

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

Anonymous Referee #2

Received and published: 22 July 2015

Summary

This is really extremely interesting, a great summary of relatively recent developments in thinking and taking the calcification/carbonate chemistry usefully further still. As a thought-provoking paper, it does not necessarily require/need much alteration to my mind, although ... there are other perspectives that need to be explored a little.

Overarching/main comments

So I find myself agreeing with the statement, which was also expressed virtually identically in a paper by Jokiel, that there is no physiological basis for tying $[\text{CO}_3^{2-}]$ or Ω to

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some measure of calcification (rate). But, I feel it is going to far to state that they are 'meaningless' in this context, as Lennart does (e.g. in Section 3.4). I have three different potted perspectives to throw out here on this – of varying helpfulness and relevance (and not necessarily in order here) – and anyone is very welcome to shoot some or all of them down. In fact, some of these thoughts have been haunting me for years and if there is a simple way of dismissing them, I'd probably sleep much better at night :)

1. Firstly, there is the question of the conditions required for the organisms to usefully precipitate calcium carbonate. (The following thoughts are arguably more applicable to hypercalcifiers such as tropical corals and maybe less so to e.g. coccolithophores.)

While the precipitation of carbonate minerals is thermodynamically favourable under conditions of $\Omega > 1$, the kinetics are not favourable for only relatively small degrees of supersaturation (although in the case of coccolithophores, presumably the kinetic barrier is considerably reduced by charged / functional groups the organic scaffolding that is layed down?). Given that surface ocean seawater is generally everywhere supersaturated (with respect to both calcite and aragonite) today, modification of the interior calcification space by e.g. corals is not done because calcium carbonate cannot be precipitated (although CO_2 released through dark respiration could potentially create under-saturated conditions) but because calcification would not otherwise occur on a biologically/ecologically useful time-scale to the organism. The faster the rate of carbonate production required, the higher the degree of super-saturation (or potentially faster the rate of seawater movement into the calcifying space) required. A thermodynamic energy difference can be assigned to the difference in modified vs. unmodified seawater, and higher super-saturation equates to a greater energy difference. Conversely, for the same internal degree of super-saturation and hence required precipitation rate, a lower saturation environment also equates to a greater external vs. internal energy difference.

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I appreciate the argument that proton transport may be the physiological relevant mechanism for maintaining internal saturation and under ocean acidification, enhancing the difference between internal and external, but saturation is still a useful concept in quantifying the thermodynamic budget. Indeed, ultimately, the thermodynamic driver for ambient seawater $[\text{CO}_3^{2-}]$ and $[\text{Ca}^{2+}]$ to precipitate as $\text{CaCO}_{3(s)}$, declines with ocean acidification and reduced ambient $[\text{CO}_3^{2-}]$. This increased energetic cost (or reduced benefit) can be encapsulated in the saturation concept regardless of whether this represents the full physiological/energetic cost to the organism or not.

In summary: I see Ω as a thermodynamically relevant measure that changes in a mechanistic interpretable way with ocean acidification, even if it is not the entire story, and hence should not be discarded in its entirety from usage.

2. There are important past implications of how impacts/controls on calcification are described and understood.

Consider the Cenozoic projections of seawater carbonate chemistry of Tyrrell and Zeebe [2004] and Ridgwell [2005]. At higher past (earlier Cenozoic) atmospheric pCO_2 concentrations (as all proxies generally agree on), ocean surface $[\text{H}^+]$ is rather higher. Multiple proxies also suggest higher $[\text{Ca}^{2+}]$ (and lower $[\text{Mg}^{2+}]$) earlier in the Cenozoic. Now given an 'adequate' global biogenic production rate of calcium carbonate, carbonate dissolution in marine sediments will control the mean saturation state of the ocean and in fact, regulate it to be relatively similar to modern (given that preservation is much more sensitive to changes in ocean saturation than global rates of weathering and hence global burial are likely to vary through time). At high $[\text{Ca}^{2+}]$, similar-to-modern Ω requires lower $[\text{CO}_3^{2-}]$. The upshot is that earlier in the Cenozoic (and e.g. later Cretaceous), pH would have been lower, $[\text{H}^+]$ much higher, but $[\text{HCO}_3^-]$ similar to modern.

The implications are: assuming that the proxies are even vaguely 'correct' (they need be only 'correct' in the signs of their respective trends with time through the

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Cenozoic for the argument to hold) and these carbonate chemistry / carbon cycle model assumptions and calculations are also not fundamentally flawed:

- That saturation is an important concept because it helps explain abundant global calcification under conditions of much lower past $[\text{HCO}_3^-]/[\text{H}^+]$ (but similar to modern surface Ω).
- $[\text{HCO}_3^-]/[\text{H}^+]$ is the only game in town (in terms of dictating the cost of calcification), but given the higher projected past $[\text{HCO}_3^-]/[\text{H}^+]$ ratios as compared to may occur in the future (end of century), future ocean acidification will have no impact on calcifying organisms. i.e. past high $[\text{HCO}_3^-]/[\text{H}^+]$ plus abundant calcification implies not future impact.
- $[\text{HCO}_3^-]/[\text{H}^+]$ is the only game in town, but the physiology of past calcifiers was very different and they have undergone fundamental evolutionary changes since, and have lost their ability to calcify well at low $[\text{HCO}_3^-]/[\text{H}^+]$. (This then requires some suggestion as to how their calcification physiological was so fundamentally different.)

or some combination, of none of the above. The point being to explain that if the $[\text{HCO}_3^-]/[\text{H}^+]$ ratio is the sole determining factor to consider, how can we reconcile low past $[\text{HCO}_3^-]/[\text{H}^+]$ ratios with abundant calcification, with concerns for the future?

3. Lastly, it is worth considering what is the barrier to globally abundant calcification occurring by e.g. benthic foraminifera (or other calcifiers) at great depth in the ocean. $[\text{HCO}_3^-]/[\text{H}^+]$ may not be drastically different on the abyssal seafloor compared to the surface, and given a protective membrane, dissolution would not be an issue. This tends to suggest to me that low external saturation (even undersaturation) and at great depth is indeed a relevant and mechanistically (even if not physiologically) based factor in understanding calcification and calcification rates.

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My overall summary comment would be: Do we not need to take into consideration and appreciate both facets of the carbonate chemistry system and both physiological and thermodynamic energy costs? The challenge might then be to combine their different facets in understanding ocean acidification controls on biogenic calcification, particularly as Lennart so eloquently argues and illustrates as with their (experimental) co-variance(?)

Interactive comment on Biogeosciences Discuss., 12, 6689, 2015.

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