The influence of C_4 photosynthesis during the Miocene

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The evolution of the C_4 photosynthetic pathway was driven by specific environmental conditions and thus reflects a record of global environmental change. Given the distinct stable carbon isotopic compositions ($\delta^{13}C_{org}$) of C_3 and C_4 flora, terrestrial $\delta^{13}C_{org}$ can be applied to assess the relative proportion of C_4 plant input with time. Estimates of the C_4 plant biomass by this approach require an understanding of changes in the $\delta^{13}C$ of atmospheric carbon dioxide ($\delta^{13}C_{CO2}$) with time. In this on-going study, we evaluate the history of C_4 photosynthesis by measuring the $\delta^{13}C$ of terrestrially-derived *n*-alkanes from a globally distributed set of oligotropic and marginal DSDP/ODP marine sediments. Estimates of paleo-$\delta^{13}C_{CO2}$ are established from (1) the $\delta^{13}C$ of C_3 plant organic matter from Paleogene-age sediments from the Isle of Wight, UK, assuming a constant carbon isotopic discrimination between CO_2 and bulk C_3 plant organic matter, and (2) from published $\delta^{13}C$ records of planktonic foraminifera. From our data we model C_3 and C_4 $\delta^{13}C_{alkane}$ values and calculate the percent abundance of C_4 plant input for a given sedimentary $\delta^{13}C_{alkane}$ composition.

Our preliminary results from the Atlantic and Indian Oceans indicate that terrestrial C_4 photosynthesis was persistent during the Miocene (~25-5 Ma), constituting ~20 to 30% of aeolian-derived organic material. These results are broadly consistent with recent pCO_2 records that indicate a rapid decline in carbon dioxide between ~34-25 Ma, reaching near-modern levels by the latest Oligocene. Such low levels would have enhanced rates of photorespiration, favoring the evolution and expansion of the C_4 pathway prior to the Miocene.

Using carbon and hydrogen isotope ratios of terrestrial organic matter to understand climate change at the PETM

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The Paleocene Eocene Thermal Maximum (PETM) is a period of abrupt and extreme warming (5-10˚C) associated with a postulated catastrophic release of methane from gas hydrates. This event is marked by a large negative carbon isotope excursion that is twice as large in paleosol carbonates (6 to 8‰) as it is in marine carbonates (3 to 4‰). Organic carbon from paleosols demonstrates an excursion of intermediate magnitude (4 to 5 ‰) (This study and Magioncalda et al., 2004). One recent hypothesis for the greater magnitude of excursion in terrestrial than marine reservoirs calls for increased carbon isotope discrimination in plants resulting from a ~20% increase in available moisture combined with an accelerated soil carbon cycle (Bowen et al. 2004). Using the carbon and hydrogen isotope signatures of plant lipids, we can test this hypothesis. The δD record of *n*-alkanes should record increases in available moisture, and their $\delta^{13}C$ values should record plant carbon isotope discrimination.

The compound-specific approach to characterizing the terrestrial carbon isotope excursion during this climatic event avoids the problem of preservational biases common to bulk measurements. In the Bighorn Basin, WY, we observe that the carbon isotope ratio of bulk organic matter in paleosols is variable and inversely correlated with the percent carbon by weight. This correlation may be the result of preferential removal of 13C-depleted carbon during decay, and/or depositional or preservational biases in different settings (oxic vs. anoxic conditions).

Leaf wax *n*-alkanes are preserved in organic-rich Paleocene and Eocene sediments from the Bighorn Basin, WY, and do not represent modern contamination. The carbon isotope ratios of *n*-alkanes are depleted relative to bulk organic carbon values by 3 to 5 ‰ and show considerably less short-term variation. Thus, the variability in bulk values reflects variable degradational or depositional conditions rather than variation in the carbon isotope signature of the vegetation input.