

$\delta^{13}\text{C}$ of opal-bound organic matter and opal B content in fossil diatoms of different sizes and geometries

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Diatom cell geometry and size limit CO_2 availability by diffusion, which has been shown to be an important factor, together with growth rate, in controlling $\delta^{13}\text{C}$ and ϵ_p . Large centric diatoms (CD) may be more sensitive to CO_2 limitation and use a higher proportion of HCO_3^- for photosynthesis at low $[\text{CO}_2]$. Consequently, bulk diatom $\delta^{13}\text{C}$ may differ from that of diatoms with different geometries and/or sizes, whose ϵ_p may depend on form/size-specific adaptations to variable atmospheric $[\text{CO}_2]$.

Diatoms from sediments in the Eastern Equatorial Pacific (EEP) over the last ~ 13 Ma were separated into pennate (PD) and different size fractions of centric (20-41, 41-70, 70-100 and 100-150 μm) diatoms by microfiltration, centrifugation and/or settling. Diatoms were cleaned to remove clays and external organic matter. $\delta^{13}\text{C}$ was measured in small samples (typically 500-1000 μg) using a NanoEA-IRMS and foraminiferal (*Globigerinoides sacculifer* and *Neogloboquadrina dutertrei*) $\delta^{13}\text{C}$ values were used to calculate diatom ϵ_p .

Radiolaria contamination was significant in the > 70 μm fraction and its $\delta^{13}\text{C}$ values were used to correct $\delta^{13}\text{C}$ of the more pure 41-70 μm CD. Different approaches to correct $\delta^{13}\text{C}$ from PD, either using the corrected $\delta^{13}\text{C}$ from 41-70 μm CD or $\delta^{13}\text{C}$ from 20-41 μm CD produced similar PD trends.

Overall, PD were found to have ϵ_p several permil higher than CD. Whereas ϵ_p in CD is nearly invariant, PD show a significant temporal evolution in ϵ_p . PD may be more sensitive to $\text{CO}_{2\text{aq}}$ variations due to their comparatively higher surface area to volume ratio (1.0 for PD vs. 0.3 for smallest CD measured). Efficient carbon concentration mechanisms may have already been in operation in the 41-150 μm CD by ~ 13 Ma and therefore, size does not appear to impose a primary control on CO_2 supply for these cells.

Since B content of diatom opal has been reported to potentially record the extent of active HCO_3^- uptake in cultured diatoms, B being positively correlated with pH and active HCO_3^- uptake [1], we present preliminary [B] in EEP fossil diatoms, which may give an insight into HCO_3^- uptake for photosynthesis under variable $[\text{CO}_2]$.

[1] Mejía, Isensee, Méndez-Vicente, Pisonero, Shimizu, González, Monteleone & Stoll (2013), *GCA* **123**, 322-337