

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

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I thank Reviewer #2 for the motivating comments and the interesting perspectives she/he raised.

In general, I think that the questions raised by Reviewer 2 can be answered when strengthening the necessary distinction between gross calcification (CaCO_3 precipitation) and net calcification (CaCO_3 precipitation + dissolution). $[\text{HCO}_3^-]/[\text{H}^+]$ would only be applicable to explain gross calcification (which usually equals net calcification if $\Omega_{\text{CaCO}_3} > 1$). I emphasized the distinction between gross and net calcification in the revised version of the manuscript. In section 3.6.1, for example, I changed the headline and wrote:

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Discussion Paper



“3.6.1. Corrosive conditions - accounting for the difference between gross and net calcification

When discussing the influence of carbonate chemistry on calcification, distinction needs to be made between formation and dissolution of CaCO_3 since these two processes are possibly controlled by different carbonate chemistry parameters. The roles of CaCO_3 formation and dissolution are incorporated into the terms gross and net calcification. The former exclusively refers to the precipitation of CaCO_3 whereas the latter accounts for both precipitation and dissolution. The ratio of $[\text{HCO}_3^-]$ and $[\text{H}^+]$ can potentially be very useful to determine gross calcification which equals net calcification under non-corrosive conditions (i.e. $\Omega_{\text{CaCO}_3} > 1$). When Ω_{CaCO_3} falls below 1, however, the control of $[\text{HCO}_3^-]/[\text{H}^+]$ on gross calcification would be obscured by the abiotic influence of Ω_{CaCO_3} on dissolution. Accordingly, corrosive conditions would require consideration of both $[\text{HCO}_3^-]/[\text{H}^+]$ and Ω_{CaCO_3} in order to correctly estimate the impact of carbonate chemistry on net biotic CaCO_3 formation.”

Comment 1 by REVIEWER 2: *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 > 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) to-day, 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 timescale to the organism. The faster the rate of carbonate production required, the higher the degree of*

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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. 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 $[CO_3^{2-}]$ and $[Ca^{2+}]$ to precipitate as $CaCO_3(s)$, declines with ocean acidification and reduced ambient $[CO_3^{2-}]$. 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.

REPLY: I agree with Reviewer #2 that $\Omega CaCO_3$ can be a useful parameter for correlations with calcification, when considering net calcification and not only gross calcification. The term ‘meaningless’ was used in a context where I addressed gross calcification (see section 3.2). To avoid confusion, I changed ‘meaningless’ to ‘not useful’ to account for the fact that (1) $\Omega CaCO_3$ co-correlates with $[HCO_3^-]/[H^+]$ under constant T, S, and P and may therefore often (indirectly) explain gross calcification (section 3.2) and (2) that $\Omega CaCO_3$ contains information on the corrosiveness of seawater and is therefore the key parameter to correlate calcification with when dissolution processes are much more important than precipitation. This has been addressed in sections 3.6.1 and 3.6.2 of the revised version of the manuscript.

Reviewer 2 argues that $\Omega CaCO_3$ could be an appropriate measure for the carbonate

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chemistry control on calcification as it addresses calcification rates from a thermodynamic point of view. I agree with this statement as long as it refers to abiotic dissolution processes under corrosive conditions (see above). I disagree with this statement when arguing for CaCO_3 formation, because how would we be able to explain that many calcifiers are able to precipitate CaCO_3 when Ω_{CaCO_3} is below 1 and conditions therefore thermodynamically unfavorable? In the coccolithophore *Emiliania huxleyi*, for example, we detected calcification at Ω_{calcite} of as low as 0.16 in case there was sufficient HCO_3^- substrate available but could not detect any signs of calcification at Ω_{calcite} of 4.3 in case $[\text{HCO}_3^-]$ was low (Bach et al., 2015).

Comment 2 by REVIEWER #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 $p\text{CO}_2$ 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 Cenozoic for the argument to hold) and these carbonate chemistry/carbon cycle model assumptions and calculations are also not fundamentally flawed:*

1) 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

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surface Ω).

2)[HCO_3^-]/[H^+] is the only game in town (in terms of dictating the cost of calcification), but given the higher projected past [HCO_3^-]/[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 [HCO_3^-]/[H^+] plus abundant calcification implies not future impact.

3)[HCO_3^-]/[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 [HCO_3^-]/[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 [HCO_3^-]/[H^+] ratio is the sole determining factor to consider, how can we reconcile low past [HCO_3^-]/[H^+] ratios with abundant calcification, with concerns for the future?

REPLY: Reviewer 2 argues that the Cenozoic was characterized by lower than modern [HCO_3^-]/[H^+] but still had abundant calcification which would argue against the relevance of [HCO_3^-]/[H^+] to explain calcification rates. I was struggling a bit with the term 'abundant' in this context because it could either refer to the relatively high diversity of calcifiers during this time (Martin, 1995) or relatively high CaCO_3 accumulation rates (Ridgwell, 2005).

Diversity: [HCO_3^-]/[H^+] would probably not be a very useful measure to assess the diversity of calcifiers as it determines a rate. Diversity can be independent of the calcification rate and is probably related to paleogeography rather than carbonate chemistry (Martin, 1995).

CaCO_3 accumulation rate: The amount of CaCO_3 accumulating on the sea floor is balanced by CaCO_3 precipitation, post-production dissolution, and alterations during

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12, C3905–C3912, 2015

Interactive
Comment

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Interactive Discussion

Discussion Paper

diagenesis. Accordingly, CaCO_3 accumulation can be relatively high even if precipitation is low in case dissolution is also low. Thus, $[\text{HCO}_3^-]/[\text{H}^+]$ cannot be used to explain CaCO_3 accumulation in the geological record as it would be only applicable for biogenic precipitation rates (gross calcification).

Reviewer #2 addressed an important question in comment 2 and I therefore added a new section (3.6.2, see below) to the manuscript which explicitly addresses the applicability of $[\text{HCO}_3^-]/[\text{H}^+]$ in the geological record.

“3.6.2 The Applicability of $[\text{HCO}_3^-]/[\text{H}^+]$ in the geological record

The restriction of $[\text{HCO}_3^-]/[\text{H}^+]$ to gross calcification rates (see previous section) limits its applicability in the geological record because the information on CaCO_3 accumulation conserved in the sediments is not only affected by gross calcification but also by post-production dissolution and abiotic modifications of CaCO_3 during diagenesis which are both controlled by ΩCaCO_3 . Thus, in order to verify the substrate-inhibitor concept for the geological record we would need a reliable proxy for biogenic gross calcification exclusively. Conversely, the application of ΩCaCO_3 to investigate trends in CaCO_3 sedimentation (e.g. Ridgwell 2005; Hönisch et al. 2012) would be reasonable because sedimentation involves both precipitation and dissolution and ΩCaCO_3 is a good indicator for the former (under constant T, S, P) and the key parameter for the latter.”

Comment 3a by REVIEWER #2: *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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REPLY: Although the vertical decline is more pronounced in ΩCaCO_3 , it is also present in $[\text{HCO}_3^-]/[\text{H}^+]$ (Fig. 7). I think on this basis it cannot be determined whether carbonate chemistry conditions for calcification deteriorate because of ΩCaCO_3 or $[\text{HCO}_3^-]/[\text{H}^+]$.

Comment 3b by REVIEWER #2 *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(?)*

REPLY: From my point of view (but see also papers by Jokiel), we would need to take into consideration that CaCO_3 precipitation is controlled by other carbonate chemistry parameters than dissolution. The common application of ΩCaCO_3 as carbonate chemistry indicator for calcification would only be useful to elucidate dissolution processes but its application would be limited with respect to the biotic formation of CaCO_3 due to the differences in latitudinal and vertical gradients (section 3.5.1). With respect to ocean acidification research it should then be distinguished more clearly whether a measured (or computed) response to changing carbonate chemistry was driven by impacts on the formation or dissolution of CaCO_3 . So I agree with Reviewer 2 that we need to appreciate the different roles of different carbonate chemistry parameters on biotic calcification. This aspect has been strengthened in section 3.6.1 in the revised version of the manuscript.

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