

Carbon Isotope Fractionation of Leaf Wax *n*-alkanes and Implications for Terrestrial Paleoclimates

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The carbon isotope values ($\delta^{13}\text{C}$) of long chain *n*-alkanes in sediments have been utilized as a proxy for carbon isotope values of higher plants in the geological past. For example, a negative carbon isotope excursion in *n*-alkane $\delta^{13}\text{C}$ values coincident with the PETM can be used to estimate the magnitude of isotopically light carbon released into the atmosphere. It is often assumed that carbon in plant waxes is ^{13}C -depleted relative to leaf tissues by a more-or-less constant amount. However, the $\delta^{13}\text{C}$ values of individual leaf wax *n*-alkanes could be affected by shifts in metabolic carbon flow as part of a physiological response to physical conditions, including temperature, or resources such as water and light availability. In this study, we compiled and analyzed a data set of the isotopic composition of leaf tissues and *n*-alkanes in modern plants to distinguish various factors that may affect the relationship between lipid and leaf tissue $\delta^{13}\text{C}$ values, and their isotopic offset from atmospheric carbon.

Our results show that the $\delta^{13}\text{C}$ values of leaf tissue and *n*-alkanes are strongly correlated with mean annual temperature (MAT) and annual aridity index (AAI). In subhumid and humid locations (defined by $\text{AAI} > 0.5$), $\delta^{13}\text{C}$ values decrease with increasing MAT, and the $\delta^{13}\text{C}$ value of *n*-C₂₉ alkane changes more than twice as much as the $\delta^{13}\text{C}$ value of whole leaf tissue per degree C. The steeper slope of *n*-alkane $\delta^{13}\text{C}$ suggests an additional, variable isotopic discrimination mechanism beyond initial carbon assimilation. We suggest two possible causes: 1) mitochondrial respiration switching substrates to lipid at higher temperature, and 2) increased emission of volatile organic carbon at higher temperature. A multiple linear regression analysis indicates that the temperature dependence of *n*-alkane $\delta^{13}\text{C}$ is approximately -0.3 to -0.4 ‰ per °C. Therefore, a temperature effect could contribute to the larger decrease in *n*-alkane $\delta^{13}\text{C}$ (relative to bulk organic matter and carbonates) at the PETM. If so, for warming events, carbon release emissions constrained by plant wax *n*-alkane $\delta^{13}\text{C}$ values may be overestimated.