Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.31701

A global core-top calibration for the chlorophyll-based CO_2 proxy

OLIVIA GRAHAM[1], **CAITLYN WITKOWSKI**[1], MARK STEVENSON[2], FRANCIEN PETERSE[3] AND DAVID NAAFS[1]

[1]University of Bristol
[2]Durham University
[3]Utrecht University

Proxy-based reconstructions of past changes in atmospheric carbon dioxide concentrations (pCO$_2$) are essential for understanding climate dynamics. A common method for reconstructing past pCO$_2$ is based on the carbon isotopic fractionation during photosynthesis by Rubisco (ε_p). This proxy method is based upon the difference (ε_p) between the stable carbon isotopic composition (δ^{13}C) of dissolved CO_2 and the δ^{13}C of marine photoautotroph biomass, which depends on the concentration of dissolved CO_2, related to pCO$_2$ through Henry's Law. This method has been applied to the general phytoplankton biomarker chlorophyll (preserved as phytol, phytane, and pristane in the sedimentary record) to reconstruct photoautotroph biomass δ^{13}C. The stability of these chlorophyll-derived biomarkers in the sedimentary record has currently allowed the reconstruction of pCO$_2$ across the Phanerozoic (~540 million years). However, the chlorophyll-derived biomarker proxy currently lacks a robust validation within modern settings. Here we investigate the relationship between the δ^{13}C of chlorophyll (as phytol) and the concentration of dissolved CO_2 in the modern ocean using a globally distributed set of 30 marine core top sediments and 75 suspended particulate matter samples. Our results demonstrate a positive relationship between the extent of fractionation (higher phytol ε_p) and dissolved CO_2 concentration and hence we derive the first empirical calibration between phytol ε_p and the concentration of dissolved CO_2. We find that terrestrial input negatively affects this observed relationship, and that excluding coastal sites from our dataset improves the correlation. When applied to previously published Pleistocene proxy data, our new calibration provides an improved pCO$_2$ reconstruction with estimates that are statistically like direct pCO$_2$ measurements from the Antarctic ice cores. When applied to published data from the entire Phanerozoic, our calibration provides estimates in line with those of other proxy methods, emphasizing its potential for reconstructions of pCO$_2$ across geological time.