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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 CO<sub>2</sub> levels and ocean acidification, but the chemical modifications tested here transcend simple scenarios of rising CO<sub>2</sub> 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, CO<sub>2</sub>, or HCO<sub>3</sub><sup>-</sup>. CO<sub>3</sub><sup>=</sup> may present a simpler situation, although the curve would be more definitive if it had more intermediate points. Ca<sup>2+</sup> concentration is presumably constant in these experiments, so CO<sub>3</sub><sup>=</sup> determines the CaCO<sub>3</sub> saturation state  $\Omega$ . So maybe ambient  $\Omega$  determines mussel calcification rate. The

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simpler experiment of altering seawater  $\text{Ca}^{2+}$  concentrations might clarify this. Yet ambient  $\text{CaCO}_3$  saturation is just part of the story. Inorganic (non-biological) calcification ceases in undersaturated waters ( $\Omega < 1$ ), yet mussels continue to calcify at  $\Omega = 0.15$  and pH 7.16. Inorganic calcification increases faster with  $\Omega$  than does biological calcification. Biological calcification also plateaus at  $\text{CO}_3^{2-}$  levels above normal ambient, while inorganic calcification rates would increase exponentially. Mollusk calcification therefore depends on more than ambient  $\text{CO}_3^{2-}$  or  $\Omega$ . Thomsen et al. note that mussels calcify within semi-isolated environments where  $\Omega$  is probably elevated, but don't say how mollusks might elevate  $\Omega$ . 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  $\text{CO}_3^{2-}$  elevation.  $\text{HCO}_3^-$  converts to  $\text{CO}_3^{2-}$ , and  $\text{CO}_2$  diffuses into the alkaline fluid (across biologically permeable membranes) and ionizes to produce more  $\text{CO}_3^{2-}$ .  $\text{CO}_3^{2-}$  accumulation is probably the main factor elevating  $\Omega$ , even more important than  $\text{Ca}^{2+}$  pumping. Furthermore, both  $\text{Ca}^{2+}$  pumping and pH elevation likely occur through a single mechanism:  $\text{Ca}^{2+}/2\text{H}^+$  exchange catalyzed by the enzyme  $\text{Ca}^{2+}$  ATPase.  $\text{CO}_3^{2-}$  accumulation is not itself an energy dependent "active" transport process, but it occurs because of active  $\text{H}^+$  export from the calcification site, likely catalyzed by  $\text{Ca}^{2+}$  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  $\text{HCO}_3^-$  or CT.) Mollusks generally have high levels of the enzyme carbonic anhydrase. It speeds carbon transport through tissues by converting  $\text{HCO}_3^-$  to  $\text{CO}_2$ , which permeates biological membranes more quickly. The need to accelerate  $\text{CO}_2$  movement provides a possible reason for the carbonic anhydrase. The strong  $^{18}\text{O}$  and  $^{13}\text{C}$  deficiencies observed in many biological carbonates also suggest some degree of carbon limitation. Mollusks generally don't show

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these isotopic disequilibria, perhaps because they use carbonic anhydrase rather than high pH at the calcification site to speed CO<sub>2</sub> reactions, and a have physically “thick” extrapallial space. Nevertheless, the existence of <sup>18</sup>O and <sup>13</sup>C deficiencies in various biological carbonates argues for some degree of carbon limitation. Thomsen et al. suggest that ambient HCO<sub>3</sub><sup>-</sup> is likely the main carbon source for mussel calcification. This is likely true. McConaughey 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 CO<sub>3</sub>=? Probably not because the mussels preferentially bring CO<sub>3</sub>= to the calcification site. No enzyme preferentially transports CO<sub>3</sub>=, as far as I know. Even if some enzyme did, CO<sub>3</sub>= would still convert to HCO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>3</sub>=. Ted McConaughey (mcconnat@gmail.com)

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