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Paleogene plants fractionated carbon isotopes similar to modern plants

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ABSTRACT

The carbon isotope composition ($\delta^{13}C$) of terrestrial plant biomarkers, such as leaf waxes and terpenoids, provides insights into past carbon cycling. The $\delta^{13}C$ values of modern plant biomarkers are known to be sensitive to climate and vegetation type, both of which influence fractionation during lipid biosynthesis by altering plant carbon supply and its biochemical allocation. It is not known if fractionation observed in living plants can be used to interpret fossil lipids because plant biochemical characteristics may have evolved during the Cenozoic in response to changes in global climate and atmospheric CO_2. The goal of this study was to determine if fractionation during photosynthesis (Δ_{leaf}) in the Paleogene was consistent with expectations based on living plants. To study plant fractionation during the Paleogene, we collected samples from eight stratigraphic beds in the Bighorn Basin (Wyoming, USA) that ranged in age from 63 to 53 Ma. For each sample, we measured the $\delta^{13}C$ of angiosperm biomarkers (triterpenoids and *n*-alkanes) and, abundance permitting, conifer biomarkers (diterpenoids). Leaf $\delta^{13}C$ values estimated from different angiosperms biomarkers were consistently 2‰ lower than leaf $\delta^{13}C$ values for conifers calculated from diterpenoids. This difference is consistent with observations of living conifers and angiosperms and the consistency among different biomarkers suggests ancient ε_{lipid} values were similar to those in living plants. From these biomarker-based $\delta^{13}C_{leaf}$ values and independent records of atmospheric $\delta^{13}C$ values, we calculated Δ_{leaf}. These calculated Δ_{leaf} values were then compared to Δ_{leaf} values modeled by applying the effects that precipitation and major taxonomic group in living plants have on Δ_{leaf} values. Calculated and modeled Δ_{leaf} values were offset by less than a permil. This similarity suggests that carbon fractionation in Paleogene plants changed with water availability and major taxonomic group to about the same degree it does today. Further, paleoproxy data suggest at least two of the stratigraphic beds were deposited at times when pCO_2 levels were higher than today. Biomarker data from these beds are not consistent with elevated Δ_{leaf} values, possibly because plants adapted carbon uptake and assimilation characteristics to pCO_2 changes over long timescales.

1. Introduction

Terrestrial plant biomarkers, and their carbon isotope ratios ($\delta^{13}C$), provide insights into ecosystems and carbon cycling from local to global scales (e.g., McInerney and Wing, 2011; Bowen, 2013). Considerable efforts have been made to constrain carbon sources, fluxes and fates, especially during periods of rapid climate change, such as hyperthermal events at the beginning of the Eocene (cf., McInerney and Wing, 2011; Bowen, 2013). Carbon isotope excursions (CIEs) during critical time intervals, such as during the Paleocene–Eocene Thermal Maximum, provide similar records of CIE shape and direction at different sites, but the CIE magnitude and shape differ, causing uncertainty in the size and timing of the carbon perturbation. This disagreement among records has led to questions about the degree to which local records of $\delta^{13}C$ record shifts in the isotopic composition of the atmosphere (e.g., McInerney and Wing, 2011). It also implies plant $\delta^{13}C$ records have variable sensitivities to changing climate and plant communities (Diefendorf et al., 2010).

Changes in the $\delta^{13}C$ of terrestrial organic matter (and especially plant biomarkers) through geologic time are often used as proxies for atmospheric $\delta^{13}C$, because having been fixed from atmospheric

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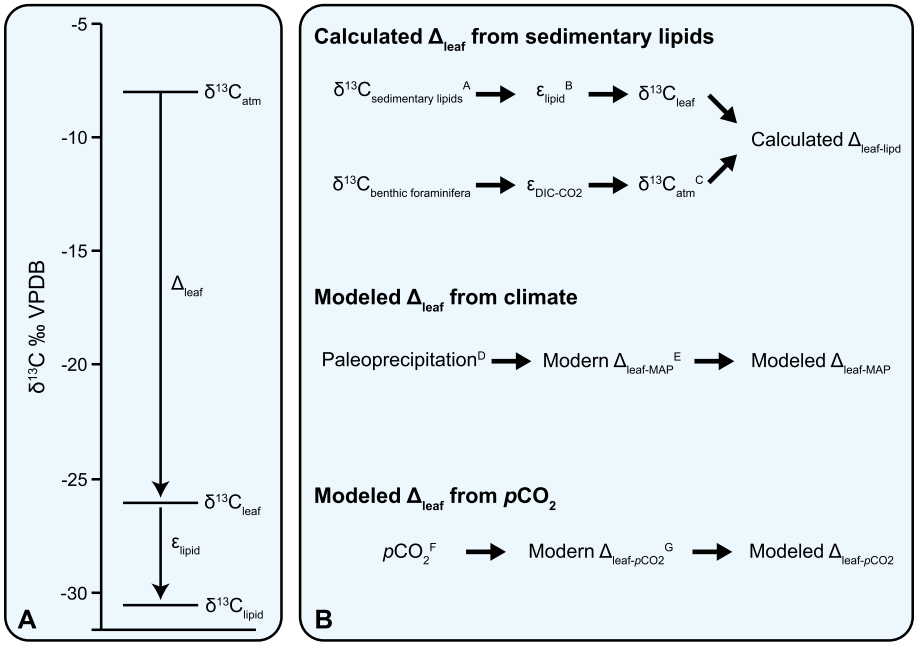

Fig. 1. A) Lipids and their carbon isotope ($\delta^{13}C_{lipid}$) values are preserved in the geologic record and provide a link to leaf $\delta^{13}C$ ($\delta^{13}C_{leaf}$), after constraining for fractionation that occurs during lipid biosynthesis (ε_{lipid}), or to atmospheric CO_2 $\delta^{13}C$ values ($\delta^{13}C_{atm}$), after constraining for fractionation that occurs during photosynthesis (Δ_{leaf}). Alternatively, Δ_{leaf} can be calculated if $\delta^{13}C_{atm}$ is known, and this provides a measure of discrimination which can be useful for interpreting water availability, ecophysiology, vegetation information, etc. (see text for details). B) In this study, Δ_{leaf} is calculated (calculated $\Delta_{leaf\text{-}lipid}$) from sedimentary lipid $\delta^{13}C$ values, after controlling for fractionation during lipid biosynthesis and using $\delta^{13}C_{atm}$ values derived from benthic foraminifera. Calculated $\Delta_{leaf\text{-}lipid}$ values are then compared to modeled Δ_{leaf} values based on modern plant studies. Δ_{leaf} values are modeled for both angiosperms and conifers using modern relationships between Δ_{leaf} and plant type and paleoprecipitation (modeled $\Delta_{leaf\text{-}MAP}$). Also, Δ_{leaf} values are modeled for angiosperms using modern Δ_{leaf} relationships between Δ_{leaf} and pCO_2. The various sources of inputs are as follows: [A] This study; [B] Diefendorf et al. (2011, 2012); [C] Tipple et al. (2010); [D] Currano et al. (2008, 2010); [E] Diefendorf et al. (2010); [F] Beerling and Royer (2011); [G] Schubert and Jahren (2012).

CO_2 through photosynthesis, plant carbon should reflect the $\delta^{13}C$ of the atmosphere. This process assumes that the many sources of fractionation between atmosphere and plant are constant or can be corrected for (Diefendorf et al., 2010; Freeman et al., 2011; Cernusak et al., 2013). During carbon fixation, atmospheric CO_2 is converted to sugars by the enzyme Rubisco, which fractionates strongly against ^{13}C; this enzymatic discrimination, along with other factors (diffusion, mesophyll and stomatal conductance), results in a large net isotope effect (e.g., Farquhar et al., 1989). Fractionation during photosynthesis (Δ_{leaf}), also referred to as carbon isotope discrimination, is quantified as

$$\Delta_{leaf} = \frac{\delta^{13}C_{atm} - \delta^{13}C_{leaf}}{1 + (\delta^{13}C_{leaf}/1000)} \quad (1)$$

Theoretical and empirical studies show that fractionation during carbon assimilation and fixation is sensitive to many factors including water availability, major taxonomic group, light intensity, photosynthetic pathway, and carbon dioxide partial pressure (Farquhar et al., 1989; Diefendorf et al., 2010; Schubert and Jahren, 2012; Cernusak et al., 2013; Graham et al., 2014).

For studies using lipid biomarkers, carbon isotope fractionation during biomarker synthesis is also important (Fig. 1A), but it is less constrained than photosynthetic fractionation. Isotope fractionation occurs during biochemical reactions and the net fractionation is a function of carbon source, the availability of the reactant, and down-stream reactions that influence fractionation (Hayes, 2001). Fractionation during biosynthesis (ε_{lipid}) is quantified by:

$$\varepsilon_{lipid} = \left(\frac{\delta^{13}C_{lipid} + 1000}{\delta^{13}C_{leaf} + 1000} - 1\right) \times 10^3 \approx \left(\delta^{13}C_{lipid} - \delta^{13}C_{leaf}\right) \quad (2)$$

The purpose of this study was to improve our ability to interpret past changes in carbon isotope composition of land plant biomarkers by establishing if Δ_{leaf} was different during the Paleogene when climate and atmospheric conditions deviated, sometimes greatly, from modern conditions. To accomplish our goal, we focused on sediments collected from the Paleocene (63 Ma) to early Eocene (53 Ma) from the Bighorn Basin (Wyoming, USA). This area was chosen because of the detailed climate and floral information that has been the focus of many studies. Samples were collected from eight stratigraphic beds, with multiple horizons sampled from within beds, yielding fifteen horizons. A companion study focused on terpenoid biomarkers as fossil vegetation proxies (Diefendorf et al., 2014). We measured $\delta^{13}C$ values of leaf wax *n*-alkanes, one of the most commonly used biomarkers, and di- and triterpenoids that are specific to conifers and angiosperms, respectively, from the same rocks samples. Although terpenoid compounds are not as well preserved as *n*-alkanes (Diefendorf et al., 2014), they provide unaltered taxon-specific $\delta^{13}C$ values (Freeman et al., 1994). We measured them in this study to compare conifers and angiosperms, which are known to have different Δ_{leaf} values when grown under similar conditions (see Diefendorf et al., 2010; 2011 and references therein).

We calculated Δ_{leaf} values from the $\delta^{13}C$ values of individual plant biomarkers ($\Delta_{leaf\text{-}lipid}$; Fig. 1B), after correcting for biosynthetic fractionation, and from estimates of $\delta^{13}C_{atm}$ based on benthic foraminifera (Tipple et al., 2010). These calculated $\Delta_{leaf\text{-}lipid}$ values were then compared to estimated, or "modeled", Δ_{leaf} values that were determined using two approaches (Fig. 1B). The first approach, denoted as $\Delta_{leaf\text{-}MAP}$, models Δ_{leaf} values as a function of the potential effects of precipitation on Δ_{leaf}, following a meta-analysis of Δ_{leaf} values from 334 living woody plant species that also accounts for effects of major taxonomic group on Δ_{leaf} (i.e. it