Invited research article

Towards determination of the source and magnitude of atmospheric $pCO_2$ change across the early Paleogene hyperthermals

Ying Cui$^a$*, Brian A. Schubert$^b$

$^a$ Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, United States
$^b$ School of Geosciences, University of Louisiana at Lafayette, LA 70504, United States

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ABSTRACT

The early Paleogene greenhouse climate is punctuated by a series of extreme global warming events known as hyperthermals that are associated with massive additions of carbon to the ocean-atmosphere system. However, no existing proxies have suitable resolution to capture the change in atmospheric carbon dioxide ($pCO_2$) across these events. Here, we reconstruct a nearly continuous record of $pCO_2$ during the early Paleogene based on changes in terrestrial carbon isotope discrimination calculated from published high-resolution marine and terrestrial carbon isotope records. We calculate relatively stable baseline $pCO_2 = 569 + 250/\Delta ^{14}C_{\text{pCO}_2}$ with significant increases in $pCO_2$ at each of four hyperthermals. These background levels are significantly higher than most existing proxy estimates, but still lower than levels commonly assumed within carbon cycle models. Based on the $pCO_2$ levels we calculate across each hyperthermal, we show that these events are associated with carbon additions most likely dominated by terrestrial organic matter oxidation or mantle-derived CO$_2$. By matching the new high-resolution $pCO_2$ data with global temperature data we calculate Earth-system sensitivity of $-0.8$ to $1.6KW^{-1}m^2$ across these hyperthermals. The slightly elevated ESS during the PETM and H2 suggests positive feedbacks through other greenhouse gases, changes in vegetation and/or oxidation of organic matter/methane may have amplified the temperature response to $CO_2$ addition.

1. Introduction

Climate sensitivity (CS; the equilibrium temperature increase due to a doubling of CO$_2$) has important implications for policy makers (Knutti and Hegerl, 2008; Rohling et al., 2012; Rogelj et al., 2014; Knutti et al., 2017; Cox et al., 2018). Current understanding of pre-Quaternary climate sensitivity (or Earth-system sensitivity) is based on individual estimates of $pCO_2$ from at least six different proxies (Royer, 2006; Park and Royer, 2011; Martínez-Botí et al., 2015; Anagnostou et al., 2016; Royer, 2016). Taken together, these data reveal Earth-system sensitivity of 1.6 to 9.6 °C during the Cenozoic (Hoffert and Covey, 1992; Hansen et al., 1993; Covey et al., 1996; Bijl et al., 2016; Lunt et al., 2010; Pagani et al., 2010; Royer, 2016), which includes both fast and slow feedbacks. The data used for these estimates are generally based on intervals of Earth history with stable levels of $pCO_2$; the temperature response to a rapid CO$_2$ increase is perhaps fundamentally different from long-term equilibrium Earth-system sensitivity (Zachos et al., 2008; Royer, 2016). Although some workers have studied past intervals of rapid $pCO_2$ and temperature increases as analogs for anthropogenic climate change (e.g., the Paleocene-Eocene Thermal Maximum, PETM; Zachos et al., 2008), existing proxies are generally unable to resolve the shape or magnitude of $pCO_2$ change across these events. The source of these events is also widely debated (Dickens, 2000; Kurtz et al., 2003; Higgins and Schrag, 2006), which leads to large uncertainty when modeling the $pCO_2$ change associated with these events (Panchuk et al., 2008; Zeebe et al., 2009; Cui et al., 2011). For this reason, a new high-resolution $pCO_2$ proxy capable of resolving $pCO_2$ across sub-million year timescales is needed.

The early Paleogene contains at least four such intervals of significant carbon release between 56 and 53.5 Ma, marked by significant negative carbon isotope excursions (CIEs) identified within both marine and terrestrial substrates (Cramer et al., 2003; Nicolo et al., 2007; Abels et al., 2016; Lauretano et al., 2016). High-resolution oxygen isotope measurements on foraminifera preserved within marine sediments suggest global deep sea temperature increases of as much as 11 °C associated with the largest one of these events (Thomas et al., 2002; Zachos et al., 2003; Tripati and Elderfield, 2004; McCarren et al., 2008; Zachos et al., 2008; Dunkley Jones et al., 2013; Hansen et al., 2013; Lauretano et al., 2015). Existing $pCO_2$ proxies, however, generally fail to precisely resolve the $pCO_2$ rise associated with these events (e.g.,
Gehler et al., 2016), which makes comparison to present-day anthropogenic CO₂ release difficult (Zeebe et al., 2016). Furthermore, modeling efforts to simulate pCO₂ levels across these events commonly set background pCO₂ = ~750 to 1000 ppmv (Panchuk et al., 2008; Zeebe et al., 2009; Cui et al., 2011; Zeebe et al., 2017), higher than any existing proxy-based value in order to simulate reasonable late Paleocene deep ocean temperature; these simulations may result in overestimations of peak pCO₂.

In this study, we present a high-resolution pCO₂ record across the early Paleogene hyperthermals based on changes in carbon isotope discrimination between the δ¹³C value of terrestrial organic matter and that of atmospheric CO₂ (Δ¹³C = (δ¹³C_CO₂ – δ¹³C_org)/(1 + δ¹³C_org/1000) (Schubert and Jahren, 2012). The effect of pCO₂ on carbon isotope discrimination has shown potential for reconstructing geologically short (< 1 Myr) timescales (Schubert and Jahren, 2015; Cui and Schubert, 2016), including the determination of background and peak levels of pCO₂ during the Paleogene hyperthermals (Schubert and Jahren, 2013; Abels et al., 2016; Cui and Schubert, 2017). Here, we demonstrate a new application of this approach towards generating a nearly continuous record of pCO₂ change across these events. These results allow for improved understanding of climate sensitivity in response to geologically rapid (i.e., < 1 Myr) pCO₂ rise, and comparison of pCO₂ proxy results with model predictions.

2. Methods

Schubert and Jahren (2015) showed how pCO₂ can be quantified based on a relative change in carbon isotope discrimination between some time t and a reference time (t = 0), designated as Δ(Δ¹³C):

\[
\Delta(\Delta^{13}C) = \frac{|(A)(B)(pCO_{2t}) + C|}{|(A + (B)(pCO_{2t}) + C)|} - \frac{|(A)B(pCO_{2t=0}) + C|}{|(A + (B)(pCO_{2t=0}) + C)|}
\]

(1)

where

\[
\Delta(\Delta^{13}C) = \Delta^{13}C_{(t)} - \Delta^{13}C_{(t=0)}
\]

(2)

which can be expanded as:

\[
\Delta(\Delta^{13}C) = \frac{(\delta^{13}C_{CO₂(t)} - \delta^{13}C_{org(t)})}{(1 + \delta^{13}C_{org(t)/1000})} - \frac{(\delta^{13}C_{CO₂(t=0)} - \delta^{13}C_{org(t=0)})}{(1 + \delta^{13}C_{org(t=0)/1000})}
\]

(3)

By rearranging Eq. (1), one can therefore quantify pCO₂(t) using the following equation:

\[
\Delta(\Delta^{13}C) \times A^2 + \Delta(\Delta^{13}C) \times A \times B \times pCO_{2t} + 2 \times \Delta(\Delta^{13}C) \times A \times B \times C + \Delta(\Delta^{13}C) \times B^2 \times C \times pCO_{2t=0} + \Delta(\Delta^{13}C) \times B^2 \times C^2 + A^2 \times B \times pCO_{2t=0} + \Delta(\Delta^{13}C) \times B^2 \times C
\]

(4)

where values for A, B, and C are curve fitting parameters (Schubert and Jahren, 2012; Cui and Schubert, 2016) (Table 1). Here, pCO₂(t=0) is equal to pre-PETM levels, determined from existing, independent proxies (Table 1 and Table S1-a), δ¹³C_org is the δ¹³C value of terrestrial organic matter measured from a site in northeast China with high water availability (Chen et al., 2014), and therefore δ¹³C_org was not likely affected by increases in precipitation (after Schubert and Jahren, 2012), which characterizes some hyperthermal sites (e.g., Pagan et al., 2006). δ¹³C_CO₂ is the δ¹³C value of CO₂ in the atmosphere determined from the δ¹³C value of benthi foraminifera (δ¹³C_benthic) from two deep sea drilling sites (ODP Site 1263 and 1262) at Walvis Ridge, following the approach of Tipple et al. (2010) (Fig. 1; see SI text for detail). We chose these two marine records because they provide the highest sampling resolution across the early Eocene hyperthermals.

Because each of the hyperthermals are defined at multiple sites from the Ocean Drilling Program by their negative carbon isotope excursions (i.e., Cramer et al., 2003), we use carbon isotope stratigraphy to align the marine-derived δ¹³C_CO₂ record (Fig. 1A) with the terrestrial record (Fig. 1B) in order to calculate net carbon isotope discrimination (Eqs. (2) and (3)) (Fig. 1C). This alignment assumes that the onset and peak of each CIE occur simultaneously in marine and terrestrial substrates (Abels et al., 2012, 2016; Chen et al., 2014). Linear interpolation between these tie points was performed to construct the age model for the terrestrial site.

Median pCO₂(t) and 68% confidence interval for each time t was determined using 10,000 Monte Carlo uncertainty propagation following the method described in Cui and Schubert (2016). Uncertainty in pCO₂(t) includes potential changes in photosynthetic rate or stomatal conductance in response to changing environmental conditions (Schubert and Jahren, 2012; Cui and Schubert, 2016), which occur independent of changes in pCO₂ (Schubert and Jahren, 2015). This method, unlike the method described in Schubert and Jahren (2013) and Cui and Schubert (2017), does not require estimates of the total mass of carbon within the ocean-atmosphere system (M₀) and the δ¹³C value of the source (δ¹³C_source), or the change in pCO₂ across each event (ΔpCO₂), and is preferred when background pCO₂ can be independently constrained (Schubert and Jahren, 2015; Cui and Schubert, 2016). This method further allows for reconstruction of pCO₂ across the entirety of an event (and independent determination of ΔpCO₂, which can be used to infer possible sources of the event), compared with our previous work, which quantified only background and peak pCO₂ across a wide

<table>
<thead>
<tr>
<th>Inputs used to calculate pCO₂(t) (Eq. (4)) with reference period 56.4–56.5 Ma (t = 0).</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>pCO₂(t=0) 338 ppmv</td>
<td>Koch et al. (1992); Sinha and Stott (1994); Royer et al. (2001); and McCarren et al. (2008)</td>
</tr>
<tr>
<td>Δ¹³C_CO₂(t=0) −5.2‰</td>
<td>This study (data based on Lauretano et al., 2015 and McCarren et al., 2008)</td>
</tr>
<tr>
<td>Δ¹³C_org(t=0) −22.04‰</td>
<td>Chen et al. (2014)</td>
</tr>
<tr>
<td>Δ¹³C_CO₂(t=0) Variable</td>
<td>This study (data based on Lauretano et al., 2015 and McCarren et al., 2008)</td>
</tr>
<tr>
<td>Δ¹³C_org(t=0) Variable</td>
<td>Chen et al. (2014)</td>
</tr>
<tr>
<td>A 28.26</td>
<td>Schubert and Jahren (2012)</td>
</tr>
<tr>
<td>B 0.22</td>
<td>Cui and Schubert (2016)</td>
</tr>
<tr>
<td>C Median value determined in Monte Carlo analysis</td>
<td>Cui and Schubert (2016)</td>
</tr>
</tbody>
</table>

* Reconstructed pCO₂(t) and its 1σ uncertainty are listed in Table S2.

† 54 ppmv represents the ± error because of a need to assume Gaussian distribution.

§ Calculated by solving Eq. (2) with pCO₂ = 0 and Δ¹³C = 4.4, such that C = [4.4 × (A)] / [(A − 4.4) × (B)].
Atmospheric CO₂ (Δ13C) and terrestrial CIEs (Bowen et al., 2004; McInerney and Wing, 2011; Abels et al., 2012, 2016), we observed smaller magnitude changes in Δ13C value inferred from the marine record (Fig. 1A) compared with the terrestrial record (Fig. 1B) across each event. After correcting for changes in Δ13C, we observed an increase in carbon isotope discrimination (Δ13C) across each of the four CIEs (Fig. 1C), consistent with elevated levels of pCO₂ at each event. Using these data and Eq. (4) we present a nearly continuous record of pCO₂ across 56 to 53.5 Ma (Fig. 2). These data indicate background pCO₂ = 569 + 250/−146 ppmv punctuated by brief (< 200 kyr) intervals with higher pCO₂ at each hyperthermal. These new background pCO₂ estimates are significantly lower than those used in carbon cycle models (750 to 1000 ppmv, Cui et al., 2011; Panchuk et al., 2008; Zeebe et al., 2009, 2017), but are also notably higher than existing low-resolution proxy estimates that collectively indicate pCO₂ = 348 ± 112/−76 ppmv (average value between 56 and 53.5 Ma from compiled proxies, n = 29; Fig. 2, Table S1-b). In contrast to previous proxy estimates, these new data are able to resolve the brief (< 200 kyr) pCO₂ increases associated with each hyperthermal. As expected based on the size of the recorded CIEs, maximum pCO₂ occurred during the PETM (average pCO₂ from 55.8 to 55.9 Ma is 1323 + 1317/−487 ppmv), followed by H1 (pCO₂ = 989 + 676/−315 ppmv), I1 (pCO₂ = 962 + 592/−299 ppmv), and H2 (pCO₂ = 796 + 403/−224 ppmv).

Fig. 3 shows the results of our previous work (Cui and Schubert, 2017), which calculated background and peak levels of pCO₂ for each of the four hyperthermals and two carbon release scenarios: methane hydrate (Δ13C = −60 ± 10‰) and organic matter oxidation (Δ13C = −26 ± 5‰), with the addition of a new analysis based on a substantial volcanic source component (Δ13C value = −11 to −17‰), as proposed by Gutjahr et al. (2017) for the PETM. These results show that lower Δ13C source values require lower background and peak pCO₂ levels in order to reconcile the marine-terrestrial offset observed across as many as 16 different combinations of available marine and terrestrial Δ13C records. By plotting the source-independent baseline and peak pCO₂ values calculated here with our previous source-dependent pCO₂ results, we find that the pCO₂ levels determined here are most consistent with results calculated assuming an organic matter source, and that a significant contribution from methane hydrate appears unlikely (Fig. 3). Given our high upper errors for peak pCO₂, a scenario requiring a substantial CO₂ contribution from volcanism cannot be ruled out; however, methane hydrate as a sole source of the CIEs is incompatible with our results (Fig. 3).

4. Discussion

Available proxy data suggest relatively low pCO₂ (348 + 112/−76 ppmv) during the early Paleogene (i.e., similar to 20th and 21st century levels) while model simulations generally set background pCO₂ during this interval ~2 to 3 × higher than these proxies suggest (Cui et al., 2011; Panchuk et al., 2008; Zeebe et al., 2009, 2017). The lowest pCO₂ estimates (< 300 ppmv) are primarily based on paleosol carbonate (Cerling, 1992; Sinha and Stott, 1994; Royer et al., 2001) and the revised stomatal proxy (Barclay and Wing, 2016); the highest pCO₂ estimates from this time interval are from the Δ13CO₂ proxy (Gehler et al., 2016), but include the PETM interval, and are therefore excluded from this calculation of background pCO₂. Our new data suggest higher background pCO₂ (569 + 250/−146) that are more in line with global surface temperatures that are > 10 °C warmer than today (Hansen et al., 2013). These data also represent the first high-resolution pCO₂ record across the early Paleogene hyperthermals and allow for direct comparison with temperature records derived from oxygen isotope measurements in foraminifera (Fig. 4). As expected, both pCO₂ and temperature increase substantially at each CIE, but the data also resolve a small but significant long-term increase in background pCO₂ (22 ppmv per 10⁶ years, p = .01) consistent with a small increase in temperature (0.5 °C per 10⁶ years, p < .001) across the record (56 to 53.5 Ma) (Fig. 4).

3. Results

Consistent with previous studies comparing the size of the marine and terrestrial CIEs (Bowen et al., 2004; McInerney and Wing, 2011; Y. Cui, B.A. Schubert

Fig. 1. Carbon isotope records across the four early Paleogene hyperthermals (56 to 53.5 Ma, using age option 2 of Westerhold et al., 2007). (A) Δ13C in atmospheric CO₂ (Δ13C CO₂) determined following the approach of Tipple et al. (2010) using Δ13C values measured in benthic foraminifera from Site 1263 and Site 1262 at Walvis Ridge (data from McCarren et al., 2008, Lauretano et al., 2015 and Litjler et al., 2014); (B) Δ13C values measured in terrestrial bulk organic matter (Δ13C org) from Fushun Basin, North China (from Chen et al., 2014); (C) Net carbon isotope discrimination (Δ13C) calculated from Δ13C CO₂ and Δ13C org. Note that the Δ13C value increases across each hyperthermal, consistent with elevated pCO₂; excluding the transient excursions, there is a small (0.2‰ per 10⁶ years) increase in Δ13C value across the study interval (56 to 53.5 Ma) (p = .005).
Determination of the source of the hyperthermals is complex. Careful analysis of chemical and biotic records of environmental change across the PETM suggests warming preceded the carbon addition and may have been a trigger for the carbon release (Sluijs et al., 2007). Subsequent studies indicate that orbital changes in insolation could be a trigger for massive releases of methane hydrate (Lunt et al., 2011) or soil organic carbon (Deconto et al., 2012) and match observed patterns in the magnitude and timing of the subsequent hyperthermals. More recently, Gutjahr et al. (2017) provided evidence of volcanic CO2 as a primary trigger of the PETM specifically, but also recognized that thawing permafrost or methane hydrate destabilization may have been an important amplifying feedback that contributed anywhere from ~10 to 60% of the total carbon released. Our data can be used to generally rule out a pure methane hydrate source, which requires significantly lower levels of pCO2 than determined here in order to reconcile the observed marine-terrestrial offsets (Fig. 3). However, it is reasonable to expect that multiple factors may have contributed to the total carbon released, through various scenarios of initial triggers and/or amplifying feedbacks. As such, scenarios with ~30 to 45% contribution from methane hydrate ($\delta^{13}C = -60\%$) with the remainder from mantle-derived carbon ($\delta^{13}C = -6\%$) can yield an overall isotopic value similar to that of oxidized organic matter. Our data therefore support scenarios that include methane hydrate in no more than a minority role, with the majority of the carbon originating from isotopically heavier sources (e.g., terrestrial organic matter, volcanic CO2).

Our new high-resolution source-independent pCO2 estimates reported here can provide an independent estimate of Earth system sensitivity (ESS), which includes both long- and short-term feedbacks...
5. Conclusions

These data represent the first high-resolution pCO2 record across the early Paleogene hyperthermals and show that pCO2 tracks temperature changes across the entirety of this interval. Background pCO2 was likely ~1.5× higher than that determined using other proxies; we assert that these new estimates are more in line with global surface temperatures that are >10°C warmer than today (Hansen et al., 2013). Revision of the background pCO2 used in model simulations of these events will serve to lower the predicted peak pCO2 and thus affect interpretations of climate sensitivity across these events (Dunkley Jones et al., 2010, 2013).

Identification of organic matter oxidation as an important driver (or feedback) in these hyperthermals has significant implications for anthropogenic climate change. The world’s permafrost regions currently store 1672 Pg C (Tarnocai et al., 2009), of which ~30% may be released by the year 2100 (MacDougall et al., 2012). Experiments indicate that this carbon release is not being offset through enhanced plant growth via CO2 fertilization or warming temperatures, resulting in the Arctic becoming a net flux, rather than sink for CO2 (Webb et al., 2016). Because warming will continue long after fossil fuel emissions level off or decline (Archer et al., 2009), CO2 released from permafrost is likely to contribute elevated pCO2 and temperature through at least the year 2300 (MacDougall et al., 2012). Regardless of the cause of early warming, oxidation of organic matter is therefore likely to serve as an important feedback on climate change in the coming centuries (Schuur et al., 2008).

Acknowledgement

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gloplacha.2018.08.011.

References

Cerling, T.E., 1992. Use of carbon isotopes in paleosols as an indicator of the P(CO2) of oxidation of organic matter or methane may have amplified the global temperature response to changes in CO2. However, it is important to note that estimates of ESS across all the hyperthermals depend heavily on changes in global mean surface temperature, but to date only the PETM has substantial global coverage, and is subject to large uncertainty (Dunkley Jones et al., 2013). This suggests a need for future studies constraining global mean surface temperature across H1, H2 and I1.

(Stubley et al., 2013). This result is also similar to the estimates for the PETM (1.0 to 1.8 KW m⁻²) and early Eocene (0.65 ± 0.25 KW m⁻²) from Rohling et al. (2012), and a recent Eocene sensitivity estimate of 4.6 K per doubling of CO2 when CO2 levels are below 1000 ppmv by Keery et al. (2018). The elevated ESS during the PETM and H2 relative to other hyperthermals suggests positive feedbacks through other greenhouse gases, changes in vegetation (Kiehl and Shields, 2013), and/or