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Interactive comment on "Impact of seawater carbonate chemistry on the calcification of marine bivalves" *by* J. Thomsen et al.

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Thomsen et al. measured the calcification rates of mussel larvae in waters of highly modified carbonate chemistries. This is relevant to rising CO2 levels and ocean acidification, but the chemical modifications tested here transcend simple scenarios of rising CO2 levels. Instead, they are designed to tease out some of the chemical controls on biological calcification. In particular, Thomsen et al. hope to learn about the carbon sources for calcification. Mussel calcification does not increase monotonically with ambient pH, CO2, or HCO3-. CO3= may present a simpler situation, although the curve would be more definitive if it had more intermediate points. Ca2+ concentration is presumably constant in these experiments, so CO3= determines the CaCO3 saturation state Ω. So maybe ambient Ω determines mussel calcification rate. The simpler experiment of altering seawater Ca2+ concentrations might clarify this. Yet ambient CaCO3 saturation is just part of the story. Inorganic (non-biological) calcification ceases in undersaturated waters (Ω<1), yet mussels continue to calcify at Ω=0.15 and pH 7.16. Inorganic calcification increases faster with Ω than does biological calcification. Biological calcification also plateaus at CO3= levels above normal ambient, while inorganic calcification rates would increase exponentially. Mollusk calcification therefore depends on more than ambient CO3= or Ω. Thomsen et al. note that mussels calcify within semi-isolated environments where Ω is probably elevated, but don't say how mollusks might elevate Ω. Proton removal is probably the key. Why? Because pH elevation is biologically common, can occur through many possible mechanisms, and has been observed in many calcifying organisms including the extrapallial space of mollusks. pH elevation guarantees CO3= elevation. HCO3- converts to CO3=, and CO2 diffuses into the alkaline fluid (across biologically permeable membranes) and ionizes to produce more CO3=. CO3= accumulation is probably the main factor elevating Ω, even more important than Ca2+ pumping. Furthermore, both Ca2+ pumping and pH elevation likely occur through a single mechanism: Ca2+/2H+ exchange catalyzed by the enzyme Ca2+ ATPase. CO3= accumulation is not itself an energy dependent "active" transport process, but it occurs because of active H+ export from the calcification site, likely catalyzed by Ca2+ ATPase. Biological processes, ranging from ion transport to respiration, therefore control mussel calcification rates. Why does ambient carbonate chemistry matter? Perhaps carbon transport limits calcification at low carbon concentrations. Thomsen et al show that calcification rate plateaus at high carbonate levels, suggesting some degree of carbon limitation at lower carbonate levels. (Please present the same data plotted against HCO3- or CT.) Mollusks generally have high levels of the enzyme carbonic anhydrase. It speeds carbon transport through tissues by converting HCO3- to CO2, which permeates biological membranes more quickly. The need to accelerate CO2 movement provides a possible reason for the carbonic anhydrase. The strong 18O and 13C deficiencies observed in many biological carbonates also suggest some degree of carbon limitation. Mollusks generally don't show these isotopic disequilibria, perhaps because they use carbonic anhydrase rather than high pH at the calcification site to speed CO2 reactions, and a have physically “thick” extrapallial space. Nevertheless, the existence of 18O and 13C deficiencies in various biological carbonates argues for some degree of carbon limitation. Thomsen et al. suggest that ambient HCO3- is likely the main carbon source for mussel calcification. This is likely true. McConnaughey and Gillikin (2008), and papers referenced therein model how and when this might come about. So why do Thomsen’s mussels calcify most linearly when plotted against CO3=? Probably not because the mussels preferentially bring CO3= to the calcification site. No enzyme preferentially transports CO3=, as far as I know. Even if some enzyme did, CO3= would still convert to HCO3- and CO2 before it reached the calcification site. The situation may be fairly complicated. After all, the calcification site is largely isolated from ambient water by the intervening tissue layers, whose pH and CO2 levels may be different from both the ambient waters and the calcification site. Tissue pH is tightly regulated. So it may take some clever models and experiments to figure out why calcification rate appears to increase with CO3=. Ted McConnaughey (mcconnat@gmail.com)

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