Carbon stable isotope fractionation during C_3 photosynthesis and its use in probing the terrestrial rock record

A. Hope Jahren and Brian A. Schubert

Because atmospheric carbon dioxide is the ultimate source of all land-plant carbon, workers have long suggested that pCO_2 level may exert control over the amount of ^{13}C incorporated into plant tissues. Prior to our work supported by the current grant period, there was no experimental observation of isotope fractionation during C_3 photosynthesis ($\Delta\delta^{13}C = \delta^{13}C_{CO2} - \delta^{13}C_{plant\ tissue}$) across multiple levels of highly elevated pCO_2. While records of $\Delta\delta^{13}C$ in modern wood had been observed to show a positive correlation with increasing pCO_2 over the last 160 years, early meta-analyses of published data revealed no correlation with pCO_2. However, these laboratory and field experiments were relatively uncontrolled across treatments (especially with respect to water availability), therefore any direct influence of pCO_2 on $\Delta\delta^{13}C$ was subject to being masked or cancelled by the multiple direct and indirect effects of environmental heterogeneity on stomatal conductance. During the current grant period we engineered growth chambers that feature enhanced dynamic stabilization of moisture availability and relative humidity, as well as provide constant light, nutrient, $\delta^{13}C_{CO2}$, and pCO_2 levels for up to four weeks of plant growth. This unprecedented level of environmental stabilization allowed us to quantify the fundamental relationship between pCO_2 and carbon isotope fractionation in C_3 land plants. Here we report upon a total of 191 C_3 plants (128 *Raphanus sativus* plants and 63 *Arabidopsis thaliana*) grown across fifteen different levels of pCO_2 ranging from 370 to 4200 ppm (Schubert and Jahren, 2012). From each plant we isolated several substrates for carbon isotope analysis, including leaf-extracted nC_{31}-alkanes, a specific compound commonly isolated from terrestrial sediments of various ages. All of our substrates showed an increase in carbon isotope discrimination ($\Delta\delta^{13}C$) with increasing pCO_2 that closely fitted (i.e., $R \geq 0.94$) the hyperbolic relationship:

$$\Delta\delta^{13}C = [(A)(B)(pCO_2 + C)] / [A + (B)(pCO_2 + C)] \quad (1)$$

where *A* is the asymptote; *B* is a measure of the responsiveness; pCO_2 is offset by the value *C*, such that $\Delta\delta^{13}C = 4.4‰$ at $pCO_2 = 0$ ppm (after Farquhar et al., 1989). Values for *A* and *B* were determined by iterative optimization to minimize the sum of the residuals squared (Schubert and Jahren, 2011b). On the basis of our experiments on *A. thaliana* and *R. sativus* as well as published data across small changes (<350 ppm) in pCO_2 we optimized the variables in Equation 1 to produce a single equation describing the relationship between $\Delta\delta^{13}C$ and pCO_2 (Figure 1 inset):

$$\Delta\delta^{13}C = [(28.26)(0.21)(pCO_2 + 25)] / [28.26 + (0.21)(pCO_2 + 25)] \quad (2)$$

This quantification of the pCO_2-dependency of carbon isotopic fractionation during photosynthesis has far-reaching ramifications for the interpretation of carbon isotope measurements in terrestrial C_{org}; it suggests that for any large release of isotopically depleted carbon to the ocean or atmosphere, the isotopic composition of resultant terrestrial photosynthetic tissues will be affected both by the change in atmospheric $\delta^{13}C_{CO2}$ and by changes in pCO_2. We have successfully quantitatively reconciled differences in magnitude in terrestrial *versus* marine carbon isotope excursions ("CIE") by incorporating the effect of changing pCO_2 on terrestrial carbon isotope fractionation. In this presentation we will show our calculations for the well-studied, globally widespread terrestrial CIE that marks the Paleocene-Eocene Thermal Maximum (PETM).

Figure:

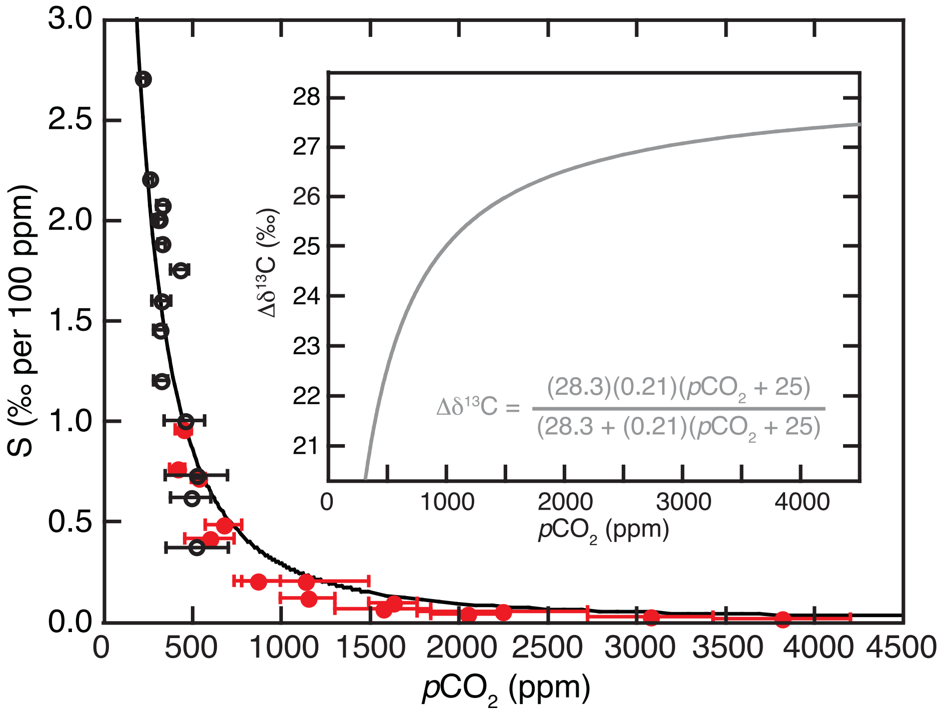

Figure 1. The effect of pCO_2 concentration on C_3 land-plant carbon isotope fractionation across the entire range of Late Paleozoic, Mesozoic, and Cenozoic estimates of pCO_2 (200 – 4200 ppm). The amount of carbon isotope fractionation per change in pCO_2 (*S*, ‰/ppm) decreases within increasing pCO_2 level (black curve; $R = 0.95$; n=28). Red closed circles reflect data from our experiments (Schubert and Jahren, 2012); open black circles represent data compiled from published studies. Horizontal bars encompass the range of pCO_2 levels variation within each experiment; the circle is plotted at the midpoint of the range. The gray curve (inset) represents the integral of the black curve, and follows the relationships described by Equations 1 and 2 within the text.

<u>Most Important Publications Supported by the Funding Period:</u>

"The effect of atmospheric CO_2 concentration on carbon isotope fractionation in C_3 land plants," (B.A. Schubert and A.H. Jahren, 2012. *Geochimica et Cosmochimica Acta*, 96: 29-43).

"Practical considerations for the use of pollen $\delta^{13}C$ value as a paleoclimate indicator," (D.C. King, B.A. Schubert, and A.H. Jahren. 2012, *Rapid Communications in Mass Spectrometry*, 26: 2165-2172, doi: 10.1002/rcm.6333).

"Quantifying seasonal precipitation using high-resolution carbon isotope analyses in evergreen wood," (B.A. Schubert and A.H. Jahren. 2011a, *Geochimica et Cosmochimica Acta*, 75(22): 7291-7303).

"Fertilization trajectory of the root crop *Raphanus sativus* across atmospheric pCO_2 estimates of the next 300 years," (B.A. Schubert and A.H. Jahren. 2011b, *Agriculture, Ecosystems, and Environment*, 140(1-2): 174-181).