Very large release of mostly volcanic carbon during the Paleocene-Eocene Thermal Maximum

By

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Earth system modelling – further model and model-data analysis

In our main analysis, we noted that the predicted peak increase in global surface temperature is close to estimates derived from compilations of available proxy records, while our inferred source and total emissions of carbon falls within existing estimates of volcanic and/or volcanic driven activity and carbon release adding plausibility to our inferences. We furthermore noted that none of: uncertainties in the age model, uncertainties in the boron proxy pH reconstruction, or whether assimilation is carried out on smoothed vs. 'raw' data, unduly affect our conclusions. In this section, we greatly extend the scope of model-data assessment to span a range of sites and proxies in order to provide a more in-depth and independent test of our preferred model-generated scenario of PETM carbon release as well as elucidate model uncertainties.

Our primary data assimilated in the model is the reconstructed ocean surface pH at Site 401, and this leads directly to our reconstruction of total carbon release via determination of the source isotopic composition of this carbon. To date, four deep ocean sites exist for which pH has been reconstructed by means of boron isotopes (shown in Fig. 2) – 401, 865, 1209, and 1263. Comparison of the model-projected evolution of surface ocean pH for each of the four locations vs. the data reconstructions, is shown in Extended Data Fig. 9 (and see Extended Data Fig. 6). To this comparison we also add model-projected (also for experiment ID 'R07sm_Corg') vs. observed evolution of sedimentary carbonate ($CaCO_3$) content (e.g. Extended Data Fig. 7), as this relates to (but does not directly reflect) carbon emissions, plus a comparison of modelled and observed bulk carbonate $\delta^{13}C$ for completeness.

For Site 401, the model matches the observed pH (excepting a small deviation during PETM recovery), but as this data is assimilated in the model, this is expected. The available observed wt% $CaCO_3$ data at Site 401 is patchy, but from what exists spanning pre-event to peak event, the model projected evolution of wt% $CaCO_3$ closely matches the data. However, during PETM recovery when the model predicts (and one would *a priori* expect) a prolonged overshoot in wt% $CaCO_3$, the data exhibits an unexpected decline to below pre-event values, not reproduced by the model. One possible explanation is that evidence for an increase in the hydrological cycle following peak warming of the PETM drove increased input of terrestrial (clay) materials (not accounted for in the model simulation), thereby diluting the carbonate

content in the upper part of the early Eocene section at Site 401[1]. Lastly, the model parallels (with an offset) the bulk carbonate $\delta^{13}C$ response except during the recovery, which the bulk $CaCO_3$ $\delta^{13}C$ does not appear to record (potentially also related to a higher clay input to the depositional site[1]). Note that monospecific planktic foraminiferal $\delta^{13}C$ data was assimilated in the model as reflecting surface ocean geochemistry. In contrast, the bulk observed and modelled records in this analysis, also reflect sedimentary preservation and plankton assemblage effects.

For Site 865, pH data is extremely sparse and suggests that the model slightly underestimates the magnitude of the pH change (although taking into account the uncertainty in the data (Fig. 2), the model projection of the peak excursion value is consistent with the data) as well as the rapidity of its recovery. Only pre-event wt% $CaCO_3$ data is available, which the model closely reproduces at this site. For bulk $CaCO_3$ $\delta^{13}C$ – the model matches almost exactly the data across the onset and peak of the event given a very sparse sampling density, but slightly over-predicts the recovery in $\delta^{13}C$ as compared to the single available recovery interval data point.

For Site 1209, the model shows a visually very good correspondence with the pH data, except for two points during the peak which on face value suggest a partial recovery before renewal of low pH values. Again, in this simple comparative analysis we have not taken into account data uncertainty (plotted in Fig. 2) and much of the remaining model-data misfit can be account for by this uncertainty. Little response is seen in either the model or data with respect to wt% $CaCO_3$. For bulk carbonate $\delta^{13}C$, the modelled excursion is slightly smaller and lagged as compared to the data.

Finally, for Site 1263, the pH recovery is a little too slow in the model compared to the data (but again, this is without taking into account any data uncertainty) although what peak PETM conditions might have been are not resolved in the data. As per Site 1209, bulk carbonate $\delta^{13}C$ is lagged in the model and the excursion a little smaller than observed. However, there is a stark misfit with respect to the observed wt% $CaCO_3$ response across the event (discussed in detail below).

What can this analysis tell us about how confident we can be in the inferred emissions scenario and about model uncertainly in general? Firstly, there does not seem to be any systematic bias in the evolution of surface ocean pH in the model as compared to the data, with the exception that simulated pH recovery may be a little

too slow. The most likely explanation for this would be that the rate of carbon removal via silicate weathering and/or organic matter burial is being underestimated. While bulk $CaCO_3$ $\delta^{13}C$ records indicate that the model response is broadly consistent with observations, there is a tendency for the modelled excursion to be lagged and narrower than observed. This may simply reflect differences between the internal age model in the simulations, which assumes a constant detrital sedimentation rate (following *Jennions et al.*[2]) and the Site 690 tied age models applied to the four sites. Changes in the intensity and nature of bioturbation and in the assumptions of which fraction of $CaCO_3$ is being dissolved, may also play a role (see ref. 2 for a discussion of similar phenomena in respect to a subsequent hyperthermal event). The wt% $CaCO_3$ records are a little more revealing, particularly for Site 1263 and to a lesser extent, in the recovery at Site 401. While the deep sea faunal and hence bioturbation response may be important (see ref. 3), model-data misfits likely indicate changes occurring in the ventilation and ocean circulation patterns that are not being appropriately reproduced in the model. This does not necessarily imply a significant uncertainty then exists in the diagnosed total carbon release across the PETM because of the relatively good model-data correspondence in pH – a surface property unlikely significantly impacted by changes in interior ocean ventilation patterns. Considerably more detailed and spatially resolved model-data analysis of the evolving patterns of carbonate preservation and burial would be needed to fully elucidate and quantify the implications of model biases in this respect (hence falling beyond the scope of this present study).

We can also look at how sedimentary carbonate content evolves in another way. Extended Data Fig. 7 shows the pre-event pattern of the $CaCO_3$ content of surface sediments together with a series of anomalies in wt% $CaCO_3$, using the same time-points as for the surface ocean pH analysis (Extended Data Fig. 6) (and still focussing on experiment ID 'R07sm_Corg'). We find an initial decline in wt% $CaCO_3$, reaching a nadir around 15-20 kyr after PETM onset. Mean global carbonate content then recovers and over-shoots (recorded in the 58.2 and 71.5 ka time-slices). Although the full spatial extent of $CaCO_3$ dissolution is not captured in the spatial snap-shots, our modelling indicates an early impact in the North Atlantic and Tethys, followed by an early recovery in those regions. In contrast, the full dissolution impact in the Pacific, Southern Atlantic, and Indian Oceans takes longer to develop and is

apparently more intense. Out of the latter three regions, reduced sedimentary carbonate content is greatest and most widespread in the Southern Atlantic and Indian Oceans as expected (e.g. Zeebe and Zachos[4]). We note that in the South Atlantic Ocean and in the vicinity of Walvis Ridge, enhanced carbonate dissolution is widespread, <u>except</u> at shallower depths such as the location of Site 1263. It should be noted that the bathymetry shown in Extended Data Fig. 7g and used for calculating the solubility of $CaCO_3$, deviates from the ocean circulation model bathymetry at the model locations of key deep-sea drilling sites, to facilitate model-data comparison. This is apparent in the existence of a 'plateau' at Shatsky Rise, and somewhat also at Walvis Ridge. Hence the partial model-data failure apparent in Figure Extended Data Fig. 9 may primarily reflect a model failure to correctly project intermediate water mass changes and characteristics (e.g. see *Jennions et al.*[2]), rather than a failure to account for carbonate dissolution and buffering in the deep South Atlantic as a whole.

Earth system modelling – uncertainty in projections

As in all numerical modelling and particularly for time-periods outside of the observational era, uncertainties in model projections exist and need to be recognized. These uncertainties can be minimized, as we have done here, by enforcing traceability to observed modern climatology and carbon cycling dynamics:

1. Employing a representation of ocean circulation and climate feedback calibrated and assessed against modern observational data[5,6], and making the minimal possible changes for the late Paleocene, namely: adjusted continental configuration and bathymetry, adjusted wind stress and wind speed, adjusted planetary albedo, reduced solar constant[7].

2. Employing a representation of ocean carbon, nutrient (here: just phosphate), and carbon isotope cycling calibrated and assessed against modern observational data[8-10], here adjusting only: atmospheric pCO_2 and $\delta^{13}C$, and ocean DIC, ALK, and Mg/Ca ratios, as described earlier[7,10].

3. Employing a representation of calcium carbonate ($CaCO_3$) production, preservation, and burial, that has been calibrated and assessed against modern observational data[11], and here adjusting only global weathering rates and the biological export $CaCO_3$:POC 'rain ratio' in the ocean, as described in references 17 and 19.

However, a number of areas of potential uncertainty remain (excepting ocean pH, which has been discussed in depth earlier):

- **Climate sensitivity**. The cGENIE model employs a fixed relationship between changes in CO_2 and radiative forcing, meaning that its climate sensitivity is effectively prescribed in our experiments. Paleogene climate sensitivity is potentially different from modern[12]. Our diagnosed change in atmosphere pCO_2 induces a global mean increase increase in ocean surface temperature across the PETM slightly lower than observations, allowing for climate sensitivity to be slightly higher than programmed into the model. Regardless, it is unlikely that Paleogene climate sensitivity uncertainty significantly impacts our findings as the contribution of climate-carbon cycle feedbacks are relatively small compared to emissions[13].

- **Surface climate**. The magnitude of surface ocean warming across the PETM simulated by cGENIE (2.3-6.0°C) is similar to recent proxy compilations (4-5°C)[14]. However, as compared to Mg/Ca and $\delta^{18}O$ reconstructed temperatures (Extended Data Fig. 8), ocean surface temperatures at the location of Site 401 in cGENIE are persistently about 7°C too low. Given that the magnitude of global mean warming is approximately correct, it is not obvious that the existence of a high Northern latitude cold bias leads to significant error in our deduced carbon emissions.

- **Ocean circulation**. Although cGENIE can reproduce observed gradients in benthic $\delta^{13}C$ and hence by inference, large scale ocean circulation patterns in the early Eocene[15], there is little constraint on the details of ocean circulation patterns and model-data misfits in the South Atlantic as revealed in our Site 1263 analysis reflecting substantial uncertainty here. However, because our inversion rests on surface seawater proxy data, uncertainty in (intermediate or deep) model circulation will be less critical to our conclusions.

- **Ocean geochemistry**. The assumed values for pre PETM ocean DIC and ALK, arise from assumptions regarding pCO_2 (itself constrained by matching observed deep ocean temperatures in the model) and the pattern of carbonate burial in the deep ocean (following ref. 17). Significant uncertainties exist on past ocean Mg/Ca ratios, which in turn influence the relationship between carbonate burial, DIC and ALK. However, radically different DIC inventories

(and hence isotopic buffering) are unlikely – a variety of previously published (and widely differing in methodology) analyses all produce a relatively consistent history of DIC, ALK, and surface ocean pH through the Cenozoic[7]. Furthermore, our initial pCO$_2$ assumption agrees with independent constraints[16].

- **Ocean productivity**. Both the initial state, and response across the PETM, is highly uncertain in both data and model. Changes in productivity not correctly accounted for in the model could impact the interpretation of both pH and δ^{13}C, although given the relative uniformity of the surface ocean pH response, the greater potential for our conclusions to be affected would be in respect of δ^{13}C. However, ocean surface δ^{13}C gradients (today) are much smaller than the total magnitude of the CIE lessening the impact that productivity uncertainty might have. Furthermore, we have already assumed and accounted for a significant uncertainty due to how the CIE is recorded and assimilated in the model.

- **The 'CCD' and carbonate buffering**. How well the deposition and preservation of CaCO$_3$ on the ocean floor is represented is arguably the most significant uncertainty. Although the model has been calibrated to an extensive paleo dataset[17], the CaCO$_3$:POC export ratio is assumed uniform and invariant. Errors in this would propagate through to errors (likely overestimates) in diagnosed carbon release[18], although we note that less buffered (and hence more sensitive to carbon release) models and associated scenarios, fail to fit observed pH proxy data[19].

Weathering and recovery feedbacks. Finally, the parameterizations of carbonate (F$_{CaCO3}$) and silicate (F$_{CaSiO3}$) weathering we assume are:

$$F_{CaCO_3} = F_{CaCO_3,0} \left(1 + k_{Ca}\left(T - T_0\right)\right)$$

$$F_{CaSiO_3} = F_{CaSiO_3,0}\, e^{\frac{1000E_a}{RT_0^2}(T-T_0)}$$

and are derived from references 15 and 20, respectively (see *Lord et al.*[21] for a complete description of terms plus discussion). These are both based solely on global mean surface land air temperature (T) and its deviation from a reference value (T_0). As such, we omit consideration of spatial patterns of temperature change, as well as runoff and plant productivity as potential modulating factors[22]. As an extreme test, in experiments with no weathering response to climate (Extended Data Table 1a), diagnosed cumulative carbon emissions are around 40% lower. A reasonable estimated uncertainty on our conclusions might then be half this: ±20% (±2000 PgC).

Overall, as might be expected for a protracted (>10 kyr total duration) geological event, the major model uncertainties likely lie in the long-term components and response of the global carbon cycle rather than details of ocean circulation or climate. Considerably more data (both spatially and temporary resolved, and for multiple proxies) and involved model-data analysis is needed for any more formal uncertainty to be placed on our model-derived PETM carbon release estimates beyond the sensitivity tests we have performed here.

References within Supplementary Information S1

1   Bornemann, A. *et al.* Persistent environmental change after the Paleocene-Eocene Thermal Maximum in the eastern North Atlantic. *Earth and Planetary Science Letters* **394**, 70-81 (2014).

2   Jennions, S. M., Thomas, E., Schmidt, D. N., Lunt, D. & Ridgwell, A. Changes in benthic ecosystems and ocean circulation in the Southeast Atlantic across Eocene Thermal Maximum 2. *Paleoceanography* **30**, 1059-1077 (2015).

3   Ridgwell, A. Interpreting transient carbonate compensation depth changes by marine sediment core modeling. *Paleoceanography* **22** (2007).

4   Zeebe, R. E. & Zachos, J. C. Reversed deep-sea carbonate ion basin gradient during Paleocene-Eocene thermal maximum. *Paleoceanography* **22**, Art. No.: PA3201 (2007).

5   Hargreaves, J. C., Annan, J. D., Edwards, N. R. & Marsh, R. An efficient climate forecasting method using an intermediate complexity Earth System Model and the ensemble Kalman filter. *Clim. Dyn.* **23**, 745-760 (2004).

6   Edwards, N. R. & Marsh, R. Uncertainties due to transport-parameter sensitivity in an efficient 3-D ocean-climate model. *Clim. Dyn.* **24**, 415-433 (2005).

7   Ridgwell, A. & Schmidt, D. N. Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release. *Nature Geoscience* **3**, 196-200 (2010).

8   Ridgwell, A. *et al.* Marine geochemical data assimilation in an efficient Earth System Model of global biogeochemical cycling. *Biogeosciences* **4**, 87-104 (2007).

9   Cao, L. *et al.* The role of ocean transport in the uptake of anthropogenic CO_2. *Biogeosciences* **6**, 375-390 (2009).

10   Turner, S. K. & Ridgwell, A. Development of a novel empirical framework for interpreting geological carbon isotope excursions, with implications for the rate of carbon injection across the PETM. *Earth and Planetary Science Letters* **435**, 1-13 (2016).

11   Ridgwell, A. & Hargreaves, J. C. Regulation of atmospheric CO_2 by deep-sea sediments in an Earth system model. *Glob. Biogeochem. Cycle* **21**, Art. No. GB2008 (2007).

12   Frieling, J. *et al.* Extreme warmth and heat-stressed plankton in the tropics during the Paleocene-Eocene Thermal Maximum. *Science Advances* **3** (2017).

13   Ridgwell, A., Zondervan, I., Hargreaves, J. C., Bijma, J. & Lenton, T. M. Assessing the potential long-term increase of oceanic fossil fuel CO_2 uptake due to CO_2-calcification feedback. *Biogeosciences* **4**, 481-492 (2007).

14   Dunkley Jones, T. *et al.* Climate model and proxy data constraints on ocean warming across the Paleocene-Eocene Thermal Maximum. *Earth-Science Reviews* **125**, 123-145 (2013).

15   Turner, S. K. & Ridgwell, A. Recovering the true size of an Eocene hyperthermal from the marine sedimentary record. *Paleoceanography* **28**, 700-712 (2013).

16   Schubert, B. A. & Jahren, A. H. Reconciliation of marine and terrestrial carbon isotope excursions based on changing atmospheric CO_2 levels. *Nature Communications* **4**, Art. No. 1653 (2013).

17   Panchuk, K., Ridgwell, A. & Kump, L. R. Sedimentary response to Paleocene-Eocene Thermal Maximum carbon release: A model-data comparison. *Geology* **36**, 315-318 (2008).

18   Zeebe, R. E., Zachos, J. C. & Dickens, G. R. Carbon dioxide forcing alone insufficient to explain Palaeocene-Eocene Thermal Maximum warming. *Nature Geoscience* **2**, 576-580 (2009).

19   Penman, D. E., Hönisch, B., Zeebe, R. E., Thomas, E. & Zachos, J. C. Rapid and sustained surface ocean acidification during the Paleocene-Eocene Thermal Maximum. *Paleoceanography* **29**, 357-369 (2014).

20   Brady, P. V. The Effect of Silicate Weathering on Global Temperature and Atmospheric CO_2. *J Geophys Res-Solid Earth* **96**, 18101-18106 (1991).

21   Lord, N. S., Ridgwell, A., Thorne, M. C. & Lunt, D. J. The 'long tail' of anthropogenic CO_2 decline in the atmosphere and its consequences for post-closure performance assessments for disposal of radioactive wastes. *Mineralogical Magazine* **79**, 1613-1623 (2015).

22   Colbourn, G., Ridgwell, A. & Lenton, T. M. The time scale of the silicate weathering negative feedback on atmospheric CO_2. *Glob. Biogeochem. Cycle* **29**, 583-596 (2015).