

# Marine calcifiers exhibit mixed responses to CO<sub>2</sub>-induced ocean acidification

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## ABSTRACT

**Anthropogenic elevation of atmospheric carbon dioxide ( $p\text{CO}_2$ ) is making the oceans more acidic, thereby reducing their degree of saturation with respect to calcium carbonate ( $\text{CaCO}_3$ ). There is mounting concern over the impact that future CO<sub>2</sub>-induced reductions in the  $\text{CaCO}_3$  saturation state of seawater will have on marine organisms that construct their shells and skeletons from this mineral. Here, we present the results of 60 d laboratory experiments in which we investigated the effects of CO<sub>2</sub>-induced ocean acidification on calcification in 18 benthic marine organisms. Species were selected to span a broad taxonomic range (crustacea, cnidaria, echinoidea, rhodophyta, chlorophyta, gastropoda, bivalvia, annelida) and included organisms producing aragonite, low-Mg calcite, and high-Mg calcite forms of  $\text{CaCO}_3$ . We show that 10 of the 18 species studied exhibited reduced rates of net calcification and, in some cases, net dissolution under elevated  $p\text{CO}_2$ . However, in seven species, net calcification increased under the intermediate and/or highest levels of  $p\text{CO}_2$ , and one species showed no response at all. These varied responses may reflect differences amongst organisms in their ability to regulate pH at the site of calcification, in the extent to which their outer shell layer is protected by an organic covering, in the solubility of their shell or skeletal mineral, and in the extent to which they utilize photosynthesis. Whatever the specific mechanism(s) involved, our results suggest that the impact of elevated atmospheric  $p\text{CO}_2$  on marine calcification is more varied than previously thought.**

## INTRODUCTION

Surface ocean pH has already decreased by 0.1 units since the industrial revolution, and it is predicted to decline another 0.3–0.4 units by the end of this century (Brewer, 1997). This translates to a nearly 50% reduction in the carbonate ion concentration [ $\text{CO}_3^{2-}$ ] of surface seawater, resulting in aragonite and high-Mg calcite undersaturation in the high-latitude oceans. The effect of CO<sub>2</sub>-induced ocean acidification on marine calcification is currently the subject of intense scientific investigation with regard to both the immediate future (cf. Gattuso et al., 1998; Langdon et al., 2000; Langdon and Atkinson, 2005; Kleypas et al., 2006; see the GSA Data Repository<sup>1</sup>) and the geologic past (Knoll et al., 2007; Zhuravlev and Wood, 2008).

## METHODS

To investigate the impact of ocean acidification on a range of benthic marine calcifiers, we reared 18 calcifying species for 60 d in isothermal (25 °C; see the Data Repository for discussion) experimental seawaters equilibrated with average  $p\text{CO}_2$  values ( $\pm\text{SD}$ ) of 409 ( $\pm 6$ ), 606 ( $\pm 7$ ), 903 ( $\pm 12$ ), and 2856 ( $\pm 54$ ) ppm, corresponding to modern  $p\text{CO}_2$ , and ~2, 3, and 10 times pre-industrial levels (~280 ppm), respectively, and yielding average seawater saturation states ( $\pm\text{SD}$ ) of 2.5 ( $\pm 0.4$ ), 2.0 ( $\pm 0.4$ ),

1.5 ( $\pm 0.3$ ), and 0.7 ( $\pm 0.2$ ) with respect to aragonite (see the Data Repository for detailed methods). These carbonate system parameters were selected to represent the range of values predicted for the coming millennium (Brewer, 1997; Feely et al., 2004) and to span those reported to have occurred since mid-Cretaceous time (ca. 110 Ma; Royer et al., 2004; Tyrrell and Zeebe, 2004). The organisms' net rates of calcification (total calcification minus total dissolution) under the various  $p\text{CO}_2$  treatments were estimated from changes in their buoyant weight and verified with dry weight measurements after harvesting (Fig. 1; see Fig. DR1, Table DR3, and additional methods in the GSA Data Repository).

## RESULTS

In ten of the 18 species (temperate corals, pencil urchins, hard clams, conchs, serpulid worms, periwinkles, bay scallops, oysters, whelks, soft clams; Figs. 1I–1R), net calcification decreased with increasing  $p\text{CO}_2$  (reduced  $\text{CaCO}_3$  saturation state). And in six of the ten negatively impacted species (pencil urchins, hard clams, conchs, periwinkles, whelks, soft clams; Figs. 1J–1L, 1N, and 1Q–1R), we observed net dissolution of the shell in the highest  $p\text{CO}_2$  treatment, for which the experimental seawater was undersaturated with respect to aragonite and high-Mg calcite. However, in four of the 18 species (limpets, purple urchins, coralline red algae, calcareous green algae; Figs. 1D–1G), net calcification increased relative to the control under intermediate  $p\text{CO}_2$  levels (605 and 903 ppm), and then declined at the highest  $p\text{CO}_2$  level (2856 ppm). In three species (crabs, lobsters, and shrimps; Figs. 1A–1C), net calcification was greatest under the highest level of  $p\text{CO}_2$  (2856 ppm). And one species, the blue mussel (Fig. 1H), exhibited no response to elevated  $p\text{CO}_2$ .

Our experiments revealed six general calcification response patterns to elevated  $p\text{CO}_2$  (Fig. 1; Fig. DR3; Table 1): positive (Figs. 1A and 1B); threshold-positive (no change under intermediate  $p\text{CO}_2$ , positive under highest  $p\text{CO}_2$ ; Fig. 1C); parabolic (positive under intermediate  $p\text{CO}_2$ , negative under highest  $p\text{CO}_2$ ; Figs. 1D–1G); neutral (no change; Fig. 1H); threshold-negative (little or no change under intermediate  $p\text{CO}_2$ , negative under highest  $p\text{CO}_2$ ; Figs. 1I–1L); and negative (Figs. 1M–1R). A combination of factors, including the organisms' ability to regulate pH at the site of calcification, the extent of organic-layer coverage of their external shell, their biomineral solubility, and whether they utilize photosynthesis, may contribute to the disparity of these response patterns.

## FACTORS EXPLAINING VARIABLE RESPONSES AMONGST ORGANISMS

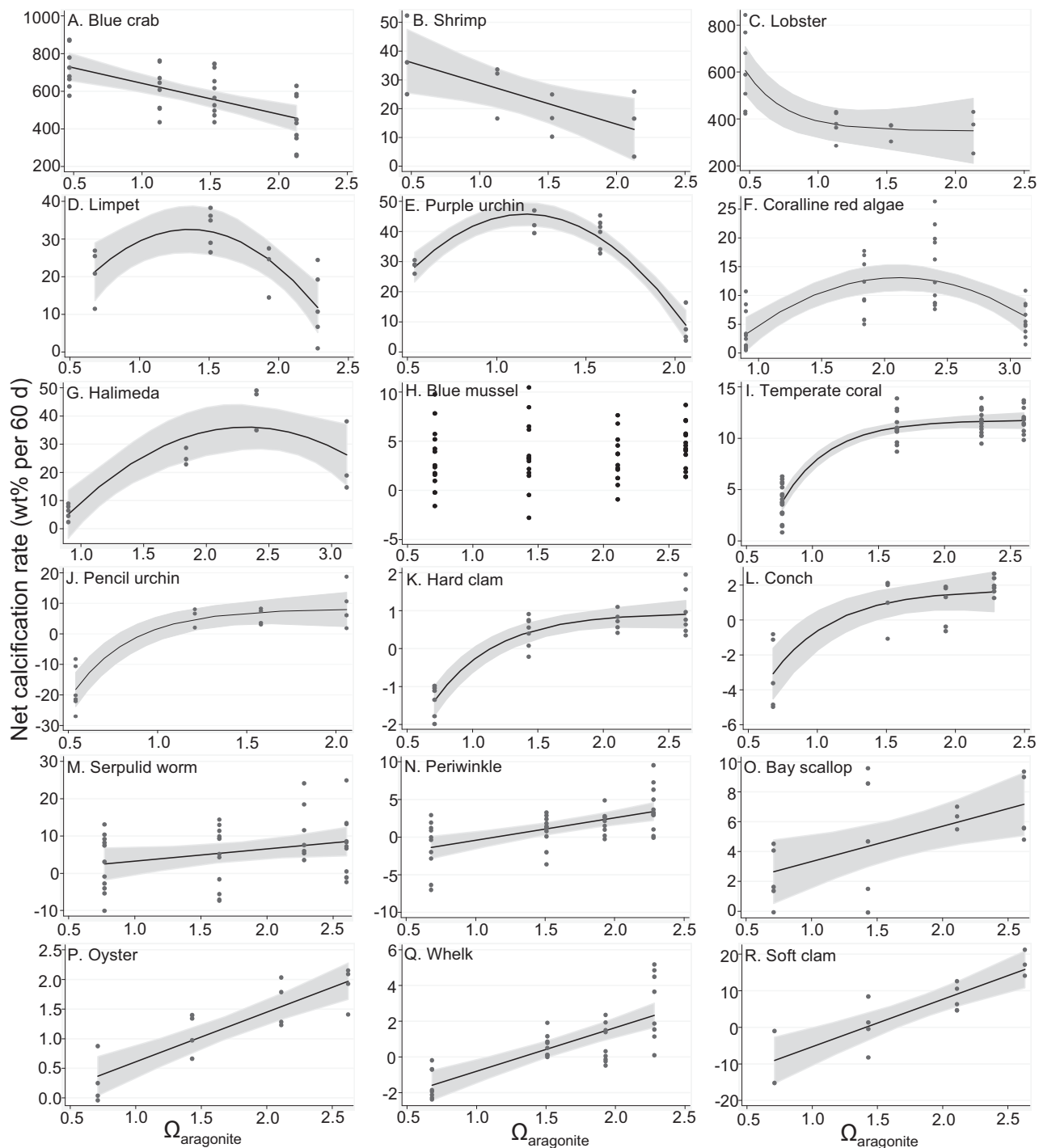
### Regulation of pH at the Site of Calcification Converts $\text{HCO}_3^-$ to $\text{CO}_3^{2-}$

Many calcifying organisms, including scleractinian corals (Al-Horani et al., 2003; Cohen and McConnaughey, 2003), coralline red algae (Borowitzka, 1987; McConnaughey and Whelan, 1997), calcareous green algae (Borowitzka, 1987; McConnaughey and Whelan, 1997; De Beer and Larkum, 2001), foraminifera (Rink et al., 1998), and crabs (Cameron, 1985) are thought to facilitate  $\text{CaCO}_3$  precipitation by elevating pH at the site of calcification. This reduction in  $[\text{H}^+]$  converts  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$ , elevating  $[\text{CO}_3^{2-}]$  within calcifying compartments.

Microelectrode data (Rink et al., 1998; De Beer and Larkum, 2001; Al-Horani et al., 2003) show elevated pH—up to 2 units above external seawater—at sites of calcification in several marine calcifiers. These

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<sup>1</sup>GSA Data Repository item 2009279, supplementary information, Table DR1, Figures DR1 and DR2, is available online at [www.geosociety.org/pubs/fl2009.htm](http://www.geosociety.org/pubs/fl2009.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1. Calcification response patterns for 18 species of calcifying organisms subjected for 60 d to  $\text{CO}_2$ -induced reductions in  $\text{CaCO}_3$  saturation state of seawater.** Net rates of calcification(+)/dissolution(-) were estimated from buoyant weighing (verified with dry weight measured after harvesting) and are expressed as a percentage of the organisms' initial buoyant weight (see GSA Data Repository Fig. DR1 and Tables DR1 and DR3 [see footnote 1]). *Halimeda* growth is in mg/day, since all measured algae emerged under experimental conditions (i.e., initial weight was zero). Linear, quadratic, and exponential regression analyses were used to examine relationship between net calcification rate and aragonite saturation state (Table 1). These regressions were calculated using least squares method and adjusted for clustering within tanks with generalized estimating equations, which employ the Huber-White sandwich estimator of variance in place of the standard estimator of variance to increase the rigor of the test for statistical significance (Rogers, 1993; see GSA Data Repository). The regression analysis (linear, quadratic, or exponential) that yielded the lowest mean squared error for each species is plotted above (see Table 1 and Table DR5). All plotted regressions are statistically significant ( $p < 0.05$ ); 95% confidence intervals are shown in gray. Regression analyses are intended to show general trends—the locations of the break-in-slope of the exponential curves (B, I-L) are not precisely constrained by the available data.  $\Omega_{\text{aragonite}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}^*$ , where  $K_{\text{sp}}^*$  is the stoichiometric solubility product of aragonite.  $\Omega_{\text{aragonite}}$  was calculated from measured values of temperature, salinity, alkalinity, and pH (see Table DR2 [see footnote 1]) using Roy et al. (1993) values for carbonic acid constants  $K_1$  and  $K_2$  (see GSA Data Repository [see footnote 1]), the Mucci (1983) value for  $K_{\text{sp}}^*$ , and pressure ( $P$ ) = 1.015 atm.

TABLE 1. REGRESSION ANALYSES OF  $\Omega_{\text{ARAGONITE}}$  VS. NET CALCIFICATION RATE AND SUMMARY OF CALCIFICATION-RELEVANT TRAITS

Organism	Scientific name	Panel (Fig. 1)	Best-fit Regression*					Response†	Mineralogy‡	Cover§	Photo**
			Regression	Type	p	R <sup>2</sup>	RMSE				
Crab	<i>Callinectes sapidus</i>	A	$y = -165x + 807$	LIN	0.00	0.41	120.71	positive	HMC	high	no
Shrimp	<i>Penaeus plebejus</i>	B	$y = -14.3x + 43.3$	LIN	0.01	0.47	9.98	positive	HMC	high	no
Lobster	<i>Homarus americanus</i>	C	$y = 1296e^{-344x} + 348$	EXP	0.00	0.57	112.11	threshold(+)	HMC	high	no
Limpet	<i>Crepidula fornicata</i>	D	$y = -24.4x^2 + 66.3x - 12.5$	QUAD	0.00	0.59	7.17	parabolic	Arag>LMC	low	no
Purple urchin	<i>Arbacia punctulata</i>	E	$y = -45.7x^2 + 106x - 15.9$	QUAD	0.00	0.91	4.65	parabolic	HMC	high	no
Coralline red alga	<i>Neogoniolithon</i> sp.	F	$y = -6.66x^2 + 28.2x + -16.7$	QUAD	0.03	0.43	4.86	parabolic	HMC	high	yes
Halimeda	<i>Halimeda incrassata</i>	G	$y = -15.4x^2 + 71.2x - 46.6$	QUAD	0.02	0.74	8.73	parabolic	Arag	high	yes
Blue mussel	<i>Mytilus edulis</i>	H	no significant trend ( $p > 0.05$ )	NONE	n/a	n/a	n/a	neutral	LMC>Arag	mod	no
Temperate coral	<i>Oculina arbuscula</i>	I	$y = -67.2e^{-277x} + 11.8$	EXP	0.00	0.87	1.43	threshold(-)	Arag	high	yes
Pencil urchin	<i>Eucidaris tribuloides</i>	J	$y = -137e^{-304x} + 8.25$	EXP	0.02	0.84	5.68	threshold(-)	HMC	low	no
Hard clam	<i>Mercenaria mercenaria</i>	K	$y = -10.3e^{210x} + 0.94$	EXP	0.00	0.83	0.44	threshold(-)	Arag>HMC	low	no
Conch	<i>Strombus alatus</i>	L	$y = -21.9e^{-222x} + 1.75$	EXP	0.00	0.69	1.37	threshold(-)	Arag>LMC	low	no
Serpulid worm	<i>Hydroides crucigera</i>	M	$y = 1.64x - 0.02$	LIN	0.05	0.08	3.93	negative	Arag + HMC	low	no
Periwinkle	<i>Littorina littorea</i>	N	$y = 2.99x - 3.41$	LIN	0.00	0.34	2.55	negative	LMC>Arag	mod	no
Bay scallop	<i>Argopecten irradians</i>	O	$y = 2.37x - 0.97$	LIN	0.00	0.34	2.61	negative	LMC	low	no
Oyster	<i>Crassostrea virginica</i>	P	$y = 0.84x - .23$	LIN	0.00	0.76	0.36	negative	LMC	low	no
Whelk	<i>Urosalpinx cinerea</i>	Q	$y = 2.45x - 3.26$	LIN	0.01	0.58	1.28	negative	Arag>LMC	low	no
Soft clam	<i>Mya arenaria</i>	R	$y = 13.0x - 18.2$	LIN	0.00	0.73	5.31	negative	Arag>HMC	low	no

\*Linear (LIN), quadratic (QUAD), and exponential (EXP) regression analyses were performed for each species using the least squares method (see Table DR5 [see footnote 1]). The regression analysis that yielded the lowest square root of the mean squared error (RMSE) for a given species and that was statistically significant ( $p \leq 0.05$ ) is listed above and plotted in Fig. 1. p—p-value; R<sup>2</sup>—correlation coefficient; y—net calcification rate; x— $\Omega_{\text{aragonite}}$ .

†Response—generalized calcification response pattern exhibited by organisms reared under elevated  $p\text{CO}_2$ ; organisms ranked in increasingly negative order.

‡Mineralogy—polymorph of  $\text{CaCO}_3$  in shell or skeleton (see GSA Data Repository for references), confirmed with X-ray diffraction and scanning electron microscopy; HMC—high-Mg calcite (>4 mol%  $\text{MgCO}_3$ ); LMC—low-Mg calcite (<4 mol%  $\text{MgCO}_3$ ); Arag—aragonite.

§Cover—extent to which shell or skeleton is covered by organic layer.

\*\*Photo— whether organism utilizes  $\text{CO}_2$  via photosynthesis.

localized increases in pH may be achieved in various ways, for example, via conventional proton channeling,  $\text{Ca}^{2+}$ -activated proton-translocating ATPase, light-induced proton-pumping, transcellular symporter and co-transporter proton-solute shuttling, cellular extrusion of hydroxyl ions ( $\text{OH}^-$ ) into the calcifying medium, and  $\text{CO}_2$  utilization via photosynthesis (Borowitzka, 1987; McConnaughey and Whelan, 1997; De Beer and Larkum, 2001; Cohen and McConnaughey, 2003).

The decrease in seawater pH that will accompany the forecasted rise in anthropogenic  $p\text{CO}_2$  will reduce the  $[\text{CO}_3^{2-}]$  of seawater, and, for many organisms, there is experimental evidence that a reduction in seawater  $[\text{CO}_3^{2-}]$  will inhibit calcification, and perhaps cause dissolution of existing shell (cf. Gattuso et al., 1998; Langdon et al., 2000; Langdon and Atkinson, 2005; Kleypas et al., 2006). It is also possible, however, that calcification in some organisms will be enhanced under elevated  $p\text{CO}_2$ . If seawater is the source of the organism's calcifying fluid, then the concentration of dissolved inorganic carbon (DIC) in this fluid will increase as  $p\text{CO}_2$  increases. Organisms able to maintain an elevated pH at their site of calcification, despite reduced external pH, will convert much of this increased DIC, occurring primarily as  $\text{HCO}_3^-$ , to  $\text{CO}_3^{2-}$ . These organisms may experience a final  $[\text{CO}_3^{2-}]$  at their site of calcification that is only slightly less than, and possibly equal to or greater than, that attained under present-day  $p\text{CO}_2$ —depending upon the efficiency of their specific proton-regulating mechanism. Alternatively, organisms such as coccolithophores may utilize  $\text{HCO}_3^-$  directly in calcification (Iglesias-Rodriguez et al., 2008), although mesocosm experiments suggest that reef-building organisms lack this ability (Langdon et al., 2000; Schneider and Erez, 2006). Nonetheless, the ability to convert  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$  via proton regulation at the site of calcification, and/or utilize  $\text{HCO}_3^-$  directly in calcification, may explain, in part, why some of the organisms investigated in our experiments exhibited enhanced calcification under conditions of elevated  $p\text{CO}_2$ .

Of the calcifiers that have been investigated in microelectrode studies, those reported to maintain their calcifying fluids at higher pH (corals: 9.3 [Al-Horani et al., 2003; Fig. 1I] and calcareous green algae: 8.8–10.5 [De Beer and Larkum, 2001; Fig. 1G]) were generally less negatively affected

by elevated  $p\text{CO}_2$  in our experiments than those reported to maintain their calcifying fluid at lower pH (bivalve molluscs: pH = 7.33–8.53 [Crenshaw, 1972; Figs. 1K, 1O–1R]). These observations are consistent with the hypothesis that organisms able to maintain an elevated pH and, thus, elevated  $[\text{CO}_3^{2-}]$  at their site of calcification could be less negatively impacted by  $\text{CO}_2$ -induced reductions in the  $\text{CaCO}_3$  saturation state of seawater.

### Protective External Organic Layer

Most calcifying marine organisms produce some type of external organic layer that separates their shell or skeleton from ambient seawater. Crustacea enclose their carapace within a relatively thick epicuticle, urchins cover their tests with an epidermis, algae precipitate  $\text{CaCO}_3$  in spaces bound by cortical tissue, corals nucleate aragonite beneath several layers of epithelial tissue, and molluscs cover their shells with periostracum. The structure and composition of these protective organic layers vary widely amongst organisms. Through visual inspection, we have classified the organisms investigated in this study by their extent of organic-layer coverage (Table 1; high = total coverage; moderate = majority coverage; low = minority coverage). Organisms that accrete shell or skeleton that remains totally covered by an external organic layer, such as the crustacea (Figs. 1A–1C), purple urchins (Fig. 1E), coralline red algae (Fig. 1F), calcareous green algae (Fig. 1G), blue mussel (Fig. 1H), and temperate corals (Fig. 1I), generally exhibited greater resilience to elevated  $p\text{CO}_2$  than those producing shell that is largely exposed to ambient seawater after deposition, such as the conchs (Fig. 1L), serpulid worms (Fig. 1M), periwinkles (Fig. 1N), scallops (Fig. 1O), oysters (Fig. 1P), whelks (Fig. 1Q), and clams (Figs. 1K and 1R).

### $\text{CaCO}_3$ Polymorph Mineralogy

It is also predicted that organisms utilizing the more soluble forms of  $\text{CaCO}_3$ —aragonite and high-Mg calcite—would be more adversely affected by elevated  $p\text{CO}_2$  than those utilizing the less soluble low-Mg calcite form (Morse et al., 2007). Although we did not observe a direct relationship between skeletal mineral solubility and vulnerability to elevated

$p\text{CO}_2$  (Table 1) under the intermediate  $p\text{CO}_2$  levels (606 and 903 ppm), mineralogy did come into play for the highest  $p\text{CO}_2$  level (2856 ppm). Of the six species that exhibited net dissolution under these conditions (pencil urchin, hard clam, conch, periwinkle, whelk, and soft clam; Figs. 1J–1L, 1N, and 1Q–1R), five of these secrete shells that are composed predominantly of the more soluble aragonite (hard clam, conch, whelk, soft clam) and high-Mg calcite (pencil urchin) polymorphs.

### Fertilization of Photosynthesis

The coralline red (Fig. 1F) and calcareous green algae (Fig. 1G) investigated in this study both exhibited increased net calcification under the intermediate  $p\text{CO}_2$  levels (606 and 903 ppm), and the temperate corals (Fig. 1I), which contain photosynthetic symbionts, exhibited no response over this range. This suggests that the direct utilization of  $\text{CO}_2$  via photosynthesis may also influence an organism's calcification response to  $\text{CO}_2$ -induced reductions in saturation state (Table 1). Although the relationship between photosynthesis and calcification is complex, increased  $\text{CO}_2$  in seawater may increase the organism's rate of photosynthesis (Bowes, 1993; Iglesias-Rodriguez et al., 2008), potentially increasing the amount of energy available for converting  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$  via pH regulation at the site of calcification. The parabolic calcification response patterns exhibited by the coralline red algae (Fig. 1F) and calcareous green algae (Fig. 1G) in our experiments, which peaked between 600 and 1100 ppm  $p\text{CO}_2$ , are consistent with previous work showing that  $p\text{CO}_2$  is only limiting for photosynthesis in marine algae at partial pressures less than 1000 ppm (Bowes, 1993).

### IDENTIFICATION OF OCEAN ACIDIFICATION EVENTS IN THE GEOLOGIC PAST

Past ocean acidification events, reportedly associated with intervals of intense global volcanism, have been invoked as potential drivers of mass extinctions that have occurred throughout Phanerozoic time (e.g., Knoll et al., 2007). The present study, by identifying both positive and negative responses to elevated  $p\text{CO}_2$  for a wide range of organisms, offers a unique, polyphyletic fingerprint for identifying such  $\text{CO}_2$ -induced extinction events in the fossil record.

### CONCLUSIONS

Our experiments suggest that the response of calcifying marine organisms to elevated atmospheric  $p\text{CO}_2$  will be variable and complex. However, with the data at hand, it is difficult to predict how these changes in calcification will impact organisms' survival, reproductive success, and overall ecosystem health. Even those organisms showing enhanced calcification under elevated  $p\text{CO}_2$  could be negatively impacted by the decline of less  $\text{CO}_2$ -tolerant species within their ecosystems. We have only begun to generate the data needed to assess  $\text{CO}_2$ -driven impacts on organisms and ecosystems in the geologic past, and to anticipate the effects of anthropogenic ocean acidification in the decades and centuries ahead.

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