

# Sedimentary response to Paleocene-Eocene Thermal Maximum carbon release: A model-data comparison

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## ABSTRACT

Possible sources of carbon that may have caused global warming at the Paleocene-Eocene boundary are constrained using an intermediate complexity Earth-system model configured with early Eocene paleogeography. We find that 6800 Pg C ( $\delta^{13}\text{C}$  of  $-22\text{‰}$ ) is the smallest pulse modeled here to reasonably reproduce observations of the extent of seafloor  $\text{CaCO}_3$  dissolution. This pulse could not have been solely the result of methane hydrate destabilization, suggesting that additional sources of  $\text{CO}_2$  such as volcanic  $\text{CO}_2$ , the oxidation of sedimentary organic carbon, or thermogenic methane must also have contributed. Observed contrasts in dissolution intensity between Atlantic and Pacific sites are reproduced in the model by reducing bioturbation in the Atlantic during the event, simulating a potential consequence of the spread of low-oxygen bottom waters.

**Keywords:** Paleocene-Eocene Thermal Maximum, model studies, carbonate compensation depth, methane, volcanism.

## INTRODUCTION

The Paleocene-Eocene boundary (ca. 55 Ma), was characterized by geologically abrupt global warming, with ocean temperatures rising by  $\sim 5^\circ\text{C}$  over as little as 10 k.y. (e.g., Kennett and Stott, 1991; Zachos et al., 2003; Sluijs et al., 2006). Well-preserved marine planktonic and benthic forams record carbon isotope ( $\delta^{13}\text{C}$ ) excursions as large as  $-4\text{‰}$  (Lu and Keller, 1993; Cramer et al., 1999; Thomas et al., 2002), and marine sediments display a marked decrease in calcium carbonate weight percent ( $\text{CaCO}_3$  wt%; e.g., Zachos et al., 2005). Together, the negative  $\delta^{13}\text{C}$  excursion and  $\text{CaCO}_3$  dissolution imply that a large pulse of  $^{13}\text{C}$ -depleted carbon to the ocean or atmosphere caused the Paleocene-Eocene Thermal Maximum (PETM) (Dickens et al., 1995).

The cause of this event has remained speculative because the isotope excursion is insufficient to constrain the potential sources of carbon addition. Additional constraints must be applied, and these require quantitative interpretation. To simultaneously address all the pertinent available geological information (sedimentary composition, isotopic, and climatic) requires analysis within an Earth-system model. Here we present the first spatially resolved model study of ocean + sediment carbon cycling and climate to be applied to the pre-Quaternary, which we ground-truth against a comprehensive compilation of late Paleocene marine sedimentary information. Using this, we compare observed spatial variations in the  $\text{CaCO}_3$  wt% of marine PETM sediments with predicted changes in  $\text{CaCO}_3$  wt% for carbon pulses spanning the full range of possible isotopically distinct sources from biogenic methane (i.e., the

methane clathrate hypothesis of Dickens et al., 1995), with  $\delta^{13}\text{C}$  of  $-60\text{‰}$ , to mantle-derived volcanic  $\text{CO}_2$  with  $\delta^{13}\text{C}$  of  $-5\text{‰}$ .

## METHODS

We use the GENIE-1 model, which consists of a three-dimensional ocean and atmosphere circulation model (Edwards and Marsh, 2005), coupled to marine carbon cycle (Ridgwell et al., 2007) and seafloor sediment models (Ridgwell and Hargreaves, 2007; Ridgwell, 2007). The sediment model simulates the preservation of carbonates in deep-sea sediments as a function of bottom-water chemistry and the rain of  $\text{CaCO}_3$  and particulate organic carbon (POC), and explicitly records the  $\text{CaCO}_3$  dissolution response to  $\text{CO}_2$  addition as a stratigraphic record of carbonate content and isotopic composition in stacked 1-cm-thick sediment layers (Ridgwell, 2007). Bioturbation is simulated by mixing adjacent layers within the sediment stack. The mixing rate is highest at the top of the sediment column with a uniform biodiffusion coefficient of  $150\text{ cm}^2\text{ k.y.}^{-1}$  (after Archer, 1991, 1996) applied over the uppermost 5 cm, decreasing below this level with an  $e$ -folding depth of 1 cm (Ridgwell, 2001, 2007). Sediments also receive a nonbiogenic, noncarbonate detrital flux of  $0.18\text{ g cm}^{-2}\text{ k.y.}^{-1}$ , a value deduced from typical late Paleocene open-ocean sedimentation rates and detrital content (Zeebe and Zachos, 2007). For this study, we apply an early Eocene bathymetry and continental configuration from Bice et al. (1998) and a zonally averaged wind-stress field from Bice and Marotzke (2002), both transformed to a  $36 \times 36$  equal-area grid. GENIE-1 was spun up for 200 k.y. to reach geochemical equilibrium between weathering

and sedimentation and to build up a sufficiently deep sediment column.

Global average concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were set to 18.2 and 29.9 mmol  $\text{kg}^{-1}$ , respectively, from the compilation of Tyrrell and Zeebe (2004) of fluid inclusion and Ca/Mg paleosalinity determinations (see GSA Data Repository Appendix DR1<sup>1</sup>). A late Paleocene  $p\text{CO}_2$  level of 750 ppm gives model global-average deep-ocean temperatures of  $\sim 7^\circ\text{C}$ , warmer than modern but cooler than temperatures derived from  $\delta^{18}\text{O}$  analyses of benthic foraminifera of  $\sim 11\text{--}12^\circ\text{C}$  (Kennett and Stott, 1991; Bralower et al., 1995; Thomas et al., 2002). A  $p\text{CO}_2$  level of 750 ppm is within the range of proxy studies and numerical models that have yielded estimates of late Paleocene  $p\text{CO}_2$  levels ranging from 300 ppm to  $>2000$  ppm (Shellito et al., 2003, and references therein; Pagani et al., 2006).

The global riverine delivery rate of  $\text{HCO}_3^-$  and the  $\text{CaCO}_3$ :POC rain ratio are important sources of uncertainty because these parameters control the  $\text{CaCO}_3$  wt% distribution. We constrain these uncertainties by comparing observed late Paleocene  $\text{CaCO}_3$  wt% to the predicted  $\text{CaCO}_3$  wt% distribution across an ensemble of simulations reflecting a range of weathering rates and spatiotemporally uniform rain ratios (Appendix DR2). We note, however, that available data are likely biased toward  $\text{CaCO}_3$ -rich sediments because those sediments are often the target for drilling.

$\text{CaCO}_3$  wt% is topographically controlled, but due to the coarse bathymetric grid, data sites do not always correspond to model cells of the appropriate depth. Substantial uncertainty is also associated with sediment paleodepths and with the reconstructed location of late Paleocene spreading ridges. Thus, we cannot expect a perfect model-data fit at all sites. We address this problem by data-rich regions and comparing the model paleodepth profile of  $\text{CaCO}_3$  wt% within

<sup>1</sup>GSA Data Repository item 2008073, Appendix DR1 (description of model modifications to accommodate varying  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), Appendix DR2 (list of observations used in this study and their sources), Appendix DR3 (description of model-data comparison methods), and Appendix DR4 (comparison of observed and model bottom water  $\delta^{13}\text{C}$  gradients), is available online at [www.geosociety.org/pubs/ft2008.htm](http://www.geosociety.org/pubs/ft2008.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

each region to the observed. The best outcome is the ensemble member with the lowest root mean squared error (RMSE) (Appendix DR3).

We assess the geochemical impacts of possible carbon sources ranging between two  $\delta^{13}\text{C}$  end members: the “methane” scenario, in which biogenic methane from clathrates ( $-60\text{‰}$ ) is presumed to oxidize immediately to  $\text{CO}_2$ ; and the “mantle  $\text{CO}_2$ ” scenario ( $-5\text{‰}$ ). Intermediate scenarios ( $-35\text{‰}$ ,  $-30\text{‰}$ ,  $-22\text{‰}$ ,  $-12\text{‰}$ ,  $-9.5\text{‰}$ , and  $-6\text{‰}$ ) represent potential sources such as thermogenic methane ( $-35\text{‰}$ ) and organic carbon ( $-22\text{‰}$ ), and/or mixtures of carbon from more than one source. The amount of  $\text{CO}_2$  added in each case is that which instantaneously decreases the  $\delta^{13}\text{C}$  of the combined atmosphere and ocean carbon reservoir by  $4\text{‰}$  (Table 1). Following Dickens (2003),  $\text{CO}_2$  was added uniformly to the atmosphere over 10 k.y., and then the model was run for an additional 90 k.y. without  $\text{CO}_2$  flux forcing. Cases were run twice: once with bioturbation of the sediments, and once without.

RESULTS

Initial Late Paleocene Conditions

Compiled observations (Appendix DR2) suggest that the pre-PETM calcite compensation depth (CCD), the depth at which  $\text{CaCO}_3$  is no longer found in sediments, was  $\sim 3500\text{--}4000\text{ m}$  (or deeper) in the central equatorial Pacific, Walvis Ridge in the Atlantic Ocean, and the southern Indian Ocean (Fig. 1, regions a, b, and c, respectively). The ensemble member best fitting the observations has a  $\text{CaCO}_3\text{:POC}$  rain ratio of 0.200, somewhat higher than estimates of the modern global average (e.g., 0.06, Sarmiento et al., 2002; 0.14, Ridgwell et al., 2007), and a global weathering rate of  $35\text{ Pmol HCO}_3^- \text{ k.y.}^{-1}$  to balance deep-sea  $\text{CaCO}_3$  sedimentation. The  $\text{CaCO}_3$  wt% is difficult to reproduce at some sites, particularly in the Indian Ocean, regardless of assumptions made about rain ratio and weathering. This may reflect insufficiently detailed representations of rapidly sloping regions by coarse model bathymetry.

Deep-ocean circulation has been inferred from gradients of benthic foraminiferal  $\delta^{13}\text{C}$  (Tripathi and Elderfield, 2005; Nunes and Norris, 2006). These data and our model results (Appendix DR4) show decreasing  $\delta^{13}\text{C}$  from the

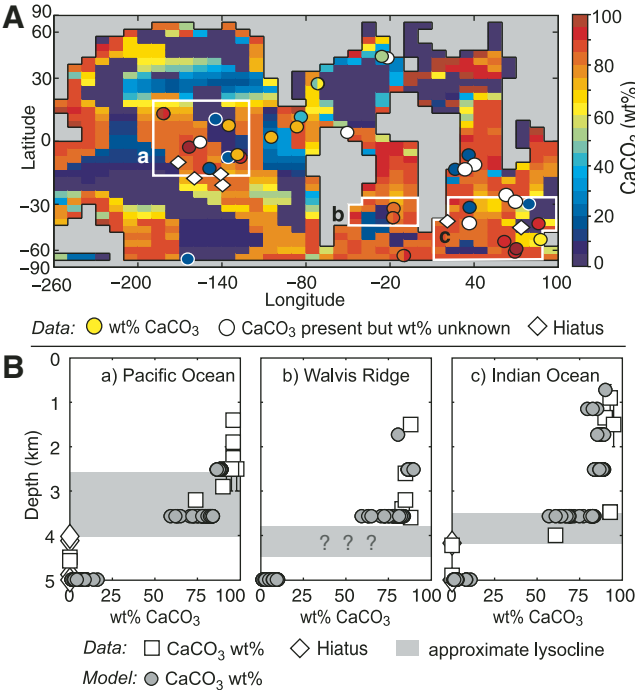


Figure 1. Pre-Paleocene-Eocene thermal maximum (PETM) model  $\text{CaCO}_3$  wt% plotted in map view (A) and versus depth (B), both with observations superimposed. Results in B are plotted for data-rich regions delineated in A by white boxes: a—central equatorial Pacific Ocean, b—Walvis Ridge, c—southern Indian Ocean. Asterisk—due to non-deposition (Van Andel, 1975).

southern Atlantic toward the northern Atlantic, and from the Indian Ocean toward the Pacific, from which a dominant Southern Ocean deep-water source region has been inferred for the late Paleocene. Nd isotopic records also support this interpretation, and suggest an intermediate water source in the North Pacific (Thomas et al., 2003; Thomas, 2004), which our model also predicts. Thus, despite the low spatial resolution of the ocean model and lack of a dynamic atmosphere, model circulation is consistent with data-based interpretations of late Paleocene circulation patterns.

PETM Results

Globally averaged whole-ocean temperatures increased by  $1.5\text{--}19\text{ °C}$  for the modeled carbon release scenarios (Fig. 2A), corresponding to increases in atmospheric  $\text{CO}_2$  from 750 to 60,000 ppm, respectively (Fig. 2B). The larger the  $\text{CO}_2$  pulse, the greater the seafloor  $\text{CaCO}_3$  dissolution (Fig. 2C); in the cases of the  $-5\text{‰}$  and  $-6\text{‰}$   $\text{CO}_2$  pulses, all seafloor  $\text{CaCO}_3$  is dissolved. With bioturbation (solid lines in Fig. 2), the globally averaged  $\text{CaCO}_3$  wt% is higher at the PETM than without (dashed lines in Fig. 2). The peak PETM atmospheric  $\text{CO}_2$  level is slightly lower for bioturbated sediments than for nonbioturbated sediments (Fig. 2B), due to the enhanced buffering capacity afforded by a continuous resupply of  $\text{CaCO}_3$  to the surface sediment layer by bioturbation.

A key feature of the observed  $\text{CaCO}_3$  wt% distribution at the PETM is the differential dissolution between the Pacific and Atlantic. Data suggest a CCD at  $<3000\text{ m}$  depth in the

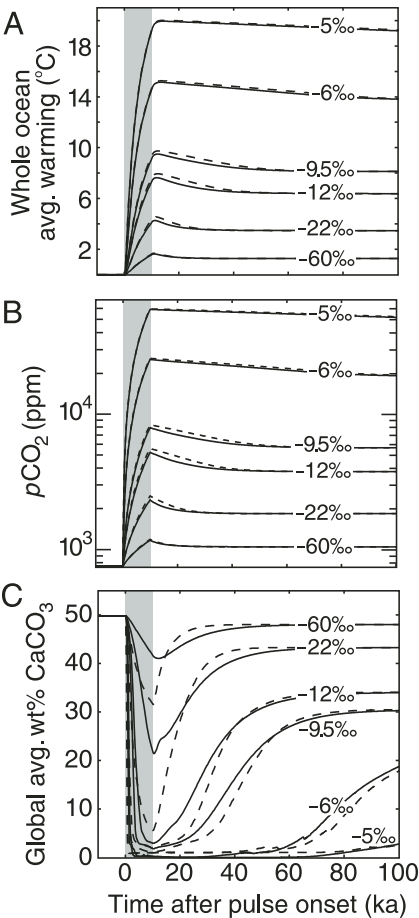
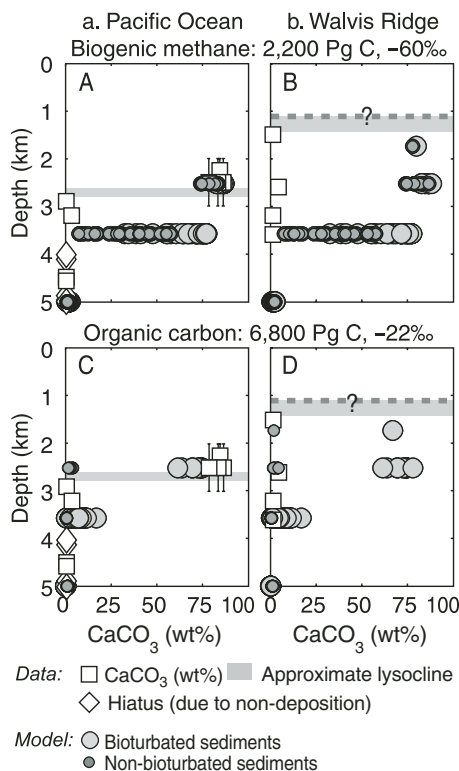


Figure 2. Global average time series of model results. Scenarios with bioturbation have solid lines and those without have dashed lines.

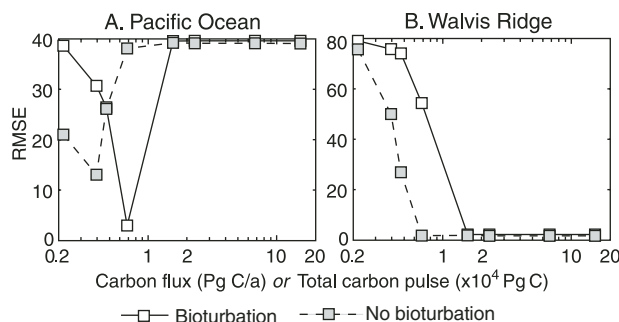
TABLE 1. REQUIRED MASSES OF CARBON		
$\delta^{13}\text{C}$ (‰)	Mass (Pg C)	Source
-60	2200	biogenic clathrate methane
-35	4000	thermogenic methane
-30	4700	mixture
-22	6800	organic carbon
-12	15,600	mixture
-9.5	23,000	mixture
-6	67,800	mixture
-5	153,000	mantle $\text{CO}_2$

central equatorial Pacific region (Fig. 3A), and a CCD at Walvis Ridge (Atlantic) of <1500 m (Fig. 3B). PETM sediments from Walvis Ridge sites have ~0 wt%  $\text{CaCO}_3$  at paleodepths ranging from 1500 to 3600 m (Zachos et al., 2005), while PETM sediments from Shatsky Rise in the Pacific (paleodepths of 2000–3000 m) retain >75 wt%  $\text{CaCO}_3$  (Colosimo et al., 2006). The model response, in contrast, is approximately the same in both regions for a given scenario. Therefore, the >75 wt%  $\text{CaCO}_3$  in the Pacific can be reproduced by the methane scenario (2200 Pg C; Fig. 3A), but then the  $\text{CaCO}_3$  wt% deeper in the Pacific and at Walvis Ridge is substantially overestimated (Figs. 3A, 3B). Alternatively, a 6800 Pg C pulse (–22‰) without bioturbation will reproduce the 0 wt%  $\text{CaCO}_3$  at depths >3000 m in the Pacific, and at Walvis Ridge, but all  $\text{CaCO}_3$  is lost at the 2500 m sites in the Pacific (Figs. 3C, 3D).

This tradeoff is reflected in the outcome of the RMSE analyses: the lowest RMSE in the central equatorial Pacific region corresponds to the 6800 Pg C carbon pulse with bioturbation (Fig. 4A), striking a compromise with 0 wt%  $\text{CaCO}_3$  at the 3600 m model layer, and 20–50 wt%  $\text{CaCO}_3$  at the 2500 m model layer. For Walvis Ridge, any scenario that dissolves all  $\text{CaCO}_3$  will have a RMSE of 0. The smallest carbon pulse to satisfy this requirement is 6800 Pg C (–22‰) without bioturbation.



**Figure 3. Modeled and observed Paleocene-Eocene thermal maximum (PETM)  $\text{CaCO}_3$  wt% plotted against depth.**



**Figure 4. Root mean squared error (RMSE) results for comparison of model Paleocene-Eocene thermal maximum (PETM) output and observations.**

These results can be reconciled if bioturbation at Walvis Ridge and at deeper Pacific sites were decreased relative to other sites during the PETM. In general, evidence appears to suggest that this was the case at Ocean Drilling Program Sites 1220 and 1221 in the Pacific (Shipboard Scientific Party, 2002; Murphy et al., 2006) at paleodepths of 2900 and 3200 m, respectively (Rea and Lyle, 2005), and at Walvis Ridge (Shipboard Scientific Party, 2002, 2004a, 2004b). In contrast, sediments at the shallower Pacific Shatsky Rise sites are reported to be strongly bioturbated (Colosimo et al., 2006).

Alternatively, a circulation reversed compared to the modern day, with deep-water formation in the North Pacific flowing at depth to the Atlantic, could generate a decreasing carbonate saturation state from the Pacific to the Atlantic (Zeebe and Zachos, 2007). Our model does not predict substantial reversal in circulation or weakening of Southern Ocean source-water production in response to PETM warming, contrary to the interpretation of Nunes and Norris (2006), but in agreement with Thomas et al. (2003) and with Bice and Marotzke (2002), who found that circulation was reversed only when the hydrologic cycle was modified and the bathymetry of the North Atlantic was altered.

## DISCUSSION AND CONCLUSIONS

Allowing that spatiotemporal variations in the rate of bioturbation can account for the very different responses of the central equatorial Pacific and Walvis Ridge sediments during the PETM, a –22‰, 6800 Pg C pulse is the smallest modeled here that dissolves enough  $\text{CaCO}_3$  to reasonably reproduce observations. The 2200 Pg C pulse of biogenic methane causes only a small decrease in  $\text{CaCO}_3$  wt%, whether bioturbation is present or not.

Our result offers an alternative to the very high climate sensitivity to  $\text{CO}_2$  doubling, 6.8–7.8 °C, estimated to be necessary to generate PETM warming and a –3‰ to –5‰  $\delta^{13}\text{C}$  excursion with biogenic methane (Pagani et al., 2006). If 6800 Pg C is the lower bound on pulse size, then the upper bound on climate sensitivity is reduced to ~4 °C (Fig. 2 of Pagani et al., 2006). The RMSE analysis and global average response of

$\text{CaCO}_3$  wt% suggest an upper limit on pulse size of between 15,600 and 23,000 Pg C, (–12‰ and –9.5‰, respectively). These pulse sizes correspond to a lower bound on the climate sensitivity to  $\text{CO}_2$  doubling of 2.5–3 °C.

The source of a pulse of 6800 Pg C with  $\delta^{13}\text{C}$  of –22‰ could be the oxidation of organic matter (Kurtz et al., 2003; Higgins and Schrag, 2006), or could reflect a combination of volcanic  $\text{CO}_2$  (i.e., mantle-derived  $\text{CO}_2$  with  $\delta^{13}\text{C}$  of –5‰) with biogenic methane or with thermogenic methane ( $\delta^{13}\text{C}$  of –35‰ to –50‰, Hunt, 1996) evolved during the emplacement of the North Atlantic Igneous Province (Svensen et al., 2004; Storey et al., 2007). The timing of the PETM appears to coincide with massive eruptions of flood basalts and the emplacement of sill complexes into organic-carbon-rich marine sediments during rifting between Greenland and Europe (Svensen et al., 2004; Storey et al., 2007), providing not only an important  $\text{CO}_2$  contribution but potentially also a trigger mechanism for both the PETM and later PETM-like Eocene hyperthermal events (e.g., Lourens et al., 2005).

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