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Interactive comment on "Reconsidering the role of carbonate ion concentration in calcification by marine organisms" *by* L. T. Bach

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Reconsidering the role of carbonate ion concentration in calcification by marine organisms

By L. T. Bach

Correlation does not prove cause and effect, yet the correlation between calcification in marine organisms and [CO32-] has led to the widespread paradigm that [CO32-] limits calcification. Adopting this idea creates conflicts because other observations indicate that HCO3- rather than CO32- is the substrate used for calcification as well as photosynthesis. Bach has made a major contribution in resolving this dilemma through

a rearrangement of the carbonate system equations to show the proportional relationship between [CO32-] and the ratio of [HCO3-] to [H+]. Due to this proportionality rule, calcification rates will always correlate well with the ratio of [HCO3-] to [H+] and equally well with the ratio of [CO32-] to Ω when temperature, salinity, and pressure are constant. Thus [CO32-] and Ω are simply good proxies for the control of calcification by [HCO3-] / [H+] where [HCO3-] is the inorganic carbon substrate and [H+] functions as a calcification inhibitor. The proportionalities between [CO32-] or Ω and the derived [HCO3-] / [H+] relationship provide the chemical basis to reconcile conflicting results. Every correlation between calcification and [CO32-] or Ω will be identical to the corresponding correlation with [HCO3-] / [H+] when T , S, and P are stable. Thus, the correlations between calcification and [CO32-] and Ω that have previously been reported are more likely attributed to the combined influence of [HCO3-] and [H+]which are the more meaningful physiological parameters.

If this "substrate-inhibitor ratio" rather than [CO32-] or Ω controls CaCO3 formation then basic paradigms in ocean acidification research need to be reconsidered. For example, the absence of a latitudinal gradient in [HCO3-] / [H+] in contrast to strong gradients in [CO32-] and Ω negates the common assumption that high latitudes will be affected most severely by ocean acidification. Bach's comparison of present and future [CO32-], Ω, and [HCO3-]/[H+] patterns in the surface ocean revealed a strong poleward decline in [CO32-] and Ω but no decline in [HCO3-] / [H+]. These highly different latitudinal patterns are conserved in models of future climate change. Thus ocean acidification may be a more uniform problem at all latitudes for biotic CaCO3 formation than previously thought.

There has been a long struggle to determine the calcification-relevant inorganic carbon species taken from seawater in order to understand the calcification response of marine organisms to changing carbonate chemistry. Many studies assume that HCO3- rather than CO32- is the primary inorganic source. However, studies undertaken to determine the inorganic carbon molecule transported by molecular transport systems

have not been successful. Bach approached this question using a carbonate chemistry approach to determine whether HCO3- or CO32- would be the more suitable inorganic carbon substrate for calcification. Three different lines of analysis led to his conclusion that HCO3- would be favored: (1) Abundance. HCO3- is the most abundant DIC species in seawater. It makes sense for an organism to rely on the largest inorganic carbon pool. (2) Homeostasis. The hydration time of CO2 is slow while the hydrolysis of HCO32- is fast. Thus CO32- transported through cytosol with a typical pH of 7.2 would quickly turn into HCO3- and bind a proton in the cytosol. The resulting HCO3- would be transported to the calcification site where the proton would be released back to the cytosol. Hence, the cytosolic pH would remain stable in case of selective CO32- uptake only when CO3- uptake and CaCO3 precipitation occur at the same rate. However, both processes probably run out of equilibrium on occasion, especially in a highly variable diurnal environment. In these cases, the utilization of CO32- as the inorganic carbon source would constitute a substantial risk for the pH homeostasis. Excess CO32- uptake would elevate cytosolic pH while excess CaCO3 precipitation would reduce it. In contrast, a selective uptake of HCO3- from seawater would not perturb the cytosolic pH as much under these conditions because HCO3- has a relatively low potential to accept or donate H+ at pH 7.2. It may therefore be easier for calcifiers to keep cytosolic pH stable at 7.2 by using HCO3-. (3) Stability. Seawater pH fluctuate substantially in a diurnal and seasonal timescale with HCO3- having a dominant stable concentration over the entire pH range encountered by marine organisms, while [CO32-] will show extreme variation. Thus HCO3- is a much more reliable inorganic carbon source for calcification.

In sum, this paper makes major contributions to our understanding of the process of calcification in marine organisms, reconciles differences in results from various studies and provides new insights into predicting future changes in marine communities due to ocean acidification.

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