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# Acid ocean cover up

The response to ocean acidification varies widely among, and even within, calcifying taxa. A study sheds light on this perplexing variability by quantifying the role of external organic layers in protecting calcified structures from corrosive sea water.

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Atmospheric carbon dioxide (CO<sub>2</sub>) levels have increased nearly 50% since the Industrial Revolution, mainly due to increased fossil fuel combustion, cement production and deforestation. Absorption of this anthropogenic CO<sub>2</sub> by the oceans lowers seawater pH — a process termed ‘ocean acidification’. Ocean acidification also reduces the abundance of carbonate ions (CO<sub>3</sub><sup>2-</sup>), which are an essential component of the mineral calcium carbonate (CaCO<sub>3</sub>) that many soft-bodied marine organisms — including corals, crabs, clams, snails, urchins and algae — use to build their protective shells and skeletons. Now, writing in *Nature Climate Change*,

Riccardo Rodolfo-Metalpa and colleagues<sup>1</sup> show that for three types of marine calcifiers — corals, mussels, and limpets — total shell growth (or total skeletal growth for corals) predictably declines under high-CO<sub>2</sub> conditions, but the rate of CaCO<sub>3</sub> accretion beneath calcifying tissue actually increases.

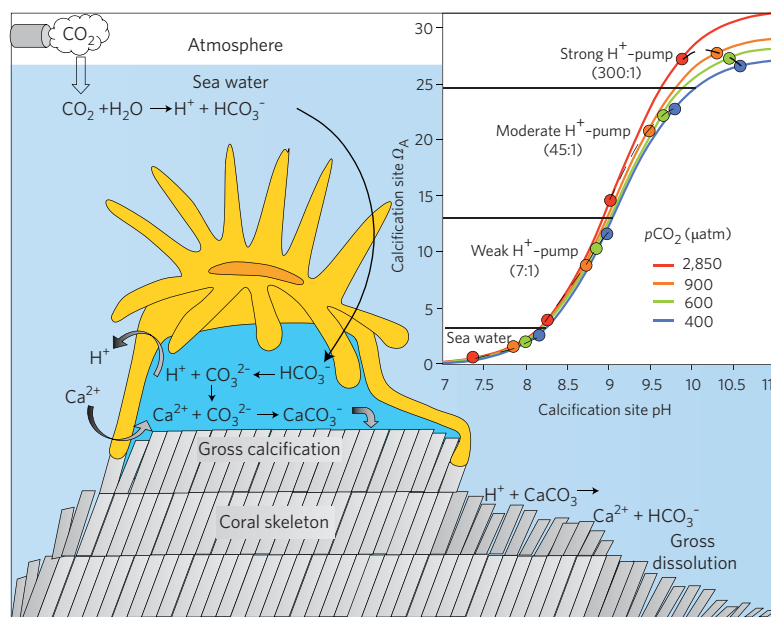
Over the past decade, a large number of field and laboratory experiments have investigated the impact of ocean acidification on the ability of marine calcifiers to build their protective shells and skeletons. The results have been highly variable: some organisms, including crabs, lobsters, urchins, limpets and various calcifying algae, seem to produce shell material faster

under moderately increased levels of CO<sub>2</sub>, whereas others, such as tropical reef-building corals, clams, oysters, scallops, snails and pteropods, calcify more slowly under such conditions<sup>2-5</sup>. To further complicate matters, certain species, such as the coccolithophore *Emiliana huxleyi*, show different responses in different laboratories<sup>6,7</sup>, raising the possibility that species’ responses in ocean acidification experiments are strain- or even protocol-dependent.

Rodolfo-Metalpa and colleagues’ study may reconcile some of this variability by distinguishing between responses in gross calcification (that is, shell or skeleton accretion beneath healthy tissue), gross dissolution (that is, loss of shell or skeleton when not protected by external organic layers) and net calcification (gross calcification minus gross dissolution) (Fig. 1). The authors make these distinctions by rearing specimens in control and high-CO<sub>2</sub> sea water spiked with the rare stable isotope <sup>45</sup>Ca, which is taken up in the coral skeletons and mussel and limpet shells as CaCO<sub>3</sub> is accreted beneath healthy tissue. Dissolving the calcified structures in acid after completion of the experiment liberates the <sup>45</sup>Ca incorporated during calcification, from which the authors were able to estimate gross shell or skeleton accretion. The authors estimated net calcification (calcification minus dissolution) by measuring the buoyant weights of the shells and skeletons at the beginning and end of the experiment.

Their experiments reveal that rates of net calcification within the Mediterranean corals *Cladocora caespitosa* and *Balanophyllia europaea* decrease with increasing atmospheric CO<sub>2</sub>. However, the corals differed in the severity of their responses: at pH 7.5, the skeleton of *C. caespitosa* begins to dissolve away, whereas *B. europaea* continues expanding its skeleton even at pH 7.3. The authors’ attribute this disparity to the fact that *B. europaea* covers a greater portion of its skeleton with tissue than *C. caespitosa*, which covers only its polyp-housing corallites.

The authors also make the important observation that calcification beneath healthy



**Figure 1** | Model of coral calcification and dissolution. The scheme shows how the rate of gross calcification for strong H<sup>+</sup>-pumping corals could increase under increased CO<sub>2</sub> levels (that is, via HCO<sub>3</sub><sup>-</sup> utilization)<sup>8,10-16</sup>, while rates of net calcification simultaneously decline owing to dissolution of exposed skeleton<sup>1</sup>. Black curves in the graph (inset) summarize changes in the calcifying fluid (dark blue region) saturation state (Ω<sub>A</sub>) of weak, moderate and strong (external:internal H<sup>+</sup> ratios are given in parentheses) H<sup>+</sup>-pumping calcifiers exposed to atmospheric pCO<sub>2</sub> of 400 (blue circles), 600 (green circles), 900 (orange circles) and 2,850 μatm (red circles)<sup>12</sup>. Gross calcification response to CO<sub>2</sub>-induced ocean acidification should be more positive for strong H<sup>+</sup>-pumping calcifiers, such as the corals investigated by Rodolfo-Metalpa and colleagues<sup>1</sup> that exhibit increased rates of gross calcification beneath protective tissue layers under high-CO<sub>2</sub> conditions. This increase, however, is offset on a net basis by enhanced dissolution of unprotected skeleton. Note: calcifying fluid dimensions are vertically exaggerated.

tissue (gross calcification) within both coral species increases at higher atmospheric CO<sub>2</sub> levels. Therefore, the net slowdown in skeletal growth by these corals under increased CO<sub>2</sub> occurs not because they are unable to calcify, but rather because their unprotected skeleton is dissolving faster (Fig. 1). The mussel *Mytilus galloprovincialis* and the limpet *Patella caerulea* showed similar trends in their ability to accrete shell under high-CO<sub>2</sub> conditions.

As net calcification represents the balance between the formation of new shell or skeleton beneath healthy tissue and the dissolution of exposed shell or skeleton, the impact of ocean acidification on a creature's net calcification may be largely controlled by the status of its protective organic cover. This varies both among and within species owing to genetic differences, as well as to the health, nutrition and handling of individual specimens. The findings of Rodolfo-Metalpa and colleagues may thus explain some of the variability in responses observed in previous experiments.

The authors also make the potentially important observation that the positive relationship between CO<sub>2</sub> and gross calcification for the coral *B. europaea* and the mussel *M. galloprovincialis* in early to mid-summer becomes negative following late summer warming of the Mediterranean Sea. They conclude that the combination of warming and acidification was simply too much for these calcifiers to overcome.

Although external organic layers should help protect calcifiers' shells and skeletons from corrosive sea water once they have formed<sup>2</sup>, their presence alone cannot explain how organisms continue calcifying — often at higher rates — in undersaturated conditions. Rodolfo-Metalpa and colleagues propose that some creatures must use bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) in

their calcification process<sup>8</sup>, which, unlike carbonate ions (CO<sub>3</sub><sup>2-</sup>), actually increase under conditions of increased CO<sub>2</sub>. But how, precisely, might calcifiers use HCO<sub>3</sub><sup>-</sup>?

As atmospheric CO<sub>2</sub> levels increase, so too does the concentration of HCO<sub>3</sub><sup>-</sup> in sea water and in organisms' calcifying fluid, which for some organisms appears to be derived from sea water<sup>9</sup>. Direct and indirect evidence suggests that many marine calcifiers use proton (H<sup>+</sup>) pumps or ATPase Ca<sup>2+</sup>-H<sup>+</sup> exchange mechanisms to elevate the pH of their calcifying fluids up to two units above that of the surrounding sea water<sup>10–16</sup>. Elevated pH at the site of calcification causes HCO<sub>3</sub><sup>-</sup> in the calcifying fluid to spontaneously dissociate into H<sup>+</sup> and CO<sub>3</sub><sup>2-</sup>, the latter of which combines with Ca<sup>2+</sup> ions to form CaCO<sub>3</sub>, which is organized into shell or skeletal structures via molecular and/or organic templates<sup>15</sup> (Fig. 1).

Recently published pH measurements of the calcifying fluid of another temperate coral, *Astrangia poculata*, under normal and acidified conditions reveal that this coral targets a fixed external:internal H<sup>+</sup> ratio (approximately 85:1), regardless of external seawater pH<sup>12</sup>. The inset of Fig. 1 illustrates the predicted change in calcifying fluid saturation state ( $\Omega_A$ ; proportional to the concentration of CO<sub>3</sub><sup>2-</sup> and Ca<sup>2+</sup> ions) for three hypothetical calcifiers that target the low (7:1), moderate (45:1) and high (300:1) external:internal H<sup>+</sup> ratios for atmospheric CO<sub>2</sub> conditions ( $p\text{CO}_2$  400–2,850  $\mu\text{atm}$ ) encompassed by the Rodolfo-Metalpa *et al.* study. Critically, the response of calcifying fluid  $\Omega_A$  to moderately increased atmospheric CO<sub>2</sub> levels ( $p\text{CO}_2$  ~400–900  $\mu\text{atm}$ ) should be neutral-to-positive for calcifiers that maintain external:internal H<sup>+</sup> ratios greater than approximately 80:1. This may explain how the organisms investigated in the study by Rodolfo-Metalpa and colleagues were able to

continue accreting new material — in some cases at elevated rates — in undersaturated, high-CO<sub>2</sub> conditions.

Nevertheless, the distinction between gross and net calcification becomes increasingly irrelevant at threshold levels of atmospheric CO<sub>2</sub>, as dissolution begins to dominate the calcification equation. Rodolfo-Metalpa and colleagues touch on this midway through their report, where they casually mention that at pH 7.3, colonies of one coral species had completely dissolved within five months of transplantation. This understated observation may prove to be the report's most dire: at certain CO<sub>2</sub> levels, even thick-skinned calcifiers can't protect themselves from the effects of ocean acidification. □

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