Enzymatic controls on carbon isotope fractionation in marine phytoplankton

E.B. WILKES[1]*, S.J. CARTER[1] AND A. PEARSON[1]

[1]Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, USA (*correspondence: elisewilkes@fas.harvard.edu)

The carbon isotopic composition of algal organic matter preserved in marine sediments provides a window into the evolution of global carbon cycling through geologic time. These archives are typically interpreted by invoking an ~25‰ kinetic fractionation factor associated with the carbon-fixing enzyme RubisCO. This value corresponds to the maximum *in vivo* expression of photosynthetic carbon isotope fractionation measured for algae (ε_f values), and its approximate agreement with isotope effects measured on RubisCO purified from higher plants (Form IB RubisCO). In practice, values of ε_f have been inferred for different species from the ε_P-intercept of chemostat culture studies as the ratio $\mu/[CO_{2(aq)}]$ approaches zero [1]. However, these culture studies have been limited to phytoplankton species employing Form ID RubisCO and do not account for the existence of other kinetically and phylogenetically distinct forms of this enzyme.

Here we present chemostat culture experiments with a marine dinoflagellate employing Form II RubisCO—a structurally and catalytically unique form of RubisCO among phytoplankton. We characterized an ε_f value of ~27‰ from the intercept of six experiments encompassing a range of growth rates and $[CO_{2(aq)}]$. This value is larger than theoretical predictions based on Form II RubisCO's substrate specificity and measurements of purified proteobacterial Form II RubisCO [2]. Thus, our study underscores a broader emerging issue with existing interpretations. As more data become available, RubisCO fractionation factors measured on the purified enzyme (*in vitro*) [3] consistently disagree with ε_f values inferred from culture studies (*in vivo*) for all investigated phytoplankton species. We discuss a revised modeling framework which may account for these differences in prominent eukaryotic phytoplankton groups. Constraining the physiological basis for this disagreement is essential for application of the proxy to ancient environments.

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