



$\delta^{13}\text{C}$ of different size fractions of biomineral-bound organic matter in fossil diatom opal measured by means of Nano Elemental Analyzer-IRMS

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Diatoms of distinct cell sizes have different surface area to volume ratios resulting in differing diffusive supply of CO_2 and different needs for active carbon acquisition mechanisms. Large cells may be more sensitive to CO_2 depletion and additionally use a higher amount of HCO_3^- as C source to increase C uptake efficiency at low CO_2 concentrations. This could result in different isotope fractionation of diatom opal-bound C of cells of variable sizes, which could change over time in response to variable atmospheric CO_2 concentrations.

The new technique of $\delta^{13}\text{C}$ measurement using the Nano Elemental Analyzer-IRMS allows obtaining results from very small sample amounts (< 1 mg), making possible to acquire $\delta^{13}\text{C}$ from fossil diatom opal of different size fractions, even in sediments of modest opal content of 30%.

Subsequent to decarbonation, opal of sediments from the Equatorial Pacific of the last 20 Ma was cleaned of clays and organics, and pennate and centric diatoms of sizes between 20-41, 41-70, 70-100 and 100-150 μm were separated to perform analysis. Reproducibility of replicates from the same size fraction analyzed over the course of a week averages 0.46 permil and the measured value is insensitive to the mass of analyzed opal in the range of 20 to 1000 μg .

The centric 40-70 μm diatoms feature $\delta^{13}\text{C}$ values up to 5 permil higher than those of pennate diatoms from the same sample. These higher values, indicating less extreme fractionation during photosynthesis, could be consistent with higher use of HCO_3^- as C source or fixation of greater fraction of total cellular C uptake by the larger cells. We will evaluate if this tendency continues in the largest sized diatoms up to 150 μm . Nonetheless the large differences already observed underscore the importance of measurement of diatom-bound organic matter on restricted size fractions in order to distinguish true temporal trends in $\delta^{13}\text{C}$ of diatom-bound organic matter from changes in the size (or species) distribution of diatoms in bulk opal fractions.