Supplementary Materials for

Regulation of calcification site pH is a polyphyletic but not always governing response to ocean acidification

Yi-Wei Liu*, Jill N. Sutton, Justin B. Ries, Robert A. Eagle*

*Corresponding author. Email: liuyiwei@earth.sinica.edu.tw (Y.-W.L.); robeagle@g.ucla.edu (R.A.E.)

Published 29 January 2020, Sci. Adv. 6, eaax1314 (2020)
DOI: 10.1126/sciadv.aax1314

This PDF file includes:

Section S1. Species selection
Section S2. Consideration of the potential for non-pH effects on calcium carbonate δ¹¹B
Fig. S1. Calcification response patterns of the full sample collection and of the subset of samples used in this study.
Table S1. Seawater chemistry (pCO₂ in μatm, total alkalinity (TA) in umol/kg-SW, pH_sw), net calcification rate (% change/60 days), δ¹¹B (‰) of biogenic CaCO₃, calcification site pH (pH_CF), and ∆pH (pH_CF – pH_sw).
Table S2. Linear and quadratic regression analysis of boron isotopic composition (δ¹¹B) of biogenic carbonates as a function of seawater pH via the least squares method.
Table S3. Linear and quadratic regression analysis of ∆pH as a function of seawater pH via the least squares method.
References (33–41)
Supplementary Materials

“Regulation of calcification site pH a polyphyletic but not always governing response to ocean acidification” by Liu, Y.-W., Sutton, J. N., Ries, J. B, and Eagle, R. A.

Section S1. Species selection

We selected species that spanned the range of net calcification rate responses patterns found in Ries, Cohen and McCorkle (5), including positive, parabolic, threshold-negative, and negative. The selected species produce their shells/skeletons from a range of polymorphs of the calcium carbonate mineral, including high-Mg calcite (purple urchin, coralline red alga, blue crab, gulf shrimp), low-Mg calcite (pencil urchin, oyster, blue mussel), a mixture of high-Mg calcite and aragonite (serpulid worm), and > 97% aragonite (temperate coral, hard clam) (33). These species are also representative of the major modes of biomineralization: intracellular (urchins), intercellular (coralline red algae) and extracellular (temperate coral, serpulid worm, bivalves, crustacea) biomineralization. By estimating calcification site pH (pH_{CF}) from the boron isotopic composition of the shells/skeletons of these divergent taxa, which were previously cultured under an equivalent range of pCO_{2} conditions, we can evaluate polyphyletic trends in the extent to which pH_{CF}-regulation influences species’ calcification response to ocean acidification.

Section S2. Consideration of the potential for non-pH effects on calcium carbonate δ^{11}B

Although correlating calcium carbonate δ^{11}B directly with net organismal calcification rate (Fig. 1) is arguably the most parsimonious way to interpret the data generated from the present study, the δ^{11}B data can also be used to calculate pH at the site of calcification.
(pH_{CF}) using established methods (see methods section, main text)—allowing direct comparison of pH_{CF} with the species’ net calcification response to OA. The assumption that calcium carbonate δ^{11}B reflects pH_{CF}—which may be offset from seawater pH—has been most widely applied to scleractinian corals (17). The validity of the boron-isotope approach to estimating coral pH_{CF} is supported by generally similar results obtained from pH-sensitive dye and pH-microelectrode analyses that indicate that corals elevate pH_{CF} above that of seawater (22, 23). This approach to estimating pH_{CF} from calcium carbonate δ^{11}B has been previously applied to a wide range of calcifying taxa, including most of the species investigated in the present study (e.g., 15, 16, 19, 20). Although the majority of work on foraminifera has focused on δ^{11}B as a potential tracer for seawater carbonate system parameters, there is a growing appreciation that organismal modulation of the calcification microenvironment influences δ^{11}B compositions of the calcium carbonate tests comprising these paleoceanographic archives (20).

Two key assumptions of the calcium carbonate δ^{11}B-based proxy of parent solution pH are that borate is the only species of boron incorporated into the calcium carbonate lattice and that there is no significant isotopic fractionation when borate is incorporated into the shell/skeleton. These assumptions are generally supported by empirical observations of marine carbonates that typically exhibit boron isotopic compositions that are not consistent with significant boric acid incorporation into the calcium carbonate lattice or with significant isotopic fractionation between the dissolved and mineralized phases of borate (15-17, 19, 20). A prior study showed that the shell/skeletal δ^{11}B compositions of six taxonomically divergent species of marine calcifiers cultured at a single pCO_2 condition
(409 ppm) revealed $\delta^{11}$B data that were, except for one species, largely inconsistent with significant boric acid incorporation into biogenic CaCO$_3$ (19). Four species, including two urchins that produce high-Mg calcite spines, a serpulid worm that produces a calcareous tube comprised of a mixture of aragonite and high-Mg calcite, and an oyster that produces a shell of predominantly low-Mg calcite, all yielded CaCO$_3$ $\delta^{11}$B at or below that predicted from the seawater borate $\delta^{11}$B-pH$_{sw}$ relationship (19)—which is not consistent with boric acid incorporation into biogenic CaCO$_3$ because boric acid has significantly higher $\delta^{11}$B than dissolved borate. However, recent studies on inorganically precipitated CaCO$_3$ suggest that some boric acid may be incorporated into CaCO$_3$ alongside borate, with the calcite polymorph of CaCO$_3$ exhibiting this tendency more than the aragonite polymorph (eg. (34-37))—thereby challenging some of the assumptions required to use CaCO$_3$ $\delta^{11}$B as a proxy for parent solution pH. Yet the synthetic solutions from which the abiogenic CaCO$_3$ minerals were precipitated are different in composition from seawater and biological calcification fluids, and are therefore not necessarily appropriate analogues for studying boron isotope systematics in calcifying fluids—leaving open the question whether these results hold for biogenic CaCO$_3$.

A recent study (38) also reported the additional complication that there can be ca. 2 to 5‰ fractionation in boron isotopes between dissolved borate and borate adsorbed onto the surface of abiogenic calcite in controlled laboratory experiments, and that this effect was influenced by NaCl concentration of the parent solution, but found no evidence that boric acid adsorbs onto the surface of calcite minerals (38). It is unclear whether these results are relevant to interpreting $\delta^{11}$B within biogenic CaCO$_3$ as the minerals investigated in this
study were precipitated in the laboratory through processes that are not necessarily representative of biogenic calcification.

Although CaCO$_3$ $\delta^{11}$B is a promising tool for estimating parent solution pH, it is clear that further work is needed to fully constrain the factors controlling the $\delta^{11}$B composition of abiogenic carbonates, and to understand how well the results of those laboratory experiments reflect mechanisms of boron isotope fractionation within biogenic CaCO$_3$.

The reliability of $\delta^{11}$B-based estimates of pH$_{CF}$ can be further assessed through comparison with independent techniques for determining the pH of internal fluid reservoirs in calcifying organisms, including pH-sensitive dyes and pH-microelectrodes. For example, pH-sensitive dyes indicate that the vesicles in which urchin calcite is produced have a pH slightly lower than seawater pH (39), consistent with the $\delta^{11}$B-based pH determinations at the control pCO$_2$ condition of 409 ppm in the present paper and in Sutton, Liu, Ries, Guillermic, Ponzevera and Eagle (19). Mollusk extrapallial fluid pH has been shown to be lower than seawater pH at ambient pCO$_2$ conditions (24), also consistent with data presented here and in Sutton, Liu, Ries, Guillermic, Ponzevera and Eagle (19). Conversely, pH-sensitive dyes and pH microelectrodes have shown that corals maintain their calcifying fluids at pH 0.5 to 1 pH units above surrounding seawater pH, which is consistent with measurements of coral $\delta^{11}$B presented here and in prior work (9, 22, 23). It has been previously noted that coralline algae have unusually high $\delta^{11}$B—higher than that published for any other species of marine calcifier (19, 20). The relatively high $\delta^{11}$B within the high-Mg calcite produced by coralline algae is potentially consistent with a small degree of boric acid incorporation (19, 20, 40), although it may simply reflect a pH near 9 at the site of
calcification—which seems reasonable given that coralline algae are likely elevating pH at their site of calcification via proton removal as well as photosynthetic drawdown of DIC. The latter scenario is also consistent with Short et al.’s (2015) observation that fluid at the diffusive boundary layer above coralline algal crust is elevated by 0.8 to 1.4 units relative to seawater pH (26), although Hoffman et al. (2018) used pH microelectrodes to show that an arctic coralline alga elevates pH at its external boundary by only ca. 0.1 units relative to seawater pH (41). The pH$_{CF}$ of the tropical coralline algal species investigated here has never been analyzed via pH-microelectrode or pH-sensitive dye.

With the possible exception of the coralline alga *Neogoniolithon* sp., which exhibited unusually high $\delta^{11}$B values compared with other species, none of the species examined here or in Sutton et al. (2018) (19) exhibit boron isotope compositions that are inconsistent with the canonical systematics of the boron isotope pH proxy. Yet even if a small fraction of the boron in the investigated biogenic carbonates was derived from boric acid, or if limited boron isotope fractionation occurred during uptake of boron into the shell/skeleton, our interpretation of trends in $\delta^{11}$B and calculated pH$_{CF}$ across experimental treatments, and their comparison with the species’ net calcification responses to ocean acidification, would only be compromised if the ratio of incorporated borate to boric acid, or the solution-mineral fractionation varied systematically across treatment conditions—which there is no evidence to suggest.
Fig. S1. Calcification response patterns of the full sample collection and of the subset of samples used in this study. Patterns in net calcification rate as a function of aragonite saturation state ($\Omega_A$) for the subset of samples selected for boron isotope analysis in the present study (right column) compared to the original experiment (left column). Ries, Cohen and McCorkle (5).
Table S1. Seawater chemistry (pCO₂ in µatm, total alkalinity (TA) in umol/kg-SW, pHsw), net calcification rate (% change/60 days), δ¹³B (‰) of biogenic CaCO₃, calcification site pH (pH_CF), and ΔpH (pH_CF − pHsw).

| Species          | pCO₂ | TA  | pHsw | Net calcification rate | δ¹³B  | pH_CF | ΔpH  |
|------------------|------|-----|------|------------------------|-------|-------|------|
| Purple urchin    | 409  | 1744| 8.04 | 16.42                  | 14.96 | 7.69  | -0.35|
| Purple urchin    | 409  | 1744| 8.04 | 7.53                   | 17.14 | 7.98  | -0.06|
| Purple urchin    | 409  | 1744| 8.04 | 5.05                   | 15.43 | 7.77  | -0.27|
| Purple urchin    | 606  | 1751| 7.90 | 39.85                  | 17.75 | 8.04  | 0.14 |
| Purple urchin    | 606  | 1751| 7.90 | 32.78                  | 17.67 | 8.03  | 0.13 |
| Purple urchin    | 606  | 1751| 7.90 | 45.34                  | 18.02 | 8.07  | 0.17 |
| Purple urchin    | 903  | 1792| 7.77 | 39.47                  | 17.35 | 8.00  | 0.23 |
| Purple urchin    | 903  | 1792| 7.77 | 46.99                  | 17.29 | 7.99  | 0.22 |
| Purple urchin    | 903  | 1792| 7.77 | 42.08                  | 19.18 | 8.17  | 0.40 |
| Purple urchin    | 2856 | 1891| 7.36 | 28.90                  | 17.95 | 8.06  | 0.70 |
| Purple urchin    | 2856 | 1891| 7.36 | 30.43                  | 17.36 | 8.00  | 0.64 |
| Pencil urchin    | 409  | 1744| 8.04 | 1.90                   | 18.64 | 8.12  | 0.08 |
| Pencil urchin    | 409  | 1744| 8.04 | 18.79                  | 18.49 | 8.11  | 0.07 |
| Pencil urchin    | 409  | 1744| 8.04 | 6.15                   | 19.00 | 8.15  | 0.11 |
| Pencil urchin    | 606  | 1751| 7.90 | 8.32                   | 18.35 | 8.10  | 0.20 |
| Pencil urchin    | 606  | 1751| 7.90 | 3.60                   | 17.10 | 7.97  | 0.07 |
| Pencil urchin    | 903  | 1792| 7.77 | 8.02                   | 17.91 | 8.06  | 0.29 |
| Pencil urchin    | 903  | 1792| 7.77 | 2.07                   | 17.39 | 8.00  | 0.23 |
| Pencil urchin    | 903  | 1792| 7.77 | 6.68                   | 17.81 | 8.05  | 0.28 |
| Pencil urchin    | 2856 | 1891| 7.36 | -20.15                 | 17.43 | 8.01  | 0.65 |
| Pencil urchin    | 2856 | 1891| 7.36 | -8.21                  | 17.45 | 8.01  | 0.65 |
| Pencil urchin    | 2856 | 1891| 7.36 | -21.41                 | 18.22 | 8.08  | 0.72 |
| Temperate coral  | 409  | 1960| 8.11 | 11.81                  | 24.04 | 8.51  | 0.40 |
| Temperate coral  | 409  | 1960| 8.11 | 12.06                  | 23.98 | 8.51  | 0.40 |
| Temperate coral  | 409  | 1960| 8.11 | 13.70                  | 24.34 | 8.53  | 0.42 |
| Temperate coral  | 606  | 2012| 8.03 | 11.76                  | 26.19 | 8.65  | 0.62 |
| Temperate coral  | 606  | 2012| 8.03 | 12.76                  | 24.79 | 8.56  | 0.53 |
| Temperate coral  | 606  | 2012| 8.03 | 13.92                  | 24.90 | 8.57  | 0.54 |
| Temperate coral  | 903  | 2027| 7.85 | 10.92                  | 24.71 | 8.56  | 0.71 |
| Temperate coral  | 903  | 2027| 7.85 | 9.60                   | 24.32 | 8.53  | 0.68 |
| Temperate coral  | 903  | 2027| 7.85 | 13.87                  | 23.79 | 8.50  | 0.65 |
|                          |     |     |     |     |     |     |     |
|--------------------------|-----|-----|-----|-----|-----|-----|-----|
| Temperate coral          | 2856| 2071| 7.48| 3.54| 24.99| 8.57| 1.09|
| Temperate coral          | 2856| 2071| 7.48| 1.53| 25.43| 8.60| 1.12|
| Temperate coral          | 2856| 2071| 7.48| 4.54| 24.35| 8.53| 1.05|
|                         |     |     |     |     |     |     |     |
| Oyster                   | 409 | 1833| 8.15| 1.92| 17.63| 8.03| -0.12|
| Oyster                   | 409 | 1833| 8.15| 1.41| 16.71| 7.93| -0.22|
| Oyster                   | 409 | 1833| 8.15| 2.15| 13.37| 7.32| -0.83|
| Oyster                   | 606 | 1862| 8.02| 1.28| 16.91| 7.95| -0.07|
| Oyster                   | 606 | 1862| 8.02| 1.79| 16.82| 7.94| -0.08|
| Oyster                   | 606 | 1862| 8.02| 2.03| 18.82| 8.14| 0.12 |
| Oyster                   | 903 | 1856| 7.83| 0.97| 16.78| 7.94| 0.11 |
| Oyster                   | 903 | 1856| 7.83| 1.34| 15.22| 7.74| -0.09|
| Oyster                   | 903 | 1856| 7.83| 0.66| 17.63| 8.03| 0.20 |
| Oyster                   | 2856| 2063| 7.45| 0.87| 15.95| 7.84| 0.39 |
| Oyster                   | 2856| 2063| 7.45|-0.04| 15.61| 7.79| 0.34 |
| Oyster                   | 2856| 2063| 7.45| 0.25| 16.66| 7.93| 0.48 |
|                         |     |     |     |     |     |     |     |
| Hard clam                | 409 | 1833| 8.15| 1.95| 18.43| 8.10| -0.05|
| Hard clam                | 409 | 1833| 8.15| 0.76| 17.53| 8.02| -0.13|
| Hard clam                | 606 | 1862| 8.02| 0.84| 14.16| 7.54| -0.48|
| Hard clam                | 606 | 1862| 8.02| 0.72| 17.54| 8.02| 0.00 |
| Hard clam                | 903 | 1856| 7.83| 0.39| 15.44| 7.77| -0.06|
| Hard clam                | 903 | 1856| 7.83| 0.72| 19.25| 8.17| 0.34 |
| Hard clam                | 2856| 2063| 7.45|-1.35| 16.66| 7.93| 0.48 |
| Hard clam                | 2856| 2063| 7.45|-1.05| 14.98| 7.70| 0.25 |
| Hard clam                | 2856| 2063| 7.45|-1.79| 16.56| 7.92| 0.47 |
|                         |     |     |     |     |     |     |     |
| Blue mussel              | 409 | 1833| 8.15| 1.87| 16.04| 7.85| -0.30|
| Blue mussel              | 409 | 1833| 8.15| 7.14| 15.65| 7.80| -0.35|
| Blue mussel              | 409 | 1833| 8.15| 4.14| 13.07| 7.20| -0.95|
| Blue mussel              | 606 | 1862| 8.02| 1.22| 14.32| 7.57| -0.45|
| Blue mussel              | 606 | 1862| 8.02| 3.69| 13.54| 7.37| -0.65|
| Blue mussel              | 606 | 1862| 8.02| 0.55| 15.57| 7.79| -0.23|
| Blue mussel              | 903 | 1856| 7.83| 10.45| 16.86| 7.95| 0.12 |
| Blue mussel              | 903 | 1856| 7.83| 2.18| 14.92| 7.69| -0.14|
| Blue mussel              | 903 | 1856| 7.83| 6.17| 14.21| 7.55| -0.28|
| Blue mussel              | 2856| 2063| 7.45|-1.61| 14.92| 7.69| 0.24 |
| Blue mussel              | 2856| 2063| 7.45| 5.19| 14.83| 7.67| 0.22 |
| Blue mussel              | 2856| 2063| 7.45| 2.36| 13.70| 7.42| -0.03|
|                         |     |     |     |     |     |     |     |
| Coralline red alga       | 409 | 2008| 8.19| 5.46| 39.94| N/A | N/A |
| Coralline red alga       | 409 | 2008| 8.19| 8.24| 32.68| 9.10| 0.91|
| Species               | Code | Year  | Size 1 | Size 2 | Size 3 | Size 4 | Size 5 |
|----------------------|------|-------|--------|--------|--------|--------|--------|
| Coralline red alga   | 409  | 2008  | 8.19   | 10.81  | 35.07  | 9.33   | 1.14   |
| Coralline red alga   | 606  | 1987  | 8.05   | 22.35  | 36.92  | 9.59   | 1.54   |
| Coralline red alga   | 606  | 1987  | 8.05   | 26.31  | 34.57  | 9.28   | 1.23   |
| Coralline red alga   | 606  | 1987  | 8.05   | 16.25  | 41.76  | N/A    | N/A    |
| Coralline red alga   | 903  | 2044  | 8.05   | 22.35  | 36.92  | 9.59   | 1.54   |
| Coralline red alga   | 903  | 2044  | 7.91   | 16.98  | 34.57  | 9.28   | 1.23   |
| Coralline red alga   | 903  | 2044  | 7.91   | 9.32   | 30.62  | 8.94   | 1.03   |
| Coralline red alga   | 903  | 2044  | 7.91   | 9.32   | 30.62  | 8.94   | 1.03   |
| Coralline red alga   | 2856 | 2354  | 7.49   | 1.34   | 24.47  | 8.54   | 1.05   |
| Coralline red alga   | 2856 | 2354  | 7.49   | 2.44   | 26.20  | 8.65   | 1.05   |
| Coralline red alga   | 2856 | 2354  | 7.49   | 3.05   | 24.70  | 8.55   | 1.06   |
| Serpulid worm        | 409  | 1960  | 8.11   | 12.45  | 19.21  | 8.17   | 0.06   |
| Serpulid worm        | 409  | 1960  | 8.11   | 6.60   | 19.44  | 8.19   | 0.08   |
| Serpulid worm        | 409  | 1960  | 8.11   | -0.61  | 19.13  | 8.16   | 0.05   |
| Serpulid worm        | 409  | 1960  | 8.11   | 3.00   | 18.59  | 8.12   | 0.09   |
| Serpulid worm        | 606  | 2012  | 8.03   | 5.76   | 18.06  | 8.07   | 0.04   |
| Serpulid worm        | 606  | 2012  | 8.03   | 12.06  | 17.52  | 8.02   | 0.01   |
| Serpulid worm        | 606  | 2012  | 8.03   | 12.06  | 17.52  | 8.02   | 0.01   |
| Serpulid worm        | 903  | 2027  | 7.85   | 4.95   | 16.50  | 7.91   | 0.06   |
| Serpulid worm        | 903  | 2027  | 7.85   | 5.68   | 18.26  | 8.09   | 0.24   |
| Serpulid worm        | 903  | 2027  | 7.85   | -0.82  | 15.17  | 7.73   | -0.12  |
| Serpulid worm        | 2856 | 2071  | 7.48   | 3.73   | 14.95  | 7.69   | 0.21   |
| Serpulid worm        | 2856 | 2071  | 7.48   | 1.53   | 14.86  | 7.68   | 0.20   |
| Serpulid worm        | 2856 | 2071  | 7.48   | -1.38  | 18.25  | 8.09   | 0.61   |
| Shrimp               | 409  | 1860  | 8.03   | 3.34   | 27.41  | 8.73   | 0.70   |
| Shrimp               | 409  | 1860  | 8.03   | 25.96  | 23.99  | 8.51   | 0.48   |
| Shrimp               | 409  | 1860  | 8.03   | 16.49  | 24.78  | 8.56   | 0.53   |
| Shrimp               | 409  | 1860  | 8.03   | 10.24  | 25.72  | 8.62   | 0.77   |
| Shrimp               | 409  | 1860  | 8.03   | 4.95   | 16.50  | 7.91   | 0.06   |
| Shrimp               | 409  | 1860  | 8.03   | 5.68   | 18.26  | 8.09   | 0.24   |
| Shrimp               | 409  | 1860  | 8.03   | -0.82  | 15.17  | 7.73   | -0.12  |
| Shrimp               | 409  | 1860  | 8.03   | 3.73   | 14.95  | 7.69   | 0.21   |
| Shrimp               | 409  | 1860  | 8.03   | 1.53   | 14.86  | 7.68   | 0.20   |
| Shrimp               | 409  | 1860  | 8.03   | -1.38  | 18.25  | 8.09   | 0.61   |
| Blue crab            | 409  | 1860  | 8.03   | 262.77 | 17.39  | 8.01   | -0.02  |
| Blue crab            | 409  | 1860  | 8.03   | 574.60 | 16.63  | 7.92   | -0.11  |
| Blue crab            | 409  | 1860  | 8.03   | 574.60 | 16.63  | 7.92   | -0.11  |
| Blue crab            | 409  | 1860  | 8.03   | 262.77 | 17.39  | 8.01   | -0.02  |
| Blue crab            | 409  | 1860  | 8.03   | 574.60 | 16.63  | 7.92   | -0.11  |
| Blue crab            | 409  | 1860  | 8.03   | 262.77 | 17.39  | 8.01   | -0.02  |
Table S2. Linear and quadratic regression analysis of boron isotopic composition ($\delta^{11}$B) of biogenic carbonates as a function of seawater pH via the least squares method. Significant regressions ($p < 0.05$) that minimized RMSE (root mean square error) were selected as optimal models (bold). N/A denotes no significant trend.

| Organism          | Linear Regression |  p   | R²   | RMSE | Quadratic Regression |  p   | R²   | RMSE | Best-fit  |
|-------------------|-------------------|------|------|------|----------------------|------|------|------|-----------|
|                   |                   |      |      |      |                      |      |      |      |           |
| Purple urchin     | $y = -1.56x + 29.16$ | 0.22 | 0.14 | 1.02 | $y = 13.36x^2 + 203.71x - 758.1$ | 0.04 | 0.51 | 0.75 | Quadratic |
| Pencil urchin     | $y = 1.57x + 5.58$  | 0.02 | 0.48 | 0.57 | $y = 5.31x^2 - 80.02x + 318.59$ | 0.01 | 0.67 | 0.48 | Quadratic |
| Temperate coral   | $y = -0.66x + 29.82$| 0.39 | 0.07 | 0.64 | $y = 1.05x^2 - 17.05x + 93.51$ | 0.69 | 0.08 | 0.64 | N/A       |
| Oyster            | $y = 0.59x + 11.91$ | 0.72 | 0.01 | 1.31 | $y = -7.08x^2 + 110.88x - 416.95$ | 0.66 | 0.09 | 1.26 | N/A       |
| Hard clam         | $y = 1.72x + 3.25$  | 0.42 | 0.10 | 1.48 | $y = 1.71x^2 - 24.85x + 106.42$ | 0.73 | 0.10 | 1.48 | N/A       |
| Blue mussel       | $y = 0.35x + 12.07$ | 0.79 | 0.01 | 1.06 | $y = -3.56x^2 + 55.75x - 203.33$ | 0.84 | 0.04 | 1.04 | N/A       |
| Coralline red alga| $y = 18.01x - 109.24$| 0.00 | 0.62 | 3.69 | $y = -33.9x^2 + 548.2x - 2179.7$ | 0.00 | 0.70 | 3.30 | Quadratic |
| Serpulid Worm     | $y = 5.54x - 26.39$ | 0.01 | 0.49 | 1.23 | $y = 15.57x^2 - 236.82x + 915.76$ | 0.02 | 0.59 | 1.11 | Quadratic |
| Shrimp            | $y = 5.02x - 15.89$ | 0.04 | 0.35 | 2.41 | $y = 4.73x^2 - 67.31x + 260.41$ | 0.13 | 0.36 | 2.43 | Linear    |
| Blue crab         | $y = 1.26x + 5.15$  | 0.64 | 0.03 | 1.63 | $y = 16.96x^2 - 257.82x + 993.36$ | 0.35 | 0.26 | 1.41 | N/A       |
Table S3. Linear and quadratic regression analysis of ∆pH as a function of seawater pH via the least squares method. Significant regressions (p < 0.05) that minimized RMSE (root mean square error) were selected as optimal models (bold). N/A denotes no significant trend.

| Organism          | Linear                           | Quadratic                           | Best-fit |
|-------------------|----------------------------------|-------------------------------------|----------|
|                   | Regression                       | Regression                          |          |
|                   | y = -1.2x + 9.53                 | y = -1.66x^2 + 24.29x - 88.25       | Quadratic |
| Purple urchin     | 0.00 0.88 0.11                   | 0.00 0.94 0.08                      |          |
| Pencil urchin     | y = -0.89x + 7.23                | y = 0.55x^2 - 9.38x + 39.79         | Quadratic |
|                   | 0.00 0.96 0.05                   | 0.00 0.97 0.04                      |          |
| Temperate coral   | y = -1.03x + 8.79                | y = 0.01x^2 - 1.25x + 9.63          | Linear   |
|                   | 0.00 0.97 0.04                   | 0.00 0.97 0.04                      |          |
| Oyster            | y = -1.01x + 7.99                | y = -1.17x^2 + 17.17x - 62.72       | Quadratic |
|                   | 0.00 0.65 0.20                   | 0.01 0.68 0.19                      |          |
| Hard clam         | y = -0.84x + 6.64                | y = 0.42x^2 - 7.36x + 31.97         | Linear   |
|                   | 0.01 0.62 0.19                   | 0.05 0.62 0.18                      |          |
| Blue mussel       | y = x + 7.64                     | y = -0.8x^2 + 11.44x - 40.74        | Quadratic |
|                   | 0.00 0.62 0.21                   | 0.01 0.63 0.20                      |          |
| Coralline red alga| y = 0.1x + 0.37                  | y = -1.23x^2 + 19.24x - 74.28       | N/A      |
|                   | 0.67 0.03 0.16                   | 0.61 0.15 0.15                      |          |
| Serpulid Worm     | y = -0.47x + 3.83                | y = 1.23x^2 - 19.55x + 77.99        | Quadratic |
|                   | 0.02 0.43 0.13                   | 0.04 0.51 0.12                      |          |
| Shrimp            | y = -0.61x + 5.51                | y = 0.01x^2 - 0.77x + 6.09          | Linear   |
|                   | 0.00 0.57 0.14                   | 0.02 0.57 0.14                      |          |
| Blue crab         | y = -0.44x + 3.28                | y = 2.15x^2 - 33.34x + 128.79       | N/A      |
|                   | 0.44 0.08 0.41                   | 0.55 0.16 0.39                      |          |