Carbon isotope fractionation in the 3HP/4HB pathway

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The 3-hydroxypropionate/4-hydroxybutyrate (3HP/4HB) pathway is utilized by Thaumarchaeota and by thermophilic Crenarchaeota of the order *Sulfolobales*. Unlike all other autotrophic carbon metabolisms, this pathway exclusively uses HCO_3^-, rather than CO_2, as the substrate for carbon fixation. Accordingly, biomass produced by the 3HB/4HP pathway is ^{13}C-enriched relative to biomass fixed by pathways containing enzymes specific for CO_2 (*e.g.*, Rubisco), with total biosynthetic isotope effects (ε_{bio}) of *ca.* 2‰ in Crenarchaeota [1] and *ca.* 19‰ in Thaumarchaeota [2]. Suggested explanations for the large difference in ε values between the two groups usually invoke the dual effects of thermophily and growth at pH ≤ 3 (low [HCO_3^-]) for the Crenarchaeota vs. mesophily and growth at pH ≥ 7.5 (high [HCO_3^-]) for the Thaumarchaeota. Here we examine the taxa *Metallosphaera sedula* and *Nitrosopumilus maritimus* using isotope flux-balance models to argue that the primary cause of different ε values more likely is the presence of carbonic anhydrase in *M. sedula* and its corresponding absence in *N. maritimus*. The pool of HCO_3^- in *N. maritimus* is predicted to be out of isotopic equilibrium with CO_2, and the value of ε_{bio} implies that little if any HCO_3^- is assimilated directly from the extracellular environment. Marine Thaumarchaeota appear to be dependent on passive CO_2 uptake and a slow rate of intracellular conversion to HCO_3^-, implying that ε_{bio} should be sensitive to growth rate and CO_2 availability (μ/CO_2). This behavior is analogous to eukaryotic algae, but is predicted to occur in the opposite direction: ε_{bio} becomes smaller as [CO_2(aq)] increases. Although the μ/CO_2 response is predicted to be a small effect on ε_{bio}, such an idea represents a testable hypothesis for the marine Thaumarchaeota, both in the laboratory and in natural systems.

[1] van der Meer et al. (2001) *FEMS Microb. Lett.*196:67-70.
[2] Könneke et al. (2012) *Org. Geochem.* 48:21-24.