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To “b“ or not to “b“: evaluating the effect of calcification on stable isotope fractionation in coccoliths and coccolithophore biomarkers (alkenones)

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Coccolilthophore algae produce alkenone biomarkers, widely used for reconstruction of carbon isotopic fractionation during photosynthesis (epsilon p) and a proxy for past pCO_2. The $CaCO_3$ coccoliths produced by the algae are also the dominant carbonate contributor to marine sediments of Paleogene age and the carbon isotopic composition of this bulk carbonate is widely used to reconstruct variations in the exogenic carbon cycle. To date, the interaction between carbon uptake for calcification and photosynthesis has not been considered quantitatively. Given recent contraints on the permeability of cell membranes to CO_2, I develop a new cellular model of carbon uptake and allocation within the coccolithophorid cell, including a separate compartment for the chloroplast and the coccolith vesicle(CV). The model can be applied to an inverse problem, to ascertain the active fluxes of HCO_3- required to simulate the epsilon p and epsilon coccolith observed in coccolithophorids grown in culture. The inverse model shows that although HCO_3- is supplied to both the chloroplast and CV, at low CO_2 concentrations the cells preferentially allocate HCO_3- to photosynthesis. This reduction in the HCO_3- to CO_2 uptake into the CV results in a negative shift in epsilon coccolith Consequently, the coccolith carbon isotopic composition is not a good proxy for the isotopic composition of marine DIC and would not be better than foraminifera for calculating epsilon p from in combination with the isotopic composition of sedimentary alkenones. The HCO_3- uptake into the CV also affects epsilon p : higher uptake of HCO_3- into the CV, at constant calcification and fixation rates, can result in shift to higher epsilonp.