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Reconciliation of marine and terrestrial carbon isotope excursions based on changing atmospheric CO₂ levels

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Negative carbon isotope excursions measured in marine and terrestrial substrates indicate large-scale changes in the global carbon cycle, yet terrestrial substrates characteristically record a larger-amplitude carbon isotope excursion than marine substrates for a single event. Here we reconcile this difference by accounting for the fundamental increase in carbon isotope fractionation by land plants in response to increasing atmospheric CO₂ concentration ($p\text{CO}_2$). We show that for any change in $p\text{CO}_2$ concentration ($\Delta p\text{CO}_2$), terrestrial and marine records can be used together to reconstruct background and maximum $p\text{CO}_2$ levels across the carbon isotope excursion. When applied to the carbon isotope excursion at the Palaeocene-Eocene boundary, we calculate $p\text{CO}_2 = 674\text{--}1,034$ p.p.m.v. during the Late Palaeocene and $1,384\text{--}3,342$ p.p.m.v. during the height of the carbon isotope excursion across all sources postulated for the carbon release. This analysis demonstrates the need to account for changing $p\text{CO}_2$ concentration when analysing large-scale changes in the carbon isotope composition of terrestrial substrates.

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Globally correlated, negative excursions in carbon isotope ($\delta^{13}\text{C}$) values measured in marine and terrestrial substrates throughout the Phanerozoic indicate episodic, massive additions of isotopically depleted carbon to the ocean-atmosphere system^{1–10}. These events not only changed the carbon isotope composition of atmospheric carbon dioxide ($\delta^{13}\text{C}_{\text{CO}_2}$), but also raised $p\text{CO}_2$ concentrations (for example, ref. 11). The magnitude of the carbon isotope excursion (CIE) and the amount of $p\text{CO}_2$ rise ($\Delta p\text{CO}_2$) calculated for such events should relate to one another, and the source of the carbon input and changes in the global carbon cycle have been reconstructed upon this premise (for example, refs 5,9,11,12). Determination of the ‘true’ magnitude of a CIE (that is, the amount of the CIE caused only by the change in $\delta^{13}\text{C}_{\text{CO}_2}$) is fundamental to calculating the amount of carbon added to the atmosphere at the event and improving our understanding of feedbacks in the climate system^{13,14}.

One complicating factor is that the magnitude of the CIE is characteristically larger when measured in terrestrial versus marine substrates by up to several per mil^{6–9,11,15}. Workers have argued that larger-magnitude negative excursions recorded in terrestrial substrates reflect increased humidity or precipitation^{6,7} based on the increased carbon isotope fractionation that modern land plants demonstrate in response to these environmental factors. Others have attributed this difference to an increased abundance of angiosperm flora, which are characteristically isotopically depleted in comparison with gymnosperm flora^{16,17}. Both of these mechanisms are problematic as general explanations for any global discrepancy between terrestrial and marine CIEs because their influences are most likely to be locally and heterogeneously expressed^{15,18} (Supplementary Information). Moreover, changes in angiosperm abundance cannot explain larger terrestrial versus marine CIEs in pre-Cretaceous substrates (for example, ref. 7). The reconciliation of terrestrial versus marine CIEs requires a mechanism fundamental to all C_3 photosynthesis, and thus globally applicable (we note that classical C_4 photosynthesis is a recent evolutionary innovation, relegated to no more than the last ~13 million years of Earth’s history^{19,20}, and that CAM photosynthesis is largely limited to aqueous and desert environments).

Previous experiments have shown that the carbon isotope value of plant tissues ($\delta^{13}\text{C}_p$) is affected by changes in $p\text{CO}_2$ concentration, independent of changes in $\delta^{13}\text{C}_{\text{CO}_2}$, and identified a positive relationship between $p\text{CO}_2$ concentration and carbon isotope fractionation ($\Delta\delta^{13}\text{C}_p \approx \delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_p$) in both angiosperm and gymnosperm taxa (for example, refs 21,22; Supplementary Information). More recently, time-series correlations between climate variables and tree-ring $\delta^{13}\text{C}_p$ values have been shown to improve when a correction proportional to the increase in $p\text{CO}_2$ is applied (for example, refs 23–25). However, a wide range of corrections for the effect of changing $p\text{CO}_2$ on $\Delta\delta^{13}\text{C}_p$ (S ; %/p.p.m.v.) have been reported and applied, typically ranging from $S=0.73$ to 2.0% per 100 p.p.m.v. increase in $p\text{CO}_2$ (for example, refs 23,24; Supplementary Information).

Our recent work growing plants under controlled environmental conditions across a wide range of $p\text{CO}_2$ levels (up to 4,200 p.p.m.v.) provided a unifying relationship for the effect of $p\text{CO}_2$ on C_3 plant tissue, showing that S decreases systematically with increasing $p\text{CO}_2$ across a wide range of C_3 plants ($R=0.96$, $n=33$) (Fig. 1) (ref. 26). This relationship suggests that for any large release of isotopically depleted carbon to the ocean or atmosphere, the land-plant-derived substrates of the terrestrial record (CIE_{terrestrial}; that is, terrestrial organic matter, soil carbonate, plant lipids and tooth enamel) will record a larger-amplitude CIE than marine substrates (CIE_{marine}; that is, benthic

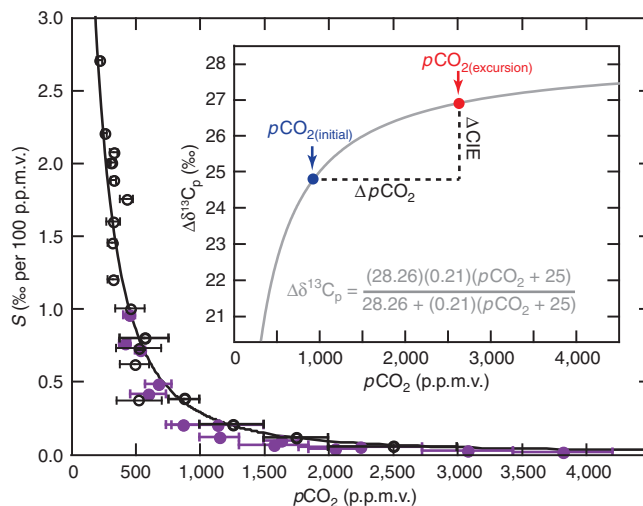


Figure 1 | The effect of $p\text{CO}_2$ concentration on C_3 land-plant carbon isotope fractionation. Across field and chamber experiments on a wide range of C_3 land-plant species, the amount of carbon-isotope fractionation per change in $p\text{CO}_2$ (S , % per p.p.m.v.) decreases within increasing $p\text{CO}_2$ level according to the following equation: $S = (B)(A^2)/[A + B(p\text{CO}_2 + C)]^2$

with $R = 0.96$ ($n = 33$) (black curve), where $A = 28.26$, $B = 0.21$ and $C = 25$. Purple closed circles reflect data from our experiments²⁶; open black circles represent data compiled from published studies (Supplementary Table S2). Horizontal bars encompass the range of $p\text{CO}_2$ levels used within each experiment; the circle is plotted at the midpoint of the range. The grey curve (inset) represents the integral of the black curve, and follows the general hyperbolic relationship: $\Delta\delta^{13}\text{C}_p = [(A)(B)(p\text{CO}_2 + C)]/[A + (B)(p\text{CO}_2 + C)]$ (see Supplementary Information). As the relationship between $p\text{CO}_2$ and $\Delta\delta^{13}\text{C}_p$ is nonlinear, absolute estimates of $p\text{CO}_2(\text{initial})$ (blue) and $p\text{CO}_2(\text{excursion})$ (red) can be calculated by solving equations (1) and (2) provided $\Delta p\text{CO}_2$ and ΔCIE are known (dashed lines); for a given magnitude CIE, the $\Delta p\text{CO}_2$ estimate is dependent on the $\delta^{13}\text{C}$ value of the source. Figure is modified from ref. 26 with new data reported in Lomax *et al.*⁵⁹ (Supplementary Information; Supplementary Table S1).

foraminifera, planktic foraminifera and bulk marine carbonate). Thus, we propose that the difference in magnitude between these two substrates ($\Delta\text{CIE} = \text{CIE}_{\text{terrestrial}} - \text{CIE}_{\text{marine}}$) results from the additional fractionation by land plants due to rising $p\text{CO}_2$ levels, which is then propagated within the terrestrial record. We apply this to the particularly well-studied and globally widespread CIE at the Palaeocene–Eocene Thermal Maximum (PETM), for which analysis of >150 CIEs shows a significant, 2.1‰ greater amplitude CIE recorded in terrestrial versus marine substrates¹¹, in order to calculate absolute $p\text{CO}_2$ levels during the Late Palaeocene and at the height of the CIE for the range of sources (and thus, $\Delta p\text{CO}_2$ values) postulated for the carbon release.

Results

Reconciliation of ΔCIE via the $p\text{CO}_2$ effect. The larger-magnitude CIE recorded in terrestrial versus marine substrates can be described by the following equation relating ΔCIE to the effect of changing $p\text{CO}_2$ levels on carbon isotope fractionation by C_3 land plants:

$$\Delta\text{CIE} = \frac{(A)(B)(p\text{CO}_2(\text{initial}) + C)}{A + (B)(p\text{CO}_2(\text{initial}) + C)} - \frac{(A)(B)(p\text{CO}_2(\text{excursion}) + C)}{A + (B)(p\text{CO}_2(\text{excursion}) + C)} \quad (1)$$

where $p\text{CO}_2(\text{initial})$ and $p\text{CO}_2(\text{excursion})$ are the $p\text{CO}_2$ levels immediately before and at the height of the CIE, respectively, and A , B and C are constants produced by the best-fit curve through the

experimental data and published values (Fig. 1 inset and Supplementary Information). For CIE events where the magnitude of both $CIE_{\text{terrestrial}}$ and CIE_{marine} are well-documented globally, knowledge of ΔCIE can be used towards the determination of both $pCO_{2(\text{initial})}$ and $pCO_{2(\text{excursion})}$ provided the change in pCO_2 (ΔpCO_2) is known (Fig. 1 inset):

$$\Delta pCO_2 = pCO_{2(\text{excursion})} - pCO_{2(\text{initial})} \quad (2)$$

Estimates of ΔpCO_2 , which are dependent on the true magnitude of the CIE and the $\delta^{13}C$ value of the source ($\delta^{13}C_{\text{source}}$), are commonly calculated using methods ranging from mass balance equations (for example, refs 5,11) to numerical models (for example, refs 12,27). Therefore, provided independent estimates of ΔCIE and ΔpCO_2 , equations (1) and (2) can be solved simultaneously for absolute estimates of $pCO_{2(\text{initial})}$ and $pCO_{2(\text{excursion})}$ (Fig. 2), allowing for a wholly new quantitative reconstruction of changes in the global carbon cycle. Although determination of $pCO_{2(\text{initial})}$ and $pCO_{2(\text{excursion})}$ requires precise estimates of ΔCIE and ΔpCO_2 , Fig. 2 shows that the value for $pCO_{2(\text{initial})}$ is more sensitive to ΔCIE than to ΔpCO_2 , while $pCO_{2(\text{excursion})}$ is more sensitive to ΔpCO_2 than to ΔCIE .

Determination of pCO_2 levels across the CIE at the PETM. The highly studied, globally widespread CIE that marks the PETM represents an ideal event upon which to first apply our methods to quantify $pCO_{2(\text{initial})}$ and $pCO_{2(\text{excursion})}$ because of the large number of $CIE_{\text{terrestrial}}$ and CIE_{marine} records that can be used to provide a robust estimate of ΔCIE globally. More than 150 total CIE_{marine} and $CIE_{\text{terrestrial}}$ records have been measured across the PETM (reviewed by McInerney and Wing¹¹); the average CIE measured in terrestrial substrates that include soil carbonate, plant lipids, bulk soil organic matter and tooth enamel ($CIE_{\text{terrestrial}} \pm 1\sigma = -4.7 \pm 1.5\%$, $n = 48$) is 2.1‰ more negative than that measured in benthic foraminifera, planktic foraminifera and bulk marine carbonate from marine environments ($CIE_{\text{marine}} \pm 1\sigma = -2.6 \pm 1.1\%$, $n = 105$) ($\Delta CIE = -2.1\%$). Bulk marine organic matter was not included in our determination of CIE_{marine} because it can include mixed pools of carbon from photosynthetic and non-photosynthetic organisms from terrestrial and marine environments^{15,28–30}. By averaging across

the large number of diverse sites and substrates available for the PETM, biasing effects of local and regional changes in climate^{6,8,31–39}, vegetation^{16,17,38}, sediment transport^{40,41}, salinity^{15,42} and dissolution^{43,44} on ΔCIE are limited. Using this ΔCIE value (-2.1%), Late Palaeocene ($pCO_{2(\text{initial})}$) and PETM ($pCO_{2(\text{excursion})}$) pCO_2 levels can be determined across a range of ΔpCO_2 estimates by simultaneously solving equations (1) and (2) (Fig. 3).

Reconstructed estimates of $pCO_{2(\text{initial})}$ and $pCO_{2(\text{excursion})}$ increase as ΔpCO_2 increases (Fig. 3); thus the solution based on a methane hydrate source ($\delta^{13}C_{\text{source}} = -60\%$, $\Delta pCO_2 = 710$ p.p.m.v.) yielded the lowest Late Palaeocene pCO_2 estimate ($pCO_{2(\text{initial})} = 674$ p.p.m.v.), followed by thermogenic methane or permafrost thawing ($\delta^{13}C_{\text{source}} = -30\%$, $\Delta pCO_2 = 1,566$ p.p.m.v.) that yielded $pCO_{2(\text{initial})} = 915$ p.p.m.v., and then wildfire or drying of epicontinental seas ($\delta^{13}C_{\text{source}} = -22\%$, $\Delta pCO_2 = 2,308$ p.p.m.v.) having the highest Late Palaeocene pCO_2 estimate ($pCO_{2(\text{initial})} = 1,034$ p.p.m.v.). If these sources can be thought to exhaust the carbon isotope range of potential sources, we calculate that Late Palaeocene pCO_2 levels may have been as low as ~ 280 p.p.m.v. higher than present, and were much lower than the recent pCO_2 estimates for the year 2300 (refs 45,46; Fig. 3). pCO_2 levels at the peak of the PETM were calculated to be 1,384, 2,481 and 3,342 p.p.m.v. for methane hydrate, thermogenic methane or permafrost thawing, and drying of epicontinental seas or wildfire sources ($\Delta pCO_2 = 710, 1,566$ and $2,308$ p.p.m.v.), respectively (Fig. 3).

Discussion

Determination of Late Palaeocene and PETM pCO_2 levels is important for quantifying climate sensitivity to CO_2 for this greenhouse period (for example, ref. 47); however, previous proxy estimates for the Late Palaeocene are highly varied, ranging from 100 to 2,400 p.p.m.v., and robust PETM pCO_2 estimates are lacking (Supplementary Information; Fig. 3). Across a wide range of increases in pCO_2 at the PETM ($\Delta pCO_2 \leq 3,000$ p.p.m.v.), our results indicate that Late Palaeocene pCO_2 levels were $\leq 1,112$ p.p.m.v. (Fig. 3). If we consider a relatively small increase in pCO_2 levels ($\Delta pCO_2 < 1,000$ p.p.m.v.), as would be attributed to a methane hydrate source, our Late Palaeocene pCO_2 estimates are consistent with values determined from liverwort, phytoplankton and stomatal proxies (Fig. 3). The boron isotope proxy, in contrast, is more consistent with our results assuming that the amount of pCO_2 increase was larger ($> 1,000$ p.p.m.v.), as would be required for the thawing permafrost model, for example (Fig. 3).

Although our reconciliation does not allow for the determination of the carbon source of the CIE at the PETM, recent work indicates significant warming before the onset of the CIE (refs 33,48), and suggests an orbitally forced mechanism for the release of carbon at the event^{49–51}. If we consider the two hypotheses suggesting that orbital forcing triggered the release of carbon through a methane hydrate release (ref. 49) ($\Delta pCO_2 = 710$ p.p.m.v.) or large-scale thawing of permafrost (ref. 50) ($\Delta pCO_2 = 1,566$ p.p.m.v.), we calculate Late Palaeocene pCO_2 levels = 674 (+159–109) or 915 (+225–153) p.p.m.v., respectively (error based on $\Delta CIE = -1.6$ to -2.6% ; Fig. 3). Notably, these calculated values for Late Palaeocene pCO_2 are consistent with the pCO_2 levels required by Lunt *et al.*⁴⁹ (~ 560 p.p.m.v.) and DeConto *et al.*⁵⁰ (~ 900 p.p.m.v.) for each of their respective models.

Many arguments have been made to explain the larger CIE measured in terrestrial versus marine substrates at the PETM^{6,8,15–18,42,43}, but each requires additional phenomena secondary to the carbon release (Supplementary Information).

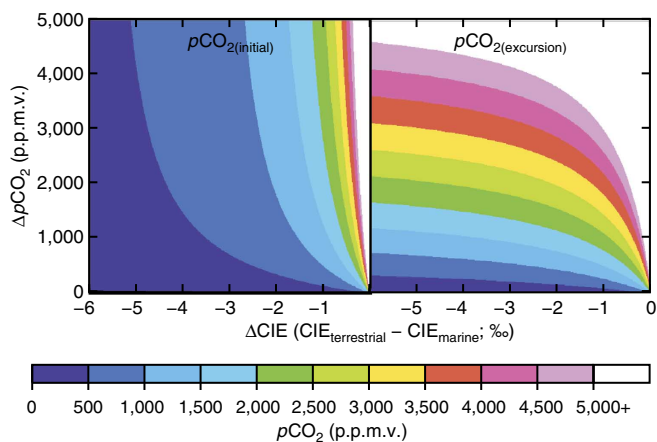


Figure 2 | Determination of pCO_2 levels as a function of ΔCIE and ΔpCO_2 .

For any hypothetical CIE, $pCO_{2(\text{initial})}$ (left) and $pCO_{2(\text{excursion})}$ (right) are a function of the difference between the terrestrial and marine CIE (ΔCIE ; $\Delta CIE = CIE_{\text{terrestrial}} - CIE_{\text{marine}}$) and the rise in pCO_2 (ΔpCO_2 ; $\Delta pCO_2 = pCO_{2(\text{excursion})} - pCO_{2(\text{initial})}$). Values for $pCO_{2(\text{initial})}$ and $pCO_{2(\text{excursion})}$ were calculated by solving equations (1) and (2) simultaneously.

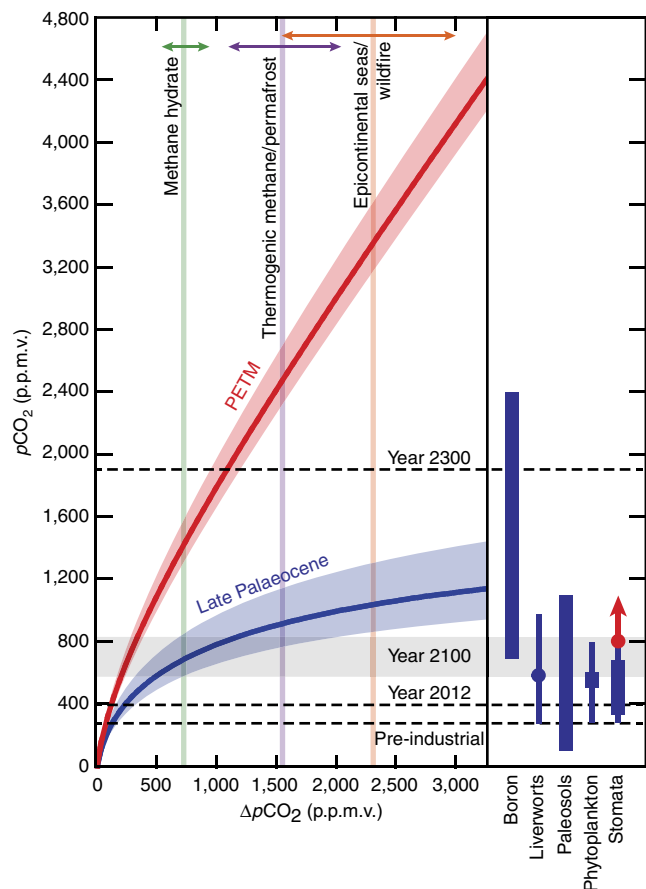


Figure 3 | Reconstruction of $p\text{CO}_2$ levels during the Late Palaeocene and PETM.

Across a range of possible $p\text{CO}_2$ increases ($\Delta p\text{CO}_2$), $p\text{CO}_2$ levels for the Late Palaeocene (blue curve; $p\text{CO}_{2(\text{initial})}$) and PETM (red curve; $p\text{CO}_{2(\text{excursion})}$) were calculated by simultaneously solving equations (1) and (2) for $\Delta p\text{CO}_2 = 0\text{--}3,600$ p.p.m.v. and $\Delta\text{CIE} = -2.1\text{‰}$ (thick curves). Blue and red shaded regions show solutions for $\Delta\text{CIE} = -1.6\text{‰}$ to -2.6‰ to illustrate the effect of ΔCIE on $p\text{CO}_2$ estimates (for a given $\Delta p\text{CO}_2$, lower ΔCIE values yield higher $p\text{CO}_2$ estimates and vice versa). $\Delta\text{CIE} = -2.5\text{‰}$ assumes that n -alkanes ($\text{CIE} = -5.1\text{‰}$; ref. 11) best represent $\text{CIE}_{\text{terrestrial}}$; $\Delta\text{CIE} = -1.6\text{‰}$ suggests a smaller offset between $\text{CIE}_{\text{terrestrial}}$ and $\text{CIE}_{\text{marine}}$ owing to an underestimation of the magnitude of $\text{CIE}_{\text{marine}}$ ($\text{CIE}_{\text{marine}} = -3.1\text{‰}$ versus -2.6‰). Vertical lines mark $\Delta p\text{CO}_2$ estimates for specific proposed sources of the event (green = methane hydrate¹⁴, $\delta^{13}\text{C}_{\text{source}} = -60\text{‰}$; purple = thermogenic methane⁵⁴ or permafrost thawing⁵⁰, $\delta^{13}\text{C}_{\text{source}} = -30\text{‰}$; and orange = wildfire burning⁵⁵ or oxidation of organic matter from drying of epicontinental seas⁵⁶, $\delta^{13}\text{C}_{\text{source}} = -22\text{‰}$) based on a mass balance equation (equation (3)) and the parameters used by McInerney and Wing¹¹ (0.3 p.p.m.v. increase in $p\text{CO}_2$ per Pg C added, $\delta^{13}\text{C}_{\text{initial}} = -2.5\text{‰}$, and $M_{\text{initial}} = 50,000$ Pg C); horizontal arrows mark the range of $\Delta p\text{CO}_2$ estimates calculated for each source (equation (3)), provided a range of estimates for the $p\text{CO}_2$ increase per Pg C added (0.23 to 0.39) and estimates of $\delta^{13}\text{C}_{\text{initial}}$ (-2.5 to -0.1‰) (Methods). The range of average Late Palaeocene (60–55Ma) $p\text{CO}_2$ estimates from other proxies (blue bars) are indicated; a single $p\text{CO}_2$ estimate from stomata provides a lower bound on $p\text{CO}_2$ during the PETM (red point and arrow) (references are provided in the Supplementary Information). Dashed lines mark pre-industrial (280 p.p.m.v.) and present-day (393 p.p.m.v.) $p\text{CO}_2$ levels, as well as a model-based projection of $p\text{CO}_2$ in the year 2300 if fossil fuel burning continues unabated (1,900 p.p.m.v.) (ref. 46). Grey-shaded region represents the range of $p\text{CO}_2$ projections for the year 2100 from the IPCC (566–821 p.p.m.v.) (ref. 60).

Based on the fundamental observation of increased carbon isotope fractionation in C_3 land plants in response to elevated $p\text{CO}_2$ levels (Fig. 1), we propose that the larger amplitude CIE recorded in terrestrial substrates results from the primary phenomenon of rising $p\text{CO}_2$ levels. We attribute deviations from the average size of the CIE measured on the same substrate at different sites to local or regional changes in water availability^{6,8,18,36}, plant composition^{16,17,38,52}, dissolution⁴³ and salinity⁴². For these reasons, the average of many CIEs measured across the planet should be used to determine the average magnitude of the marine and terrestrial signals for the purpose of reconciling the magnitude of the event and reconstructing $p\text{CO}_2$ levels.

We further note systematic differences in the magnitude of the CIE within the marine and terrestrial substrates as compiled by McInerney and Wing¹¹ in their Table 1. Within the marine record, foraminifera (benthic and planktonic) and bulk marine carbonate record the smallest CIE (-2.5 to -2.7‰), while algal lipids and bulk marine organic matter record a greater CIE (-3.5 to -4.1‰). In terrestrial systems, the smallest CIE is measured in bulk soil organic matter (-3.5‰), followed by tooth enamel and plant lipids (-4.8 to -5.1‰), with the largest CIE measured in soil carbonate (-5.5‰). The greater CIE measured in algal lipids compared with foraminifera is likely caused by elevated $p\text{CO}_2$ levels, as photosynthetic algae are also known to show increasing carbon isotope fractionation with increasing concentrations of CO_2 dissolved in water although these relationships vary widely (reviewed within ref. 53) and differ from that of higher land plants. Bulk organic matter in terrestrial and marine environments show the same median magnitude CIE (-3.5‰); the CIE measured in terrestrial bulk organic matter may be dampened relative to other terrestrial substrates by mixing of organic matter of a different age¹⁵, while the marine bulk organic matter CIE is likely augmented compared with other marine substrates by photosynthetic inputs from terrestrial and marine environments^{15,28–30}. Variability in the degree of these inputs may explain why bulk marine organic matter shows the greatest variability among all substrates ($1\sigma = \pm 2.2\text{‰}$). Within purely terrestrial systems, the median CIE recorded in plant lipids (-5.0‰) reflects the full effects of elevated $p\text{CO}_2$ levels on plant isotope fractionation (as shown here and in ref. 26); the similar median CIE recorded in fossil tooth enamel (-4.9‰) is not surprising considering that it reflects the $\delta^{13}\text{C}$ value of the plants the herbivore consumes. The very large CIE measured in paleosol carbonate (average = -5.5‰ , median = -6.3‰) may reflect a combination of the enhanced fractionation by plants under high $p\text{CO}_2$, diffusion of increased $p\text{CO}_2$ levels into the soil and increased productivity. Based on measurements of enamel carbonate, Secord *et al.*³³ attribute 1.5‰ of the CIE measured in soil carbonate to increased rates of carbon turnover, driven by warmer climate.

Our results illustrate the need to account for changes in $p\text{CO}_2$ concentration when interpreting changes in the carbon isotope composition of substrates derived at least in part from C_3 land plants, which dominate the terrestrial carbon record. Although our analysis was applied specifically to the PETM, the fundamental $p\text{CO}_2$ effect and equations presented here can be applied similarly to other global CIE events recorded in marine and terrestrial sediments (for example, Aptian–Albian, Early Toarcian, Triassic–Jurassic, Permian–Triassic and many others) in order to quantitatively reconstruct levels of $p\text{CO}_2$ before and during the CIE event.

Methods

Quantifying $\Delta p\text{CO}_2$. We used the following mass balance equation modified from McInerney and Wing¹¹ to quantify $\Delta p\text{CO}_2$ for each of the proposed sources (vertical, coloured lines in Fig. 3; green = methane hydrate¹⁴, $\delta^{13}\text{C}_{\text{source}} = -60\text{‰}$; purple = thermogenic methane⁵⁴ or permafrost thawing⁵⁰, $\delta^{13}\text{C}_{\text{source}} = -30\text{‰}$;

and orange = wildfire burning⁵⁵ or oxidation of organic matter from drying of epicontinental seas⁵⁶, $\delta^{13}\text{C}_{\text{source}} = -22\text{‰}$):

$$\Delta p\text{CO}_2 = \frac{-(\text{CIE}_{\text{marine}})(M_{\text{initial}})(0.3)}{\delta^{13}\text{C}_{\text{final}} - \delta^{13}\text{C}_{\text{source}}} \quad (3)$$

where M_{initial} is the mass of the Palaeocene surface reservoir, $\delta^{13}\text{C}_{\text{final}}$ is the $\delta^{13}\text{C}$ value at the PETM ($\delta^{13}\text{C}_{\text{final}} = \delta^{13}\text{C}_{\text{initial}} + \text{CIE}_{\text{marine}}$), $\delta^{13}\text{C}_{\text{initial}}$ is the $\delta^{13}\text{C}$ value of the Late Palaeocene carbon pool and $\delta^{13}\text{C}_{\text{source}}$ is the $\delta^{13}\text{C}$ value of the source responsible for the CIE. We used $\text{CIE}_{\text{marine}}$ (and not $\text{CIE}_{\text{terrestrial}}$) because it does not incorporate any land-plant-derived components and thus only represents changes in $\delta^{13}\text{C}_{\text{CO}_2}$. The constant 0.3 indicates that for every 1 Pg C added $p\text{CO}_2$ increases 0.3 p.p.m.v. (ref. 11); this value is within the range of values suggested from models of the carbon release at the PETM (for example, 0.23–0.39; refs 12, 27, 57). We calculated the value for $\text{CIE}_{\text{marine}}$ (–2.6‰) as the average of the CIEs measured in benthic forams (–2.5 ± 1.0‰, $n = 36$), planktic forams (–2.7 ± 1.0‰, $n = 36$) and bulk marine carbonate (–2.7 ± 1.1‰, $n = 33$) as listed in Table 1 of McInerney and Wing¹¹. Bulk marine organic matter (CIE = –4.1 ± 2.2‰, $n = 11$) was not included in the average because it may contain a mix of marine and terrestrial inputs^{28–30}; the single CIE measured on algal lipids (CIE = –3.5‰) was also excluded. Our values for $M_{\text{initial}} = 50,000$ Pg C and $\delta^{13}\text{C}_{\text{initial}} = -2.5\text{‰}$ were based on the values used by McInerney and Wing¹¹. We note, however, that the value for $\delta^{13}\text{C}_{\text{initial}} = -2.5\text{‰}$ may be too low; we estimate $\delta^{13}\text{C}_{\text{initial}}$ as high as –0.1‰ assuming a pre-industrial value of –2.1 to –2.6‰ (ref. 14) offset by +2.0‰ based on the secular change in $\delta^{13}\text{C}$ (ref. 58).

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B.A.S. and A.H.J. wrote the paper and analysed the results; B.A.S. developed the equations and methods with advice and assistance from A.H.J.

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