Hydrogen isotope fractionation is controlled by CO₂ in coccolithophore lipids

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Hydrogen isotope ratios (d²H) represent an important natural tracer of metabolic processes, but quantitative models of processes controlling H-fractionation in aquatic photosynthetic organisms are lacking. Here we elucidate the underlying physiological controls of d²H fractionation in algal lipids by systematically manipulating temperature, light and, for the first time, CO₂(aq) in continuous cultures of the haptophyte Gephyrocapsa oceanica. We analyze the hydrogen isotope fractionation in alkenones (alkenone), a class of acyl lipids specific to this species and other haptophyte algae. We find a strong decrease in the alkenone with increasing CO₂(aq), and confirm the alkenone correlates with temperature and light. Based on the known biosynthesis pathways, we develop a new cellular model of the d²H of algal acyl lipids to evaluate processes contributing to these controls on fractionation. Simulations show that longer residence times of NADPH in the chloroplast favor greater exchange of NADPH with d²H-richer intracellular water, increasing alkenone. Higher chloroplast CO₂(aq) and temperature shorten NADPH residence time by enhancing the carbon fixation and lipid synthesis rates. The inverse correlation of alkenone to CO₂(aq) in our cultures suggests that carbon concentrating mechanisms (CCM) do not achieve a constant saturation of CO₂ at the Rubisco site, but rather that chloroplast CO₂ varies with external CO₂(aq). The pervasive inverse correlation of alkenone with CO₂(aq) in the modern and preindustrial ocean also suggests that natural populations may not attain a constant saturation of Rubisco with the CCM. Rather than reconstructing growth water, alkenone may be a powerful tool to elucidate carbon limitation of photosynthesis.