2</i> (Fiji/UK)		Allison et al. 2018				
1.9×10^{-7}	<i>Porites murrayensis</i> (Fiji/UK)		Allison et al. 2018				
1.7×10^{-7}	<i>Porites murrayensis</i> (Fiji/UK)		Allison et al. 2018				
$\sim 8.1 \times 10^{-7}$	<i>Pocillopora damicornis</i> (W. Australia)		Comeau et al. 2018				
$\sim 2.0 \times 10^{-6}$	<i>Acropora youngi</i> (W. Australia)		Comeau et al. 2018				
$\delta^{13}\text{C}_\text{P}$	-10.7		-13		%		Swart et al. 2005
$\delta^{13}\text{C}_\text{G}$	-0.2		-2		%		Swart et al. 2005
pH_CF	9.4		8.4–10				Holcomb et al. 2014, Cai et al. 2016, D’Olivo and McCulloch 2017, Allison et al. 2018, Comeau et al. 2018

Fig. 1 Steady state fluxes in the five box model under normal seawater conditions. The fluxes are represented by arrows between compartments with the direction of the arrow indicating the direction of flow and the width of the arrow proportional to the magnitude of the flux (see scale arrows inside box). Solid arrows indicate active fluxes and dashed arrows indicate passive, diffusive fluxes. The solid arrow directed horizontally into the coelenteron represents fluid exchange between the gastrovascular cavity and the coelenteron



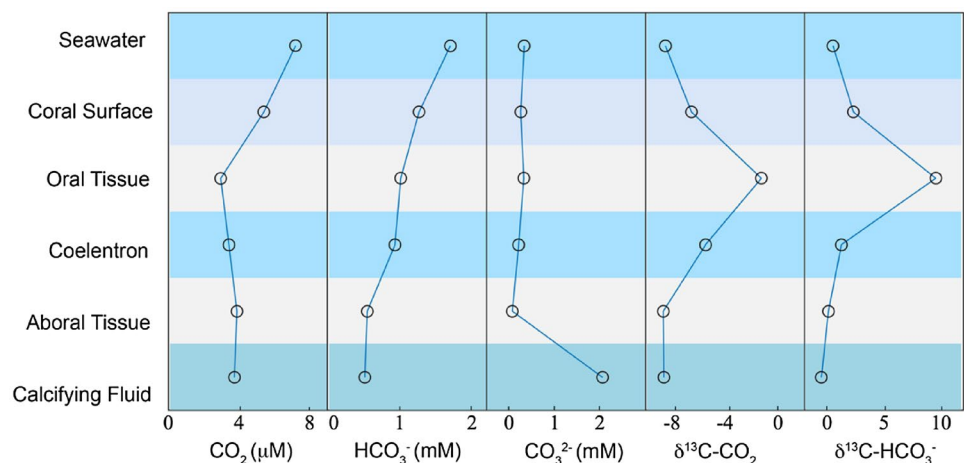
the respiration rate in the aboral tissue layer was increased substantially. The fraction of metabolic DIC used in calcification varies between coral species as a result of variable dependence on heterotrophy (Houlbrèque and Ferrier-Pagès 2009). In the model, the proximate source of DIC for calcification is primarily HCO_3^- transported from the aboral tissue layer into the calcifying fluid (Fig. 1). Contrary to previous suggestions (Cai et al. 2016), direct CO_2 flux into the calcifying fluid is not a substantial source of DIC in our model. Instead, CO_2 respired in the aboral tissue layer is rapidly converted to HCO_3^- by CA (~50%) or lost by diffusive efflux to the coelenteron (~50%). In part, this discrepancy is due to the assumption in Cai et al. (2016) that the DIC system in the calcifying fluid is in chemical equilibrium, resulting in a very low CO_2 concentration in the calcifying fluid which then pulls in CO_2 from the aboral tissue layer. In our model, rapid diffusion of CO_2 across membranes prevents the establishment of chemical equilibrium in the calcifying fluid despite high CA activity in the calcifying fluid converting the CO_2 to HCO_3^- in accordance with the speciation of DIC at high pH. This flux leads to only a small CO_2 concentration gradient between the aboral tissue layer and calcifying fluid in the model and consequently a modest CO_2 flux into the calcifying fluid (Fig. 2). Making direct CO_2 flux a significant DIC source for calcification required nearly eliminating CA activity in the aboral tissue layer of the model, which is contrary to the apparent localization of CA to this layer (Isa and Yamazato 1984, Moya et al. 2008). However, phylogenetic analysis of the CA found in the aboral tissue layer of *S. pistillata* suggests that it may be a membrane bound form facing the calcifying fluid rather than intracellular (Moya et al. 2008). Precise localization of this CA is critical to constraining proximate DIC sources (CO_2 vs HCO_3^-) for calcification. Paracellular fluxes in the model play only a minor role in DIC fluxes for calcification and the net flux of DIC through the paracellular pathway is roughly balanced between an import of HCO_3^- and an export of

CO_3^{2-} in response to the concentration gradients between the seawater and the calcifying fluid. Little is known about the permeability of these paracellular pathways, however, it has been established that the fluxes through them are based on the concentration gradients between the seawater and calcifying fluid (Tambutte et al. 2011, Venn et al. 2020).

Calcification is enabled by delivery of DIC and Ca^{2+} combined with export of protons, working to raise the pH and aragonite saturation state in the calcifying fluid. Measured values of pH in the calcifying fluid range between 8.4–10 and our modeled pH is towards the upper range of these values (Table 1). This high pH is achieved in the model by importing alkalinity to the calcifying fluid, chemically equivalent to an export of protons, which is believed to be the biological basis for elevated calcifying fluid pH (Zoccola et al. 2004, Jokiel 2011). The modeled carbonate ion concentration (~2 mM) exceeds measured concentrations (0.6–1 mM, Cai et al. 2016, Sevilgen et al. 2019) but was necessary to achieve observed calcification rates given our formulation of calcification based on inorganic aragonite precipitation experiments (Burton and Walter 1990). The organic matrix likely promotes high calcification rates at a lower degree of oversaturation, potentially explaining the discrepancy between measured and modeled carbonate concentrations in the calcifying fluid, but there are no quantitative constraints on the magnitude of this effect (Clode and Marshall 2003; Tambutte et al. 2011, von Euw et al. 2017). Similarly, the modeled aragonite saturation state (16.5) exceeds directly measured values (~12.0) (Sevilgen et al. 2019).

Recent work by Sevilgen et al. (2019) agrees with the model on the contribution of metabolic DIC for calcification. However, our model does not incorporate the organic matrix in the calcifying space on CaCO_3 mineralization and the localization of skeletal growth to sites of nucleation as little is known about the processes beyond basic descriptions (Von Euw et al. 2017). Furthermore, the exchange intensity

Fig. 2 Steady state concentrations of CO_2 , HCO_3^- and CO_3^{2-} and isotopic composition ($\delta^{13}\text{C}$) of CO_2 and HCO_3^- in the base model run



between the gastrovascular cavity and coelenteron fluid, which effectively separated DIC flow paths for photosynthesis and calcification, is based on a single observation (Taylor 1977). Refinement of coelenteron exchanges would help constrain the extent of coupling between carbon supply for photosynthesis and calcification. Further descriptions of the calcifying space, transporters and the role that the skeletal organic matrix plays in secreting aragonite are all vital areas for research to improve any model of coral carbon fluxes.

The model also tracks $^{13}\text{C}/^{12}\text{C}$ isotopes, which we used to help constrain the model and to provide insight into isotope cycling which is of biogeochemical and paleo-oceanographic interest (Grottoli 2000, Swart 2015). The model reproduces measured photosynthate isotopic composition ($\delta^{13}\text{C}_\text{P}$) (Table 1). $\delta^{13}\text{C}_\text{P}$ is substantially less than the full fractionation of Form II RubisCO (-20%) (Guy et al. 1993) and is reduced due to the restricted availability of DIC to Symbiodiniacea, manifested as DIC depletion in the oral tissue layer relative to seawater (Fig. 2). $\delta^{13}\text{C}_\text{P}$ is robust with respect to the fraction of CO_2 vs HCO_3^- taken up by Symbiodiniacea, changing by only $\pm 0.3\%$ when the fraction of CO_2 taken up ranges between 20 and 80%. The primary sources of DIC for calcification in the model are HCO_3^- from the coelenteron (1.2%) and respired CO_2 (-15.5%). A simple mixing model suggests that respired CO_2 would need to make up just 20% of the DIC for calcification to match observed values ($\delta^{13}\text{C}_\text{G} \sim -2\%$) (Swart et al. 2005), which seems obtainable given that respiration rates in the aboral tissue are $\sim 60\%$ of the calcification rate and CA in the aboral tissue layer minimizes CO_2 leakage to the coelenteron. However, photosynthetic carbon fixation results in a strong $\delta^{13}\text{C}-\text{CO}_2$ gradient driving the efflux of isotopically light CO_2 from the aboral tissue layer, making it much more difficult to achieve observed values (Fig. 2). As shown in Fig. 3, CA activity manages to recover approximately half the respired CO_2 . Although only $\sim 35\%$ of the CO_2 leaks out into the coelenteron, this leaked CO_2 is extremely

isotopically light (-32%) leaving the residual CO_2 relatively heavy. Although the simulated value of $\sim 0\%$ is heavier than the observed bulk $\delta^{13}\text{C}_\text{G}$ of $\sim -2\%$, our model represents carbon flows during the daytime when photosynthesis drives the internal $\delta^{13}\text{C}-\text{C}_\text{i}$ towards heavier values. Shutting off photosynthesis in the model lightens $\delta^{13}\text{C}_\text{G}$ to -2% illustrating that calcification at night may contribute to the lighter value of bulk $\delta^{13}\text{C}_\text{G}$.

Modeling the impact of ocean acidification on photosynthesis

Ocean acidification to end of century levels led to a nearly 20% increase in gross photosynthetic rate in the model (Fig. 4). Since photosynthetic production is dependent on having CO_2 to fix, increasing the concentration of this DIC species could plausibly lead to an increase in photosynthesis as the ocean acidifies. In our model, higher external CO_2 concentrations did drive an increased flux of CO_2 into the oral tissue layers where symbiotic algae reside, leading to higher rates of photosynthesis (Fig. 5). While this is in agreement with some longer-term studies (Langdon and Atkinson 2005, Bisc  re et al. 2019), there have also been reports of lower rates under OA (Anthony et al. 2008), or no change (Kroeker et al. 2013, Takahashi and Kurihara 2013, Hoadley et al. 2015, Comeau et al. 2016). Variation among taxa in the ability to regulate internal DIC conditions may be responsible for the observed differences. It has previously been suggested that carbon may be the limiting factor controlling coral growth (Marubini and Thake 1999, Herfort et al. 2008) and photosynthesis (Lesser et al. 1994, Goiran et al. 1996, Tansik et al. 2017). Since CO_2 diffusion is a passive process, it appears from the model that OA could induce CO_2 influxes of such magnitude that they overwhelm the host coral’s DIC control mechanisms and stimulate algal

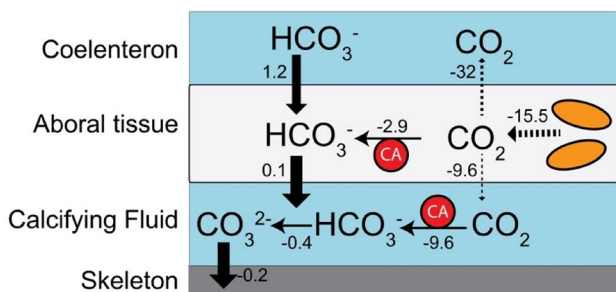


Fig. 3 $\delta^{13}\text{C}$ isotopic composition of major fluxes relevant to calcification. Arrows representing fluxes are proportional to flux rates and $\delta^{13}\text{C}$ isotopic composition of the fluxes are indicated next to the arrows. Note that only the major fluxes are shown in the figure so mass balance is not completely achieved with the fluxes shown

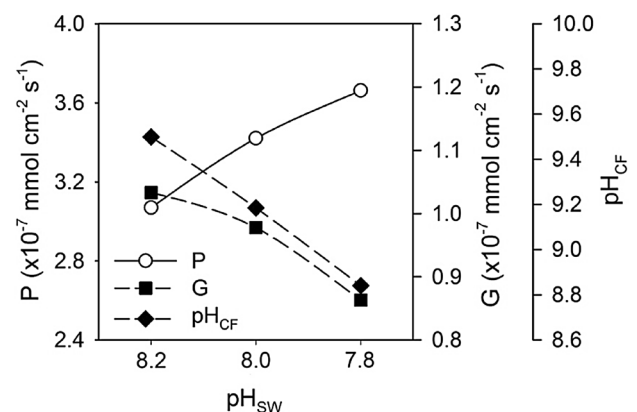
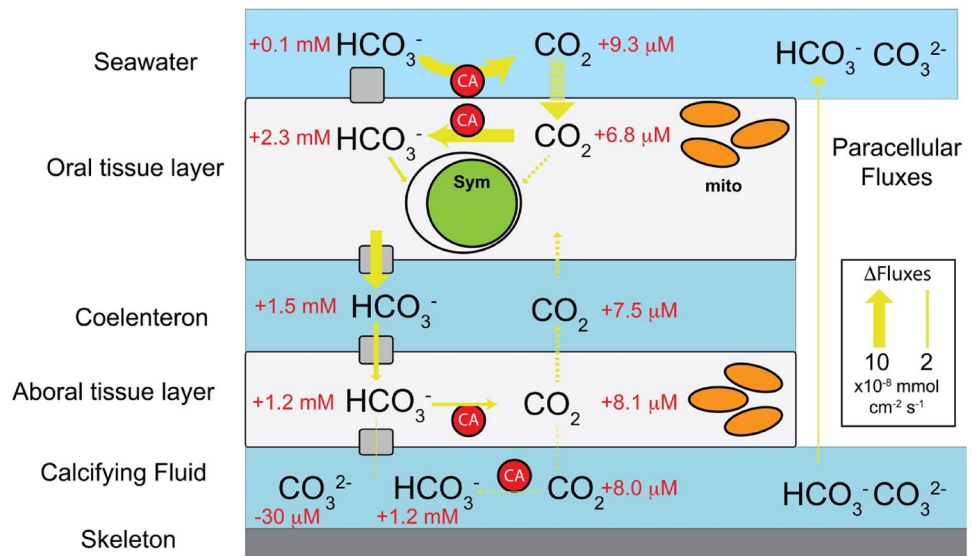


Fig. 4 Effect of OA scenarios (indicated by pH of the seawater) on photosynthesis (P), calcification (G) and pH of the calcifying fluid (pH_{CF})

Fig. 5 Changes to the steady state fluxes and concentrations in the model from normal seawater conditions to end-century seawater conditions. The flux changes are represented by arrows between compartments with the width of the arrow proportional to the magnitude of the change in flux (see scale arrows inside box). Changes in flows less than $1 \times 10^{-8} \text{ mmol cm}^{-2} \text{ s}^{-1}$ are not shown. Solid arrows indicate active fluxes and dashed arrows indicate passive, diffusive fluxes. Concentration changes are indicated next to each chemical species



photosynthesis. Without carbon limitation, growth and production thus may increase in nutrient-replete conditions, leading to a shift from mutualism to parasitism (Dubinsky and Jokiel 1994; Marubini and Thake 1999; Morris et al. 2019). Another possibility is that corals will upregulate their DIC controls, controlling symbiont abundance by limiting carbon (and other resources) needed for growth and reproduction. However, in the absence of detailed knowledge on the mechanisms of DIC regulation, this was not incorporated into the model.

Photosynthetic productivity is important for corals, as most of their energy is derived from the translocation of fixed carbon from their Symbiodiniaceae symbionts, supplemented with heterotrophic feeding (Falkowski et al. 1984). Changing oceanic conditions, especially increasing sea surface temperatures, put stress on both host and symbiont, this can disrupt photosynthate transfer, negatively impact the energy budget of the coral and cause the expulsion of the symbionts from their host (coral bleaching) (Anthony et al. 2009; Hughes et al. 2010; Morris et al. 2019; Rådecker et al. 2021). Levas et al. (2018) showed that some Caribbean corals can survive and recover from a mild bleaching event without loss of their energy stores, our modeled coral was one of them. However, an increase in the frequency of bleaching events will shift coral energy budgets away from a reliance on autotrophic carbon and towards net heterotrophy (IPCC 2014, Levas et al. 2016). There are indications that some corals, including *O. faveolata*, cannot support their carbon needs via heterotrophy when exposed to annual bleaching events (Levas et al. 2016). This reinforces the importance that autotrophic carbon plays in the energy budgets of these corals. It remains to be seen whether an increase in productivity, as seen in the model, combined with potential savings from the downregulation of carbon

concentrating processes, can produce enough fixed carbon to maintain metabolic processes and calcification despite increased bleaching frequency (Levas et al. 2016). Upregulation of pH in the calcifying fluid is not excessively energetically demanding (McCulloch et al. 2012), and so many corals are able to maintain the high pH in the calcifying fluid under OA. This suggests that, at least under some circumstances, corals may be able to maintain growth and calcification under OA conditions.

Modeling the impact of ocean acidification on calcification

Although there is variability among species (Kornder et al. 2018, Bove et al. 2020), some corals calcify at slower rates under OA, which may either be due to decreased seawater CO_3^{2-} concentration or synchronous decline of calcifying fluid pH with seawater pH (Schneider and Erez 2006, Jury et al. 2010, Comeau et al. 2017b). The simulations run here showed a decline in calcification with decreasing seawater pH, in line with some experiments (Langdon and Atkinson 2005, Okazaki et al. 2017) and one of the previous models (Hohn and Merico 2012). With a calcification rate decrease from the baseline in both the mid-century (-5.35%) and end-century runs (-16.46%), our results are within the range of experimental data across the same pH range (Marubini et al. 2008, Chan and Connolly 2013, Huang et al. 2014, Kornder et al. 2018, Bove et al. 2020), or some that include temperature manipulations as well (Kroeker et al. 2013, Okazaki et al. 2017). Though the impact modeled here is small, any reduction in calcification rate has the potential to be important, as growth must keep up with rates of erosion and sea level rise to maintain the reef structure in the surface waters (Silbiger et al. 2014, DeCarlo et al. 2015, Enochs

et al. 2015). Some corals are able to maintain constant linear extension rates by reducing skeletal density, though this makes the skeleton weak and more susceptible to breakage (Tambutte et al. 2015, Mollica et al. 2018).

In our model, the decline in calcification is attributed to a reduction in calcifying fluid pH. Of interest is that the rate of calcification decreased less than the corresponding decreases in calcifying fluid pH would suggest based on experimental results (Holcomb et al. 2014, Comeau et al. 2017a, Okazaki et al. 2017). Reductions in calcifying fluid pH were -0.31 and -0.66 pH units, under mid and end-century conditions respectively, but calcification rate declined by only 5 and 16% (Fig. 4). For comparison, Holcomb et al. (2014) found calcifying fluid pH decreases as small as 0.2 units could be associated with 35% declines in calcification rates in *Stylophora pistillata*. These differences indicate that the modeled calcification rate is less sensitive than calcifying fluid pH to the changes predicted under acidified conditions. However, this result is not without precedent. Comeau et al. (2017a) saw greater declines in the calcifying fluid pH in *Pocillopora damicornis* with no significant change in the calcification rate. They attributed this in part to slower growing corals being less sensitive to declines in seawater pH than fast growing corals due to a lower rate of proton flux (Comeau et al. 2017a). This is unlikely to be the process behind the observed trends here, however, as the calcifying fluid pH was maintained by a large proton flux.

Bove et al. (2020) showed that corals in the Caribbean show less of a response to OA than corals from other ocean basins. However, Okazaki et al. (2017) found *O. faveolata* calcification decreased by approximately a third in an end-century experiment, which would suggest that we should have seen greater declines than we did. They also had low saturation states for their treatments (Okazaki et al. 2017). In our model, although OA results in reduced calcifying fluid pH, the total concentration of DIC in the calcifying fluid increased (Fig. 5). A lower pH shifts the speciation of DIC in the calcifying fluid toward HCO_3^- and CO_2 , and away from CO_3^{2-} . The increased concentration of DIC meant that only modest declines in carbonate concentrations were seen, allowing calcification rates to remain relatively high. Even though the pH in the calcifying fluid dropped, there still remained sufficiently high aragonite saturation states to favor calcification, though less so than under non-OA conditions.

We probed the model to identify the mechanisms by which OA decreases calcifying fluid pH, using previously proposed hypotheses as a guide. The first hypothesis is that increases in seawater CO_2 will result in greater flux of this mild acid through the tissues into the calcifying fluid leading to reduced pH (Furla et al. 2000b, Sevilgen et al. 2019). This would be visible in the model results as a higher flux of DIC from the aboral tissue layer to the calcifying fluid. The second hypothesis, that of bulk seawater transport without

biological changes to the DIC (Cohen and Holcomb 2009), would be visible in the results as a larger flux from the bulk seawater to the calcifying fluid. In our model, the fluxes from the aboral tissue layer were an order of magnitude larger than those from the bulk seawater (Fig. 1). This implies that biologically mediated fluxes dominate the determination of calcifying fluid pH. In the OA simulations, the flux of CO_2 from the aboral tissue layer to the calcifying fluid increased substantially with decreasing external pH, to near double and triple the original flux under the mid and end-century scenarios, respectively (Fig. 5). The total flux of HCO_3^- to the calcifying fluid was still much greater than that of CO_2 in the model, however, the former declined with lower seawater pH as the HCO_3^- concentration in the calcifying fluid increased. This leads to a decreased HCO_3^- concentration gradient between the calcifying fluid and seawater, consequently decreasing the HCO_3^- flux into the calcifying fluid (Fig. 5). Based on the baseline fluxes and the changes to them, our model results are in line with the first hypothesis for how calcifying fluid pH declines, that of biologically mediated fluxes. This is in agreement with one of the previous models (Hohn and Merico 2012).

Future directions

Environmental pressures such as OA can stimulate acclimation of corals to altered conditions (Barkley et al. 2017), and OA is commonly coinciding with increased sea surface temperatures (Anthony et al. 2008) and/or eutrophication (Langdon and Atkinson 2005). These factors are not considered here, though the model framework may allow for those effects if the data for appropriate model parameterization is available. There is, for example, evidence for the downregulation of the CA found in the calcifying fluid of *Stylophora pistillata* with decreasing external pH (Zoccola et al. 2016). In contrast, acclimation in the photosynthetic DIC kinetics, such as an increased half-saturation constant (Wu et al. 2010, Shi et al. 2015), which has been seen in other marine primary producers has not yet experimentally been determined in corals. Increasing ion pumping from the calcifying fluid, as another example, could also be a way for corals to counteract the detrimental effects of OA on calcification (Jokiel 2011, McCulloch et al. 2012, Ohno et al. 2017, Griffiths et al. 2019). Determining the activity of such transporters would lead to a more accurate parameterization of the calcification dynamics of corals.

A number of studies have suggested that the active transport of carbon, protons and other ions can mediate the effects of declining calcifying fluid pH (McCulloch et al. 2012, Ohno et al. 2017, Griffiths et al. 2019). Our model suggests that active transport of DIC from the seawater and metabolic sources may well be a pathway of acclimation and/or adaptation, compensating for the decreases in HCO_3^- fluxes. Such

transport would further elevate the DIC concentration in the calcifying fluid and, in conjunction with an increase in ion transport (Jokiel 2011, McCulloch et al 2012, Ohno et al. 2017, Griffiths et al. 2019), support higher rates of calcification than expected without biological control.

Conclusions

Our process-based and spatially resolved model of coral metabolism accurately reproduces rates of primary production and calcification, and produces $\delta^{13}\text{C}$ values for photosynthesis and calcification similar to measured fractionations (Table 1). It shows that photosynthesis and calcification have disparate sources of DIC with photosynthesis being supported by DIC from seawater and calcification supported by metabolic CO_2 as well as DIC from the coelenteron. Our simulations show declines in calcification and calcifying fluid pH driven by increased CO_2 flux into the calcifying space. The potential to mitigate these impacts is suggested through increased photosynthetic production, creating a larger amount of energy available to the coral. However, the difficulty of the model in matching aragonite $\delta^{13}\text{C}$ values implies that more work is needed on the underlying biological and chemical processing of DIC for coral calcification, and exchange between polyps through the coelenteron. This will clarify how coral reef growth responds to a changing climate.

Data availability and material

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00227-021-03926-8>.

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Author contributions Model conceptualization: ALT, BMH, model development: CM, ALT, model runs and analysis: ALT, BMH, CM, manuscript writing and revision: ALT, BMH, CM.

Declarations

Conflicts of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Ethical approval No approval of research ethics committees was required to accomplish the goals of this study because it was solely computer-based.

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