

## **Phytoplankton CO<sub>2</sub> estimates and the carbon concentrating mechanism over Quaternary Glacial Cycles**

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Phytoplankton carbon isotopic fractionation has been widely used to indicate the ratio of carbon supply to carbon demand for photosynthesis, and thereby infer past changes in the carbon dioxide concentration of seawater and the atmosphere. However, the existing framework assumes that carbon supply for photosynthesis is regulated solely by the passive diffusive flux of CO<sub>2</sub> into the cell. However, laboratory studies show that under carbon limitation, cells actively enhance the carbon supply for photosynthesis. In laboratory culture, such carbon concentration has a clear effect on the phytoplankton isotopic concentration. If this is a widespread response of phytoplankton in the modern ocean, and an effect that varies depending on the degree of cellular C limitation and CO<sub>2</sub>, then accurate phytoplankton pCO<sub>2</sub> estimates will require accounting for this adaptation.

We review evidence for variation in the significance of carbon concentrating mechanisms in the ocean during Quaternary glacial cycles, by coupling records of alkenone carbon isotopic fractionation, independent proxy records of phytoplankton growth rate, and records of the carbon isotopic concentration in coccoliths, which may reflect the HCO<sub>3</sub> concentration allocated to calcification. These records reveal compelling evidence for increased significance of carbon concentrating mechanisms during the low pCO<sub>2</sub> glacial times, as well as evidence for growth rate forcing of carbon isotopic fractionation. We suggest that the observed range of photosynthetic fractionation in the modern photic zone is driven by both variations in growth rate and variations in the significance of carbon concentrating mechanisms forced by the range of dissolved CO<sub>2</sub> concentrations. Calibration relationships from the modern photic zone database, should not be applied for estimation of past pCO<sub>2</sub> from phytoplankton carbon isotopic fractionation without deconvolving these multiple effects.