

Coral resilience to ocean acidification and global warming through pH up-regulation

James L Falter


Nature Climate Change

Cite this paper

Downloaded from [Academia.edu](#) 

[Get the citation in MLA, APA, or Chicago styles](#)

Related papers

[Download a PDF Pack](#) of the best related papers 



[Buffer capacity, ecosystem feedbacks, and seawater chemistry under global change](#)

Christopher Jury

[Coral calcifying fluid pH dictates response to ocean acidification](#)

Denis Allemand

[Measuring gross and net calcification of a reef coral under ocean acidification conditions: methodolo...](#)

Maoz Fine

Coral resilience to ocean acidification and global warming through pH up-regulation

Malcolm McCulloch^{1,2*}, Jim Falter^{1,2}, Julie Trotter¹ and Paolo Montagna^{3,4,5}

Rapidly rising levels of atmospheric CO₂ are not only causing ocean warming, but also lowering seawater pH hence the carbonate saturation state of the oceans, on which many marine organisms depend to calcify their skeletons^{1,2}. Using boron isotope systematics³, we show how scleractinian corals up-regulate pH at their site of calcification such that internal changes are approximately one-half of those in ambient seawater. This species-dependent pH-buffering capacity enables aragonitic corals to raise the saturation state of their calcifying medium, thereby increasing calcification rates at little additional energy cost. Using a model of pH regulation combined with abiotic calcification, we show that the enhanced kinetics of calcification owing to higher temperatures has the potential to counter the effects of ocean acidification. Up-regulation of pH, however, is not ubiquitous among calcifying organisms; those lacking this ability are likely to undergo severe declines in calcification as CO₂ levels increase. The capacity to up-regulate pH is thus central to the resilience of calcifiers to ocean acidification, although the fate of zooxanthellate corals ultimately depends on the ability of both the photosymbionts and coral host to adapt to rapidly increasing ocean temperatures⁴.

The response of calcifying organisms to the accelerating effects of declining seawater pH and increasing ocean temperatures is still poorly constrained⁵. Some studies^{2,6} of warm-water zooxanthellae-bearing corals show a high degree of sensitivity to declining seawater pH. This has led to predictions of major reductions in coral calcification at atmospheric CO₂ levels (p_{CO_2}) of $\sim 450 \mu\text{atm}$ (ref. 7) and, with the additional effects of global warming, the demise of coral reefs at $\sim 560 \mu\text{atm}$ (ref. 8). However, other studies^{2,9–11} indicate a much lower range of coral sensitivities and thus predict less dramatic changes in calcification rates over the probable range of future p_{CO_2} scenarios. Uncertainties in the response of biogenic calcifiers to the combined effects of climate change and ocean acidification arise, not only from inherent limitations in experiments attempting to simulate the impacts of high p_{CO_2} , but also from the lack of a well-constrained physiologically based understanding of the links between calcification, seawater carbonate chemistry and rapidly changing thermal regimes. Here we present a new approach that effectively quantifies the response of calcification in corals and some other key biogenic calcifiers to ocean acidification and rising ocean temperatures, assuming that they are able to continue to operate within their thermal tolerance⁴.

Biogenic calcification occurs within a physiologically controlled environment^{12–14}, with scleractinian corals precipitating their calcium carbonate (CaCO₃) skeleton from an extracellular calcifying

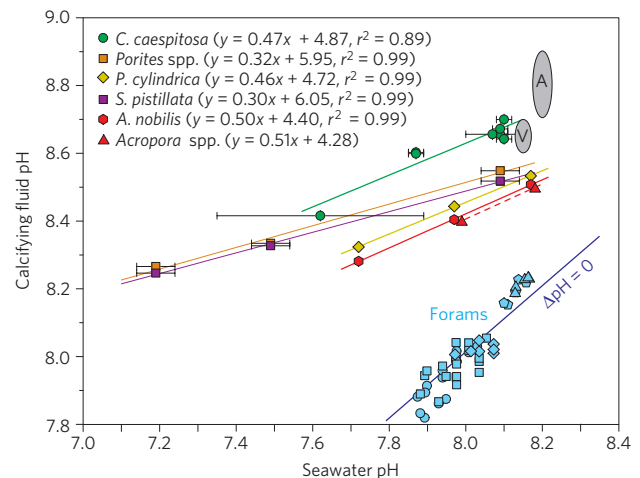


Figure 1 | Plot of pH_T relative to pH_{cf} , determined from boron isotope systematics³ (see Supplementary Information) of aragonitic corals and calcitic foraminifera¹⁷. At pH_T of 8.1, the temperate coral *Cladocora caespitosa* exhibits the greatest increase in pH_{cf} with $\Delta\text{pH} \sim 0.5$ ($\Delta\text{pH} = \text{pH}_{cf} - \text{pH}_T$), whereas the tropical corals *Porites* spp., *P. cylindrica*, *Stylophora pistillata*, *Acropora* spp. and *A. nobilis* have lower $\Delta\text{pH} \sim 0.3$ to ~ 0.4 (ref. 3). In contrast, the calcitic foraminifera¹⁷ (shown in blue) lie on or near the abiotic line with $\Delta\text{pH} \sim 0$. Ellipses show pH_{cf} values measured over daily cycles using microelectrodes (A; ref. 12) and pH-sensitive dyes (V; ref. 15), broadly consistent with the longer duration (weeks to month) represented by boron measurements.

fluid located in the semi-isolated space^{12–14} between the skeleton and the calciblastic ectoderm. During active calcification, the pH of the calcifying fluid (pH_{cf}) is often increased^{12,15} relative to ambient (that is, external) seawater pH, resulting in the equilibrium composition of dissolved inorganic carbon (DIC) being shifted in favour of CO_3^{2-} relative to HCO_3^- , thus promoting the reaction $\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$. Using boron isotope systematics, it has recently been shown³ (Fig. 1) that corals systematically increase their pH_{cf} over a wide range of seawater pH following highly correlated ($r^2 = 0.99$) linear arrays, which are approximately sub-parallel for different species. Thus, at a typical seawater pH of ~ 8.1 (total scale: pH_T), the pH_{cf} of aragonitic corals shows a species-dependent range from 8.4 to 8.7 (Fig. 1), representing a systematic increase in pH_{cf} relative to ambient sea water (ΔpH) of ~ 0.3 – 0.6 units.

¹The UWA Oceans Institute and School of Earth and Environment, University of Western Australia, Crawley, Western Australia 6009, Australia, ²ARC Centre of Excellence for Coral Reef Studies, University of Western Australia, Crawley, Western Australia 6009, Australia, ³Laboratoire des Sciences du Climat et de l'Environnement, Av. de la Terrasse, 91198, Gif-sur-Yvette, France, ⁴Institute of Marine Sciences, Bologna 40129, Italy, ⁵Lamont Doherty Earth Observatory of Columbia University, 61 Route 9W, Palisades, New York 10964, USA. *e-mail: malcolm.mcculloch@uwa.edu.au.

The validity of the boron-derived estimates of pH_{cf} (Fig. 1) is supported by the albeit still limited *in situ* measurements of pH from within the calcifying medium of live coral polyps, using microelectrodes^{12,16} and more recently with pH-sensitive dyes¹⁵. These studies indicate enhanced pH_{cf} by ~ 0.6 – 1.2 (and possibly up to 2) pH units above sea water during the daytime, when both net production and calcification are highest. These results are broadly consistent with the boron isotope systematics (see Supplementary Information) that represent the pH_{cf} integrated over at least several weeks of the calcification process. Collectively these studies indicate that pH_{cf} up-regulation is a highly resilient trait that occurs across a number of coral species, implying an inherent commonality in the physiological controls on aragonite calcification. A notable exception, however, are some species of calcitic foraminifera that have pH_{cf} similar to ambient seawater¹⁷ pH (Fig. 1), indicating that pH up-regulation is both variable in its magnitude and not universal to all marine calcifiers.

Constraining the biologically controlled pH_{cf} and, importantly, its relationship to changing external seawater pH, is profound. The calcification rates inherently attainable by different calcifying species can now be effectively quantified over a wide range of seawater conditions. To achieve this we use the well-known concept of biologically induced calcification¹⁸, where the carbonate saturation state at the site of calcification is mainly biologically controlled through the active transport of Ca^{2+} , DIC and H^+ , together with mineral precipitation rates governed by abiotic kinetics. Our approach of combining internal pH regulation of the calcifying fluid with abiotic calcification (IpHRAC model) thus enables carbonate mineral precipitation rates, G , to be quantified as a function of both seawater saturation state and temperature, where the calcification rate¹⁹ is given by: $G = k(\Omega_{\text{cf}} - 1)^n$, where k is the rate law constant, Ω_{cf} is the saturation state of the calcifying fluid and n is the order of the reaction, for which the coefficients are temperature dependent (see Methods). In contrast to previous studies^{2,8}, we use the biologically mediated Ω_{cf} value rather than the seawater value. We therefore assume that seawater-derived ions are transported to the site of calcification in the subcalicoblastic layer and its chemistry is modulated by active transport of metabolic carbon and H^+ to facilitate increased rates of precipitation.

Although there are still some uncertainties about the physiological mechanisms controlling calcification¹⁴, our IpHRAC model provides a quantitative framework against which the contrasting experimental data on calcification sensitivities can now be evaluated (Fig. 2). Our IpHRAC model identifies two distinct classes of response: first, those that exhibit a low-sensitivity response consistent with strong pH_{cf} up-regulation; and second, those showing a higher sensitivity to ocean acidification, which we attribute to an inability to up-regulate pH_{cf} , resulting in a response that closely matches abiotic rates (Fig. 2). The key reason for the lower sensitivity response of coral calcification to declining seawater pH is that pH up-regulation of the calcifying fluid results in significantly increased internal saturation states²⁰, with Ω_{cf} of ~ 25 to ~ 15 despite seawater pH_{T} decreasing from ~ 8.1 to 7.6 (Fig. 3a). This is also consistent with studies²¹ that indicate a much lower pH threshold at which corals can continue to maintain calcification. In contrast, over the same range in seawater pH_{T} , the high-sensitivity abiotic response reflects the large relative change in saturation state from $\Omega \sim 4$ to ~ 1 , the lower value being the critical limit for undersaturation and thus a strong determinant of calcification rate as Ω_{cf} approaches unity.

A key question is whether the energy requirement to increase pH_{cf} is also likely to be a critical factor in limiting rates of calcification. Biological manipulation of pH_{cf} is mainly undertaken by Ca-ATPase-driven antiporters that pump H^+ ions from the site of calcification in exchange for Ca^{2+} ions^{12,13}. The free energy¹⁶ needed to maintain this pH gradient is given by: $\Delta G_{\text{H}^+} = 2.3RT\Delta\text{pH}$, where ΔpH is the difference

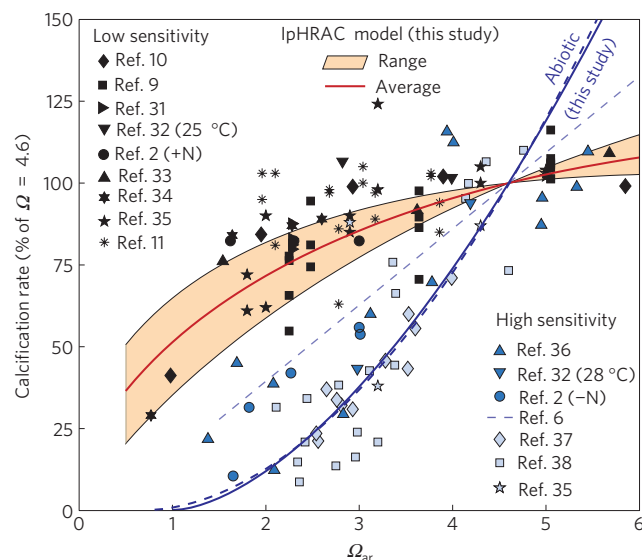


Figure 2 | Percentage change in calcification rates (relative to seawater $\Omega = 4.6$) plotted against seawater aragonite saturation state (Ω_{ar}). The IpHRAC model is compatible with the low-sensitivity coral data (black symbols). The sensitivity of abiotic aragonite precipitation (solid dark blue line) and high magnesium calcite precipitation (dashed dark blue line) represents the absence of pH up-regulation, consistent with the high-sensitivity response of some corals (blue symbols) and calcareous algae (light blue symbols) to ocean acidification. The '+N' and '-N' data represent the nutrient-increased and ambient communities, respectively².

between pH_{cf} and seawater pH_{T} , R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the temperature in Kelvin. For a typical ΔpH value of ~ 0.5 (Fig. 1), the free-energy change (ΔG_{H^+}) required to maintain the pH gradient is $\sim 3 \text{ kJ mol}^{-1}$ of H^+ transported, or roughly 3 – 6 kJ mol^{-1} of CaCO_3 precipitated, depending on whether the metabolic carbon supporting calcification is supplied in the form of CO_2 or HCO_3^- (see Methods). For example, a relatively large decrease in seawater pH_{T} from 8.1 to 7.7 would increase ΔpH to 0.7 units and would thus require an additional 1 – 2 kJ mol^{-1} of CaCO_3 precipitated. Although being a large relative change, it is insignificant when considering the total energy produced by photosynthesis ($\sim 475 \text{ kJ mol}^{-1} \text{ C}$, see Methods) and that rates of calcification are generally around one-third²² of gross primary production. So for zooxanthellae-bearing corals, the extra energy required to up-regulate pH is minor, only $<1\%$ of that generated by photosynthesis. Although it is only a relatively small proportion of the overall photosynthetically supplied energy, this is nevertheless essential for controlling physiological pH_{cf} , which further emphasizes the importance of maintaining the zooxanthellae–coral symbiosis for sustaining calcification.

The higher rates of coral calcification, production and respiration when exposed to light compared with the dark^{22,23} also indicate that calcification may be dependent on the rate of carbon supply needed to build organic templates, as well as to increase DIC_{cf} at the site of calcification. This concept is consistent with numerous studies showing that calcification is generally correlated with net photosynthesis and both occur at rates of similar magnitude on a per-mole-carbon basis^{22,23}. This further implies that higher p_{CO_2} could stimulate higher rates of zooxanthellae production, which in turn may drive higher rates of coral calcification through increasing internal DIC_{cf} and Ω_{cf} . Other factors, such as nutrients and feeding mechanisms, also play a role in the energetics of calcification, but it seems that pH up-regulation is the most critical factor determining the inherent sensitivity of calcifiers to ocean acidification.

The effects of ocean acidification on coral calcification can now be quantified using our IpHRAC model over a wide range of CO_2 scenarios. Here we consider the low p_{CO_2} conditions ($\sim 180 \mu\text{atm}$) of the Last Glacial Maximum (LGM) through to the pre-industrial period ($p_{\text{CO}_2} \sim 280 \mu\text{atm}$) and future Intergovernmental Panel on Climate Change (IPCC) A1FI year 2100 scenario ($p_{\text{CO}_2} \sim 1,000 \mu\text{atm}$). When considering the response of calcification to only ocean acidification (that is, constant temperature; Fig. 3b), the corals represented here exhibit a relatively narrow range of moderate to low sensitivities. The most sensitive is *Acropora nobilis*, which shows a decrease in calcification by $\sim 12\%$ during the LGM to pre-industrial levels, with a further $\sim 35\%$ decrease in calcification predicted from the present day to the very high p_{CO_2} levels predicted in the year 2100 by the A1FI scenario. The least sensitive are *Stylophora pistillata* and *Porites* spp., which operate at a lower gradient of ~ 0.32 for pH_{cf} relative to seawater pH (Fig. 1) and therefore show smaller decreases in calcification by only $\sim 5\%$ from the LGM to present and $\sim 15\%$ from the present day to 2100 in the A1FI scenario. Although still significant, these declines are approximately half of those based on changes in seawater saturation state.

It is also necessary to incorporate the effects of ocean warming on rates of calcification. This is most clearly evident for the LGM to late Holocene epoch, a time period characterized by warming of the planet and a concomitant expansion of tropical coral reefs. Using the experimentally determined temperature dependency of rate kinetics on calcification¹⁹ together with a simplified dependence of global warming on p_{CO_2} (see Methods), our IpHRAC model now predicts a $\sim 15\%$ increase in calcification rates from the LGM to late Holocene. This is consistent with the expansion of tropical reef habitats that occurred during this time despite p_{CO_2} increasing. Notably, the LGM to late Holocene warming occurred over a period of $\sim 10,000$ yr (that is, from $\sim 18,000$ yr BP to $\sim 8,000$ yr BP), whereas our present-day greenhouse-induced warming is occurring within 100–200 yr, thus nearly two orders of magnitude faster. This rate of anthropogenic-induced CO_2 warming is probably unprecedented and raises the crucial question of whether coral ecosystems, or more specifically the zooxanthellae photosymbionts and their coral hosts, have the ability to adapt or acclimate on such short timescales. The response of biogenic mineral precipitation to increasing temperature is therefore ultimately dictated by the limits of coral physiology to acclimate or adapt to rising temperatures rather than rate kinetics alone. This is best demonstrated by the bell-shaped (Gaussian) response of coral calcification rates with increasing temperature^{24,25}, indicating that calcification is subject to optimum temperature thresholds, such as those for coral bleaching, beyond which it rapidly declines.

With this caveat, we also model the future response of coral reefs to both global warming with mean tropical sea surface temperatures (SSTs) of $\sim 2^\circ\text{C}$ higher (see Methods) and a future scenario with p_{CO_2} increasing from present-day levels to $\sim 1,000 \mu\text{atm}$ by the year 2100 (IPCC A1FI). For this scenario, our IpHRAC model predicts either unchanged or only minimal effects on calcification rates. For example, in the case of *Stylophora pistillata* and *Porites* spp., a modest increase in calcification is predicted by the year 2100, thus the enhanced kinetics from increasing SSTs more than compensates for reduced calcification from declining seawater saturation state. This is also consistent with recent findings for long-lived *Porites* corals from Western Australia²⁶. From a strictly chemical and kinetic perspective, our IpHRAC model therefore indicates that ocean acidification combined with rising ocean temperatures should have only minimal effects on coral calcification, a direct outcome of their ability to up-regulate pH at the site of calcification. We caution, however, that our IpHRAC approach specifically addresses only the effect of rising temperature on aragonite precipitation kinetics. The inherent ability of different coral species and their symbionts to thermally

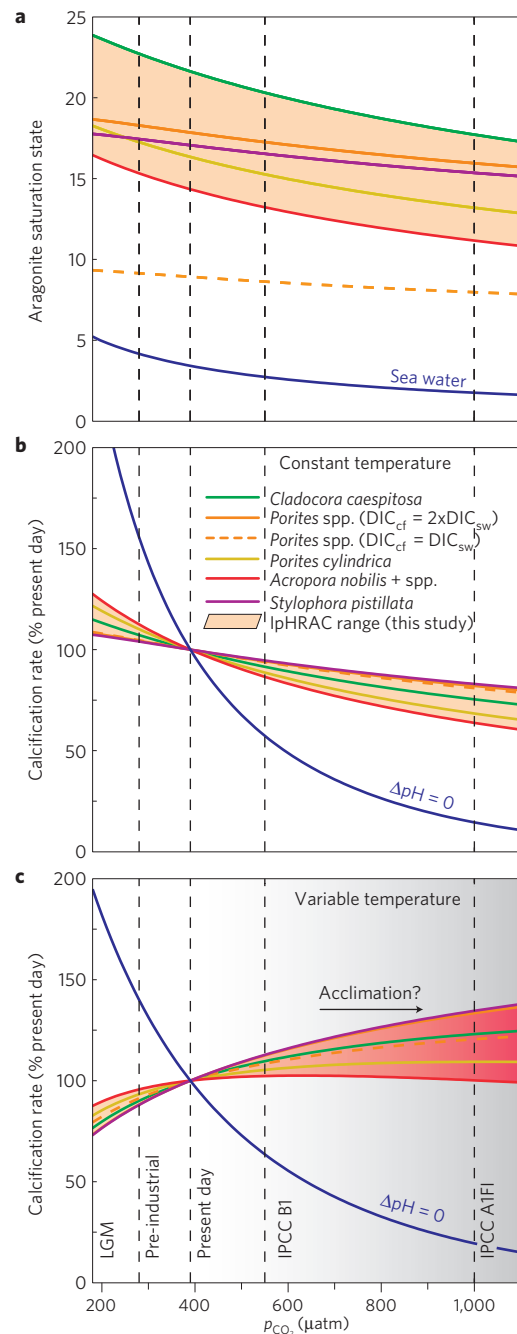


Figure 3 | Future and historical projections of changes in internal saturation state and % changes in coral calcification rates. **a**, Aragonite saturation state of the calcifying fluid and of sea water versus p_{CO_2} for IPCC A1FI projections of levels to the year 2100. Calculations based on pH_{cf} up-regulation for coral species from Fig. 1, assuming $\text{DIC}_{\text{cf}} = 2 \times \text{DIC}_{\text{sw}}$ (solid lines) and $\text{DIC}_{\text{cf}} = \text{DIC}_{\text{sw}}$ (dashed). **b**, Relative changes in calcification rates versus p_{CO_2} for constant temperatures calculated using the IpHRAC model for tropical and temperate corals. The line $\Delta\text{pH} = 0$ represents rates of abiotic aragonite precipitation at seawater pH and DIC. **c**, As for **b** but also incorporating the effects of increasing temperature on the rate kinetics of calcification. Marine calcifiers with the ability to up-regulate pH have the potential to maintain approximately constant or enhanced (that is, within $\pm 10\%$) calcification rates even at high p_{CO_2} , depending on their ability to adapt to higher temperatures from rapid climate change (shaded zone). Calcifiers lacking the ability to regulate internal pH_{cf} will follow the seawater trajectory and therefore suffer major reductions in skeletal formation.

adapt as temperatures increase under a rapidly changing climate⁴ thus remains to be the critical unknown parameter that limits quantitative predictions on the future of coral reefs. We also emphasize that calcifying organisms with minimal or no ability to regulate their pH will suffer substantial decreases in skeletal growth rates as p_{CO_2} continues to increase and seawater pH decreases. This is supported by observations²⁷ that some calcitic foraminifera have already suffered severe declines since the LGM, consistent with the rapid decline of non-regulating species predicted by our model for abiotic calcification (Fig. 3b,c). Although our results indicate that up-regulation of pH at the site of calcification provides corals with enhanced resilience to the effects of ocean acidification, the overall health of coral reef systems is still largely dependent on the compounding effects of increasing thermal stress from global warming and local environmental impacts²⁸, such as terrestrial runoff, pollution and overfishing.

Methods

The effect of internal pH regulation on the rate of coral calcification is modelled using an empirical exponential rate dependence law for carbonate precipitation¹⁹:

$$G = k(\Omega_{\text{cf}} - 1)^n$$

with the following temperature-dependence for aragonite precipitation¹⁹:

$$k_a = -0.0177T^2 + 1.47T + 14.9$$

$$n_a = 0.0628T + 0.0985$$

and for calcite precipitation¹⁹ by:

$$k_c = 0.0153T^2 - 0.968T + 18.4 \quad \text{for } T < 25^\circ\text{C}$$

and

$$k_c = -0.0167T + 4.32 \quad \text{for } T \geq 25^\circ\text{C}$$

$$n_c = 0.0543T + 0.387$$

Ω_{cf} is the saturation state of calcite or aragonite at the site of calcification and defined as:

$$\Omega_1 = [\text{Ca}^{2+}]_{\text{cf}}[\text{CO}_3^{2-}]_{\text{cf}}/K'_{\text{spx}}$$

where $[\text{Ca}^{2+}]_{\text{cf}}$ and $[\text{CO}_3^{2-}]_{\text{cf}}$ are the concentrations of dissolved calcium and carbonate ions at the site of calcification and K'_{spx} is the solubility constant for aragonite (K'_{spa}) and calcite (K'_{spc}).

Our IpHRAC model calculations assume that $\text{DIC}_{\text{cf}} = 2 \times \text{DIC}_{\text{sw}}$ and $[\text{Ca}^{2+}]_{\text{cf}} = [\text{Ca}^{2+}]_{\text{sw}} + 0.5$ (mmol kg^{-1}), where sw refers to values for sea water. For tropical waters, ambient seawater pH is calculated at temperatures of 25 °C, salinity of 35 and corresponding total alkalinity of 2,300 $\mu\text{eq kg}^{-1}$. A present-day temperature of 25 °C is used for all tropical corals and forams, whereas 20 °C is used for the Mediterranean coral *C. caespitosa*. For corals living in Mediterranean waters, both $[\text{Ca}^{2+}]_{\text{sw}}$ (11.2 mmol kg^{-1}) and total alkalinity (2,600 $\mu\text{eq kg}^{-1}$) are adjusted upwards in proportion to the higher salinity of 38. The internal pH for various coral species were then calculated as a function of seawater pH based on the relationships determined from their boron isotope systematics (Fig. 1; ref. 3). Finally, Ω_{cf} was calculated from the increased pH_{cf} , DIC_{cf} and $[\text{Ca}^{2+}]_{\text{cf}}$ using CO2SYS v1.1 and thus is enhanced five- to tenfold relative to the seawater aragonite saturation state.

For the constant-temperature simulations, temperatures were held constant at present-day values as described above. For the variable-temperature simulations, temperature was modelled using a global warming response of the form:

$$\Delta T_{\text{SST}} = S[\ln(p_{\text{CO}_2}/390)/\ln 2]$$

where: S is a climate scaling factor of $\sim 1.5^\circ\text{C}$, which is a conservative estimate of the climate sensitivity of tropical SSTs to increasing atmospheric p_{CO_2} . For the LGM ($\sim 20,000$ yr ago), early Holocene, pre-industrial (1850), present day and the year 2100 under the IPCC SRES B1 and A1FI scenarios, we assume p_{CO_2} levels of 180, 280, 390, 550 and 1,000 μatm respectively and tropical SST increases of $\sim 1.6^\circ\text{C}$ from the LGM to present and $\sim 2^\circ\text{C}$ from the present day to the A1FI scenario in 2100.

The free energy needed to maintain the extracellular pH gradient (ΔG_{H^+}) is given by:

$$\Delta G_{\text{H}^+} = RT \ln\left(\frac{[\text{H}^+]_{\text{sw}}}{[\text{H}^+]_{\text{cf}}}\right), \quad \text{or}$$

$$\Delta G_{\text{H}^+} = 2.3RT \Delta \text{pH}$$

For a typical value of $\Delta \text{pH} \sim 0.5$ (Fig. 1), the free-energy change needed to maintain the pH gradient between pH_{cf} and pH_{T} is $\Delta G_{\text{H}^+} \sim 3 \text{ kJ mol}^{-1} \text{H}^+$ transported. For metabolic carbon provided in the form of bicarbonate, the coral would need to pump only 1 $\text{H}^+ \text{mol}^{-1} \text{CaCO}_3$, but in the form of respired CO_2 the coral would need to pump out 2 $\text{H}^+ \text{mol}^{-1} \text{CaCO}_3$ precipitated. Thus, for a major decrease in seawater pH of 0.4 units for example, with pH up-regulation, ΔpH would increase by only ~ 0.2 units to $\Delta \text{pH} \sim 0.7$ (Fig. 1), thus requiring $\sim 4\text{--}8 \text{ kJ mol}^{-1}$ of H^+ .

The free energy (ΔG_{R}) available from aerobic respiration per mole of photosynthetically fixed carbon is given by:

$$\Delta G_{\text{R}} = \Delta G_{\text{R}}^0 + RT \ln\left(\frac{f_{\text{CO}_2}}{f_{\text{O}_2} \{ \text{CH}_2\text{O} \}}\right)$$

where ΔG_{R}^0 ($-480 \text{ kJ mol C}^{-1}$) is the free-energy yield for aerobic respiration at standard temperature and pressure, f_{O_2} and f_{CO_2} are the fugacities of oxygen and carbon dioxide and $\{ \text{CH}_2\text{O} \}$ is the cellular concentration of photosynthate ($\sim 0.5 \text{ mM}$; ref. 29). This corresponds to a net energy release of 475 kJ mol^{-1} of carbon fixed. Given a ratio of calcification to gross primary production of one-third^{22,30}, based on maximum rates of net production, respiration, and calcification, measured under conditions of natural diurnal light, corals need to expel 0.3–0.6 $\text{mol H}^+ \text{mol}^{-1} \text{C}$ fixed by photosynthesis, depending on whether the metabolic carbon supporting calcification is supplied in the form of CO_2 or HCO_3^- . Although this is a thermodynamic simplification, with the total energy costs of ion transport being the sum to cross each of the epithelial layers for which both active and passive transport steps are involved, nevertheless, the energy required for pH up-regulation is still relatively minor, being $< 1\%$ of that being supplied by photosynthesis.

Received 2 November 2011; accepted 5 March 2012;
published online 1 April 2012

References

- Kleypas, J. *et al.* Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* **284**, 118–120 (1999).
- Langdon, C. & Atkinson, M. J. Effect of elevated p_{CO_2} on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J. Geophys. Res.* **110**, C09S07 (2005).
- Trotter, J. A. *et al.* Quantifying the pH 'vital effect' in the temperate zooxanthellate coral *Cladocora caespitosa*: Validation of the boron seawater pH proxy. *Earth Planet. Sci. Lett.* **303**, 163–173 (2011).
- Howells, E. J. *et al.* Coral thermal tolerance shaped by local adaptation of photosymbionts. *Nature Clim. Change* **2**, 116–120 (2012).
- Pandolfi, J. M., Connolly, S. R., Marshall, D. J. & Cohen, A. L. Projecting coral reef futures under global warming and ocean acidification. *Science* **333**, 418–422 (2011).
- Schneider, K. & Erez, J. The effect of carbonate chemistry on calcification and photosynthesis in the hermatypic coral *Acropora eurystroma*. *Limnol. Oceanogr.* **51**, 1284–1293 (2006).
- Hoegh-Guldberg, O. *et al.* Coral reefs under rapid climate change and ocean acidification. *Science* **318**, 1737–1742 (2007).
- Silverman, J., Lazar, B., Cao, L., Caldeira, K. & Erez, J. Coral reefs may start dissolving when atmospheric CO_2 doubles. *Geophys. Res. Lett.* **36**, 1–5 (2009).
- Marubini, F., Barnett, H., Langdon, C. & Atkinson, M. J. Dependence of calcification on light and carbonate ion concentration for the hermatypic coral *Porites compressa*. *Mar. Ecol. Prog. Ser.* **220**, 153–162 (2001).
- Gattuso, J. P., Frankignoulle, M., Bourge, I. & Romaine, S. Effect of calcium carbonate saturation of seawater on coral calcification. *Glob. Planet. Change* **18**, 37–46 (1998).
- Rodolfo-Metalpa, R., Martin, S., Ferrier-Pages, C. & Gattuso, J. P. Response of the temperate coral *Cladocora caespitosa* to mid- and long-term exposure to p_{CO_2} and temperature levels projected for the year 2100 AD. *Biogeosciences* **7**, 289–300 (2010).
- Al-Horani, F. A., Al-Moghrabi, S. M. & de Beer, D. The mechanism of calcification and its relation to photosynthesis and respiration in the scleractinian coral *Galaxea fascicularis*. *Mar. Biol.* **142**, 419–426 (2003).
- Cohen, A. L. & McConnaughey, T. A. in *Biomining* (eds Dove, P. M., Weiner, S. & de Yoreo, J. J.) Ch. 6, 151–187 (Reviews in Mineralogy & Geochemistry, Vol. 54, Mineralogical Society of America, 2003).
- Allemand, D., Tambutté, E., Zoccola, D. & Tambutté, S. in *Coral Reefs: An Ecosystem in Transition* Vol. III (eds Dubinsky, Z. & Stambler, N.) 119–150 (Springer, 2011).
- Venn, A., Tambutté, E., Holcomb, M., Allemand, D. & Tambutté, S. Live tissue imaging shows reef corals elevate pH under their calcifying tissue relative to seawater. *PLoS ONE* **6**, e20013 (2011).
- Ries, J. B. A physicochemical framework for interpreting the biological calcification response to CO_2 -induced ocean acidification. *Geochim. Cosmochim. Acta* **75**, 4053–4064 (2011).

17. Rae, J. W. B., Foster, G. L., Schmidt, D. N. & Elliott, T. Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system. *Earth Planet. Sci. Lett.* **302**, 403–413 (2011).
18. Lowenstam, H. A. & Weiner, S. *On Biomineralization* (Oxford Univ. Press, 1989).
19. Burton, E. A. & Walter, L. M. Relative precipitation rates of aragonite and Mg calcite from seawater: Temperature or carbonate ion control? *Geology* **15**, 111–114 (1977).
20. Holcomb, M., Cohen, A. L., Gabitov, R. I. & Hutter, J. L. Compositional and morphological features of aragonite precipitated experimentally from seawater and biogenically by corals. *Geochim. Cosmochim. Acta* **73**, 4166–4179 (2009).
21. Fine, M. & Tchernov, D. Scleractinian coral species survive and recover from decalcification. *Science* **315**, 1811 (2007).
22. Gattuso, J.-P., Allemand, D. & Frankignoulle, M. Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: A review on interactions and control by carbonate chemistry. *Am. Zool.* **39**, 160–183 (1999).
23. Schneider, K., Levy, O., Dubinsky, Z. & Erez, J. *In situ* diel cycles of photosynthesis and calcification in hermatypic corals. *Limnol. Oceanogr.* **54**, 1995–2002 (2009).
24. Jokiel, P. & Coles, S. Effects of temperature on the mortality and growth of Hawaiian reef corals. *Mar. Biol.* **43**, 201–208 (1977).
25. Marshall, A. T. & Clode, P. Calcification rate and the effect of temperature in a zooxanthellate and azooxanthellate scleractinian reef coral. *Coral Reefs* **23**, 218–224 (2004).
26. Cooper, T. F., O'Leary, R. & Lough, J. M. Growth of Western Australian corals in the anthropocene. *Science* **335**, 593–596 (2012).
27. Moy, A. D., Howard, W. R., Bray, S. G. & Trull, T. W. Reduced calcification in modern Southern Ocean planktonic foraminifera. *Nature Geosci.* **2**, 276–280 (2009).
28. McCulloch, M. T. *et al.* Coral record of increased sediment flux to the inner Great Barrier Reef since European settlement. *Nature* **421**, 727–730 (2003).
29. Leggat, W., Buck, B. H., Grice, A. & Yellowlees, D. The impact of bleaching on the metabolic contribution of dinoflagellate symbionts to their giant clam host. *Plant Cell Environ.* **26**, 1951–1961 (2003).
30. Chalker, B. E. & Taylor, D. L. Light-enhanced calcification and the role of oxidative phosphorylation in calcification of the coral *Acropora cervicornis* (Lamarck). *Proc. R. Soc. Lond. B* **190**, 323–331 (1975).
31. Marubini, F., Ferrier-Pagès, C. & Cuif, J.-P. Suppression of growth in scleractinian corals by decreasing ambient carbonate ion concentration: A cross-family comparison. *Proc. R. Soc. Lond. B* **270**, 179–184 (2002).
32. Reynaud, S. *et al.* Interacting effects of CO₂ partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. *Glob. Change Biol.* **9**, 1660–1668 (2003).
33. Marubini, F., Ferrier-Pagès, C., Furla, P. & Allemand, D. Coral calcification responds to seawater acidification: A working hypothesis towards a physiological mechanism. *Coral Reefs* **27**, 491–499 (2008).
34. Ries, J. B., Cohen, A. L. & McCorkle, D. C. A nonlinear calcification response to CO₂-induced ocean acidification by the coral *Oculina arbuscula*. *Coral Reefs* **29**, 661–674 (2010).
35. Anthony, K. R. N., Kline, D. I., Diaz-Pulido, G., Dove, S. & Hoegh-Guldberg, O. Ocean acidification causes bleaching and productivity loss in coral reef builders. *Proc. Natl Acad. Sci. USA* **105**, 17442–17446 (2008).
36. Ohde, S. & Hossain, M. M. Effect of CaCO₃ (aragonite) saturation state of seawater on calcification of *Porites* coral. *Geochem. J.* **38**, 613–621 (2004).
37. Broecker, W. S., Langdon, C., Takahashi, T. & Peng, T.-S. Factors controlling the rate of CaCO₃ precipitation on the Grand Bahama Bank. *Glob. Biogeochem. Cycles* **15**, 589–596 (2001).
38. Langdon, C. *et al.* Effect of calcium carbonate saturation state on calcification rate of an experimental coral reef. *Glob. Biogeochem. Cycles* **14**, 639–654 (2000).

Acknowledgements

The authors are grateful for financial support from the Australian Research Council Discovery grant DP0986505 awarded to M.M. and J.T. and to the Australian Research Council Centre of Excellence for Coral Reef Studies for support to J.F. and M.M. P.M. is grateful for financial support from the Marie Curie International Outgoing Fellowship (MEDAT-ARCHIVES) and M.M. is supported by a Western Australian Premiers' Fellowship. This is ISMAR-CNR scientific contribution no. 1745.

Author contributions

M.M. and J.T. designed the study and J.F., M.M. and P.M. carried out the model simulations. M.M. led the writing with contributions from all authors to the analysis of the results and writing the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/natureclimatechange. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.M.