Carbon Isotope Discrimination in C3 Land Plants is Independent of Natural Variations in pCO$_2$

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Abstract

The δ13C of terrestrial C3 plant tissues and soil organic matter is important for understanding the carbon cycle, inferring past climatic and ecological conditions, and predicting responses of vegetation to future climate change. Plant δ13C depends on the δ13C of atmospheric CO2 and mean annual precipitation (MAP), but an unresolved decades-long debate centres on whether terrestrial C3 plant δ13C responds to pCO2. In this study, the pCO2-dependence of C3 land plant δ13C was tested using isotopic records from low- and high-pCO2 times spanning historical through Eocene data. Historical data do not resolve a clear pCO2-effect (~1.2 ± 1.0 to 0.6 ± 1.0 %/100 ppmv). Organic carbon records across the Pleistocene-Holocene transition are too affected by changes in MAP, carbon sources, and potential differential degradation to quantify pCO2-effects directly, but limits of ≤1.0 ‰/100 ppmv or ~0 ‰/100 ppmv are permissible. Fossil collagen and tooth enamel data constrain pCO2-effects most tightly to -0.03 ± 0.13 and -0.03 ± 0.24 %/100 ppmv between 200 and 700 ppmv. Combining all constraints yields a preferred value of 0.0 ± 0.3 %/100 ppmv (2 s.e.). Recent models of pCO2-dependence imply unrealistic MAP for Cenozoic records.

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Introduction

C3 plants (trees, shrubs, herbs and cool-climate grasses) constitute c. 95 % of terrestrial plant biomass (Still et al., 2003), so understanding C3 plant response to changes in the partial pressure of atmospheric CO2 (pCO2) is key for modelling Earth’s carbon cycle (e.g., Cao et al., 2010; Shevliakova et al., 2013). Carbon isotope compositions (δ13C) of C3 plants are a principal means of inferring water use efficiency (Farquhar et al., 1989), which is important to models of future C3 biomass, and have been proposed to allow estimation of mean annual precipitation (MAP) in the geologic past (Kohn, 2010). Plant δ13C depends on the δ13C of atmospheric CO2 (Freyer and Wiesberg, 1973), but an unresolved decades-long debate centres on whether terrestrial C3 plant δ13C responds to pCO2. Many studies have argued that increasing pCO2 increases carbon isotope discrimination (e.g., Feng and Epstein, 1995; Schubert and Jahren, 2012); others have argued for no pCO2-effect (e.g., Arens et al., 2000; Saurer et al., 2004; Frank et al., 2015). Recent work (Schubert and Jahren, 2012) integrated natural and experimental data to infer that C3 plant δ13C depends hyperbolically on pCO2 (Fig. 1a) and that changes to carbon isotope compositions in leaves and sediment organic matter over the last 30 ka parallel and predict pCO2 (Schubert and Jahren, 2015). In this study, carbon isotope records ranging from the last several decades through the early Cenozoic are critically evaluated to identify which records indeed provide quantitative constraints on pCO2-dependencies, and to provide a robust estimate of that dependence.

Multiple factors besides atmospheric CO2 can affect C3 plant δ18C, including MAP, ontogeny, light levels, genetics and fertilisation (e.g., through atmospheric nitrogen deposition; Farquhar et al., 1989; Stewart et al., 1995; McCarron and Loader, 2004; Diefendorf and Loader, 2010; Kohn, 2010; Fig. 1b). Other physical factors, including latitude and altitude, have a minor impact on C3 plant δ13C (Diefendorf et al., 2010; Kohn, 2010), but high variability both within and among trees must reflect individual responses to other, less easily identified, environmental or physiological factors (McCarron and Loader, 2004). Thus, records of natural δ13C through time, e.g., from tree rings, sediment records, etc. must account for changes to MAP and other environmental changes, most recently from anthropogenic activities, before any pCO2-dependence can be quantified.

“Modern” conditions anchor many quantitative estimates of palaeoclimate, e.g., δ13C-based estimates of MAP are normalised to AD 2000 data (pCO2 = 370 ppmv, δ13CO2 = -8.0 ‰). If C3 plant δ13C does depend on pCO2, δ13C values from periods of low pCO2 (e.g., late Pleistocene) are anomalously high, and must be downward corrected for any calculations (Δδ13C increases); conversely δ13C values from periods of high pCO2 (e.g., Eocene) must be upward corrected (Δδ13C decreases; Fig. 1a). In comparison with the modern dependence of C3 plant δ13C on MAP (Fig. 1b), uncorrected estimates of MAP must be too dry for the Pleistocene and too wet for the Eocene. Fortunately, estimates of MAP for many times are known from independent proxies (e.g., floral analysis) and general circulation models, and pCO2 is known either from measurements in ice cores or from geochemical proxies. Thus, pCO2-effects on C3 δ13C values can now be evaluated from ancient sediments and fossils, albeit with careful consideration of sometimes substantial errors in proxy estimates of pCO2 and MAP (see Supplementary Information).

This study evaluates pCO2-dependencies in the context of two endmember models – a null hypothesis of no dependence vs. a hyperbolic dependence that integrates numerous other studies (Schubert and Jahren, 2012). Ultimately four datasets are considered: modern leaves (1970 through 2007; Kohn, 2010), tropical rainforest tree rings (least susceptible to changes in MAP; Fig. 2a;
van der Sleen et al., 2015), sediment organic matter (SOM) from three representative studies of the Pleistocene-Holocene transition (Fig. 2b; C. Hatté et al., 1998; Sinninghe Damsté et al., 2011; Barker et al., 2013), and herbivore collagen and tooth enamel for especially low-preCO2 (<250 ppmv) and high-preCO2 (>500 ppmv) periods of the geologic past (Fig. 3; Supplementary Information). The overall intent of these comparisons is to correct first for factors that we know influence δ13C (especially MAP, carbon sources) and ascribe any residual effect to preCO2.

Because plants track the δ13C of atmospheric CO2, which has changed through time, data are presented in terms of isotope discrimination (Δ13C):

\[
\Delta^{13}C(CO_2) - \delta^{13}C_C = \delta^{13}C_{CO_2} - \delta^{13}C_C + \frac{\delta^{13}C_{CO_2} - \delta^{13}C_C}{1000}
\]  

Eq. 1

By correcting for secular changes to atmospheric δ13C from recent direct measurements, ice core measurements, and foraminiferal data (Supplementary Information), Equation 1 allows comparisons of data from different times.

Supplementary Information explains materials and methods, including error propagation.

### Results and Discussion

**Modern/Historical records.** Linear regression of modern leaf Δ13C (Kohn, 2010), treating preCO2 as an independent variable (Table S-1), results in a preCO2 coefficient for Δ13C of -1.2 ± 1.0 ‰/100 ppmv (2σ). These data do not generally support a positive preCO2-dependence for Δ13C but are quite imprecise. Historical cellulose data from tropical rainforests (Fig. 2a; van der Sleen et al., 2015; Table S-1) suggest a positive slope with respect to preCO2 (0.62 ± 1.05 ‰/100 ppmv, 2 s.e.; Supplementary Information), but are also strongly influenced by an up-tick in Δ13C between 2000 and 2010 AD (Fig. 2a; Toona, Chukrasia) which might reflect other factors. For example, 10-20 yr, 1-2 ‰ oscillations at all sites (e.g., Melia, Aezélia, Fig. 2a) probably reflect susceptibility to environmental factors besides precipitation and preCO2, and such an effect might explain specific slopes. Tree ring isotope data across Europe, corrected for climate variables, suggest a negative preCO2-dependence (-0.55 ± 0.67 ‰/100 ppmv; data from Frank et al., 2015).

Overall, modern/historical data are too imprecise and idiiosyncratic to either require or preclude a preCO2-effect.

**Pleistocene-Holocene sediment records.** Mid-latitude sediments from the Rhine River valley in France and Germany present one of the better cases for a preCO2-effect: a gradual 2 ‰ increase in Δ13C between 20 and 10 ka parallels preCO2 (Fig. 2b). A near doubling of MAP across the Pleistocene-Holocene transition (Bartlein et al., 2011; Alder and Hostetler, 2015), however, predicts c. 1.25 ‰ of the observed ~2 ‰ increase (Fig. 2b). A near doubling of MAP across the Pleistocene-Holocene transition (Bartlein et al., 2011; Alder and Hostetler, 2015), however, predicts c. 1.25 ‰ of the observed ~2 ‰ increase (Fig. 2b). A near doubling of MAP across the Pleistocene-Holocene transition (Bartlein et al., 2011; Alder and Hostetler, 2015), however, predicts c. 1.25 ‰ of the observed ~2 ‰ increase (Fig. 2b).

In addition, organic C content in these records increases by a factor of 9 across the Pleistocene-Holocene boundary (Hatté et al., 1998). Numerous studies show a linear correlation between Δ13C and the logarithm of soil organic C content, (e.g., Poage and Feng, 2004) with a minimum slope of c. 0.7 ‰ per logMAP (Balesdent et al., 1993). If the striking increase in organic C content in the European records represents differential degradation, Δ13C should increase by at least c. 0.65 ‰. The combined isotopic effects of changes to MAP and organic C content (c. 2 ‰) can explain the data without resort to any preCO2-effects.
Alternatively, an estimate of ecosystem impacts on Δ13C can be made for the French record in reference to the Dansgaard-Oeschger 2 (DO2) and the Belling-Allerød (B-A) warming events, which caused brief 2-2.5 % spikes in Δ13C without obvious changes to pCO2. Subtracting this (pCO2-independent) effect from the Pleistocene-Holocene transition yields a residual pCO2-effect of ~0 ‰/100 ppmv.

A large, abrupt increase in Δ13C in lowlatitude Kenyan lake data (Fig. 2c) likely reflects decreasing abundances of C4 vegetation (Sinninghe Damsté et al., 2011), rather than increasing pCO2. Increasing pCO2 tends to destabilise C4 plants (Ehleringer et al., 1997), so an abrupt decrease in C4 abundance (Prentice et al., 2011) during the Pleistocene-Holocene rise in pCO2 logically explains the observations. Changes to lake diatom abundance and preservation may also play a role (Fig. 4).

Overall, for the Pleistocene-Holocene transition, widespread increases in MAP across much of Earth (Bartlein et al., 2011) and concomitant changes to floral ecosystems (CLIMAP, 1976; Prentice et al., 2011), especially changes in C3/C4 abundances at low latitudes, generally predict an increase in Δ13C, compromising any quantitative retrieval or validation of pCO2-dependencies using these records. At present, the best constrained data imply a maximum value of ≤1.0 ‰/100 ppmv (MAP-correction alone) or possibly ~0 ‰/100 ppmv (DO-event analog, France; MAP plus organic C degradation) between 180 and 270 ppmv.

**Fossil herbivore records.** Pleistocene and Tertiary herbivore data place the most stringent constraints on a pCO2-dependence: -0.03 ± 0.13 ‰/100 ppmv between 180 and 370 ppmv, and -0.03 ± 0.24 ‰/100 ppmv between 370 and 715 ppmv. The pCO2-dependent model strongly overestimates Δ13C for the Pleistocene and underestimates Δ13C for the Tertiary (Fig. 3a,b). Similarly, isotopically-based estimates of MAP without correction of pCO2 reproduce independent estimates within uncertainties (Fig. 3c), whereas estimates from the pCO2-dependent model strongly overestimate MAP for Pleistocene data, and strongly underestimate MAP for Tertiary data (Fig. 3d). Uncertainties in estimates of MAP, pCO2, or the δ13C of atmospheric CO2 do not likely bias interpretation of Pleistocene data because pCO2 and δ13C are directly determined from ice cores, and MAP is based on large numbers of floral observations coupled to GCMs with especially well constrained boundary conditions. Large errors for Tertiary pCO2 cause the pCO2-dependent model errors to overlap independent estimates of Δ13C and MAP. The point of overlap, however, occurs only at quasi-modern pCO2 levels, which is generally inconsistent with Eocene and middle Miocene proxies (Beerling and Royer, 2011). Note that a systematic error for Pleistocene calculations operates in the opposite direction for Tertiary data, so the internal consistency of both sets of calculations (the same pCO2-coefficient suggests that systematic errors are small.

Considering calculated MAP throughout the Cenozoic, a U-shaped distribution (Fig. 4a) highlights unusually dry conditions [low Δ13C(CO2)-plant, high Δ13C(plants)] during the late Eocene and early/middle Oligocene. Aggregating Cenozoic MAP estimates, the pCO2-independent model exhibits a predominance of values between 0 and 1.0 m/yr (>80 %; Fig. 4b) with a distribution that mimics modern Earth’s area distribution of MAP (dashed line, Fig. 4b). In contrast, the pCO2-dependent model implies widespread rainforests during the Pleistocene (Fig. 4a), which contrasts starkly with global climate and vegetation syntheses that have long indicated greater aridity across much of the globe (e.g., CLIMAP, 1976; Prentice et al., 2011), especially in Europe where many of the Pleistocene fossils were collected. The pCO2-independent model also implies negative MAP during the Eocene and Oligocene (Fig. 4a). A histogram of pCO2-dependent predictions (Fig. 4e) yields unrealistically abundant hyperarid deserts (MAP < 0) and rainforests (>2.5 m/yr).

**Figure 3** Cenozoic herbivore data. (a-d) Calculated vs. measured Δ13C, and calculated vs. independently estimated MAP, showing good correspondence with pCO2-independent model. Representative error bars (2σ) reflect propagated uncertainties in isotope compositions and tissue-diet fractionations, the dependence of δ13C on MAP, and proxy estimates of MAP and pCO2 (Table S-2).

**Figure 4** (a) Estimates of MAP for the Cenozoic based on fossil herbivore isotope compositions show a U-shaped distribution, pCO2-corrections imply widespread rainforests in the Pleistocene and hyper-deserts in mid-Cenozoic. pCO2 curve simplified from Beerling and Royer (2011). (b-c) Histograms of Cenozoic MAP estimates show a better match between the global distribution (by area) of MAP (Kohn, 2010) vs. MAP estimated using the pCO2-independent model. The pCO2-dependent model predicts unusually high proportions of deserts (MAP < 0.1 m/yr) and rainforests (MAP > 2.5 m/yr) in the geologic record.
CO₂ history. But on evolutionary timescales (decades to centuries) may evolve towards an optimal physiology whose isotopic fractionation is pCO₂-independent. Short-term experiments might have relevance for modern rapid changes to pCO₂, but not for ancient isotope records.

Overall, natural data either do not resolve a pCO₂-dependence or indicate an effect far smaller than recent models. On geologic timescales, a best estimate for a pCO₂-dependence between c. 200 and c. 700 ppmv averages -0.04 ± 0.26 ‰/100 ppmv (2 s.e.; Table S-3), i.e. pCO₂-dependencies are negligible. Because no correction for pCO₂ is needed, this result vastly simplifies interpretations of past climates and carbon use by C3 land plants.

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**Additional Information**

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1604

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**References**


