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Contribution to Special Issue: 'Towards a Broader Perspective on Ocean Acidification Research' **Response**

Response to Waldbusser *et al.* (2016): "Calcium carbonate saturation state: on myths and this or that stories"

Tyler Cyronak^{1*}, Kai G. Schulz², and Paul L. Jokiel³

¹Scripps Institution of Oceanography, UC San Diego, 9500 Gilman Drive 0244, La Jolla, CA 92093-0244, USA
²Centre for Coastal Biogeochemistry, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia
³Hawaii Institute of Marine Biology, University of Hawaii, PO Box 1346, Kaneohe, HI 96744, USA

*Corresponding author: tel: +1 610 701 1117; fax: +1 858 822 3310; e-mail: tcyronak@gmail.com

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Currently, almost any article searched with the keywords "calcification" and "ocean acidification" (OA) will inevitably bring up a link between calcification and bulk seawater carbonate saturation state (Ω) as a justification for the study. Therefore, it seems timely to highlight that from a physiological point of view, there are mechanisms that invoke control of calcification by seawater bicarbonate (HCO₃⁻) and proton (H⁺) concentrations rather than Ω in many marine organisms. While we agree with Waldbusser et al. (2016) that there is a vast diversity of marine calcification, it seems adequate to assume a similar underlying physiological response to OA unless shown otherwise.

We do not necessarily interpret the seeming Ω sensitivity of calcification as substrate limitation, as suggested by Waldbusser et al. (2016), we simply question the mechanisms that would invoke bulk seawater Ω as a driving force of calcification in the first place. Waldbusser et al. (2016) rightfully note the co-variability of seawater Ω with the ratio of [HCO₃⁻] to [H⁺]. Recently, Bach (2015) demonstrated that a rearrangement of carbonate system equations results in an inevitable proportionality between Ω and the ratio of [HCO₃⁻] to [H⁺]. Owing to this proportionality, calcification rates will always correlate as well with $[HCO_3^-]/[H^+]$ as they do with $[CO_3^{2-}]$ or Ω when temperature, salinity, and pressure are constant (Figure 1). Hence, the good correlations with bulk seawater $[{\rm CO_3}^{2-}]$ or Ω that have previously been reported [examples given in Waldbusser et al. (2016)] can equally be interpreted as the influence of [HCO₃⁻] and [H⁺], which are physiologically more meaningful carbonate system parameters.

We acknowledge that Ω influences calcification rates in accordance with the kinetic mechanism invoked by Waldbusser et al. (2016), the difference being that it is the internal Ω (not bulk seawater Ω) that is important, which is most likely modulated by bulk seawater $[HCO_3^{-}]$ and $[H^+]$ and not bulk seawater Ω . The ratio of $[HCO_3^{-}]$ to $[H^+]$ incorporates both the substrate (needed to be supplied from bulk seawater to the site of calcification) and waste product (needed to be removed from the site of calcification to bulk seawater) during the biogenic production of CaCO₃. It must be emphasized that both parameters should be included when looking at the effects of seawater carbonate chemistry on calcification because increasing seawater HCO₃⁻ concentrations could compensate for unfavourable pH ([H⁺]) conditions (see Bach, 2015). In essence, the more substrate (e.g. HCO3⁻) is available for uptake from bulk seawater the better a calcifying organisms is able to cope with lowered pH levels by keeping internal Ω at the site of calcification favourable for CaCO3 precipitation. Low substrate availability together with low pH (high [H⁺]) levels would make calcification more difficult. In general, high [HCO₃⁻]/[H⁺] ratios would be favourable to calcification while low ones become detrimental. In this respect, it also does not matter how well an organism, or ontogenetic life stage, is able to separate the internal calcifying fluid from external seawater as suggested by Waldbusser et al. (2016), its sensitivity to external carbonate chemistry changes will simply scale with its ability to modulate internal carbonate chemistry. We also acknowledge that there are other processes involved in calcification such as protein synthesis, however, bulk seawater HCO₃⁻ and H⁺ concentrations or its ratio ultimately influence the energetic demands of calcification.

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Figure 1. Mussel shell length vs. (a) aragonite saturation state (Ω_{ar}), (b) the ratio of bicarbonate (HCO₃⁻⁻) to proton (H⁺) concentration in the



Figure 2. Plot showing the mass normalized dissolution rate (d^{-1}) of biogenic aragonites derived from $R = k \times (1 - \Omega)^{2.5}$ at the two extreme k values from Walter and Morse (1985). The black lines show the range of mass normalized calcification rates of larval mussels from Waldbusser *et al.* (2013). From this, it is obvious that dissolution rates can account for changes in bivalve net calcification once Ω drops below 1, which may happen in the calcifying fluid before in the external seawater (Thomsen *et al.*, 2010; Heinemann *et al.*, 2012). The proportion of normal (PN) mussel larvae (Waldbusser *et al.*, 2015b) is plotted to demonstrate how changes in mussel shell development could be related to dissolution rates.

Another potential issue concerning the influence of Ω on calcification rates is that CaCO₃ dissolution becomes thermodynamically favourable at $\Omega < 1$. If dissolution is not accounted for, it would enhance relationships between the biologically mediated process of calcification (gross calcification) and Ω [HCO₃⁻]/[H⁺], Waldbusser et al. (2016) briefly discuss that CaCO₃ dissolution rates cannot account for changes in calcification under elevated CO₂ reported in several studies on bivalve larvae. However, they report no quantitative analysis of this except to say that dissolution follows the kinetic rate equation;

$$R = k \times (1 - \Omega)^n,$$

where *R* is the dissolution rate (μ mol g⁻¹ h⁻¹), *k* the rate constant (μ mol g⁻¹ h⁻¹), and *n* the reaction order. Using a reaction order of *n* = 2.5 and a range of *k* values (467.7–1258.9 μ mol m⁻² h⁻¹) for biogenic aragonites taken from Table 6 in Walter and Morse (1985) demonstrates that dissolution may in fact be very important in controlling a bivalve's response to increasing seawater CO₂ (Figure 2). At the highest *k* value, dissolution rates of aragonite exceed the mass normalized measured net calcification rates of larval mussels (0.45 d⁻¹) around an aragonite saturation state (Ω_{ar}) of 0.5, while at the lowest *k* value, dissolution exceeds measured net calcification around a seawater Ω_{ar} of 0.3 also coincides with the point at which the proportion of

total scale, and (c) $\Omega_{\rm ar}$ vs. [HCO₃⁻]/[H⁺]. Data from Waldbusser *et al.* (2015b) were downloaded from the Biological and Chemical Oceanography Data Management website (http://www.bco-dmo .org/dataset/557253) and carbonate chemistry parameters were recalculated using the TA and DIC data at a salinity of 31 and temperature of 18°C.

normal larval mussel shells approaches zero (Waldbusser et al., 2015a, b, 2016). Therefore, this mass balance lends support to dissolution being a potential driver of changes in larval mussel shell development in high CO2 seawater. In support of this, it has been demonstrated that internal (within the calcifying fluid) and external shell dissolution significantly affect the mortality of juvenile and adult bivalves at low Ω (Green *et al.*, 2004; Melzner *et al.*, 2011). As pointed out by Waldbusser et al. (2016), the response of larval mussels to Ω seems to have a threshold where shell development becomes severely compromised (Waldbusser et al., 2015a, b). Considering the response of mussel larvae to seawater Ω occurs very close to a bulk seawater Ω of 1, and continues after $\Omega < 1$, perhaps the threshold is a response due to dissolution becoming thermodynamically favourable either inside or outside of the calcifying fluid. Therefore, the possibility that changes in CaCO₃ dissolution rates drive changes in larval mussel shell development when Ω of the calcifying fluid or external seawater <1 cannot be excluded.

We do not dispute the fact that Ω can, and does, affect the biogenic CaCO₃ budgets of marine organisms. However, it must be emphasized that, ultimately, it is the Ω of the calcifying fluid that controls precipitation kinetics, and not the bulk seawater. Furthermore, when Ω of either the calcifying fluid or bulk seawater is <1, dissolution of CaCO₃ could become important. Future studies should attempt to tease apart the influence of changes in bulk seawater chemistry on the chemistry of the calcifying fluid, and therefore, internal CaCO₃ precipitation kinetics, along with any changes in CaCO₃ dissolution. Organisms that are able to actively control carbonate chemistry at the site of calcification are most likely responding to changes in bulk seawater carbonate chemistry that affect their ability to maintain that physiological control. As outlined above and in the original paper, there is no clear physiological basis as to why seawater Ω should be one of these variables, but rather seawater $[HCO_3^-]$ and $[H^+]$.

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