



Penman, D. E., Turner, S. K., Sexton, P. F., Norris, R. D., Dickson, A. J., Boulila, S., ... Röhl, U. (2016). An abyssal carbonate compensation depth overshoot in the aftermath of the Palaeocene-Eocene Thermal Maximum. *Nature Geoscience*, 9(8), 575-580. <https://doi.org/10.1038/ngeo2757>

Peer reviewed version

Link to published version (if available):
[10.1038/ngeo2757](https://doi.org/10.1038/ngeo2757)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via nature at www.nature.com/articles/ngeo2757. Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

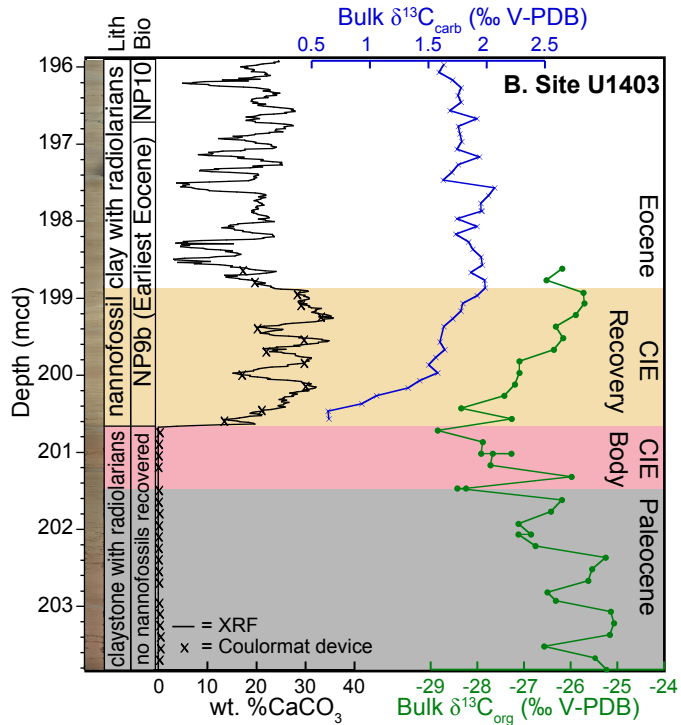
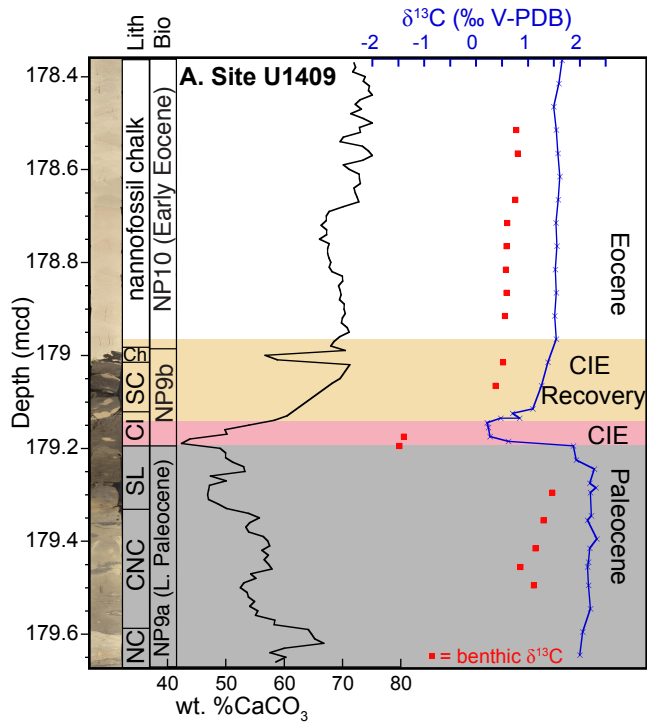
General rights

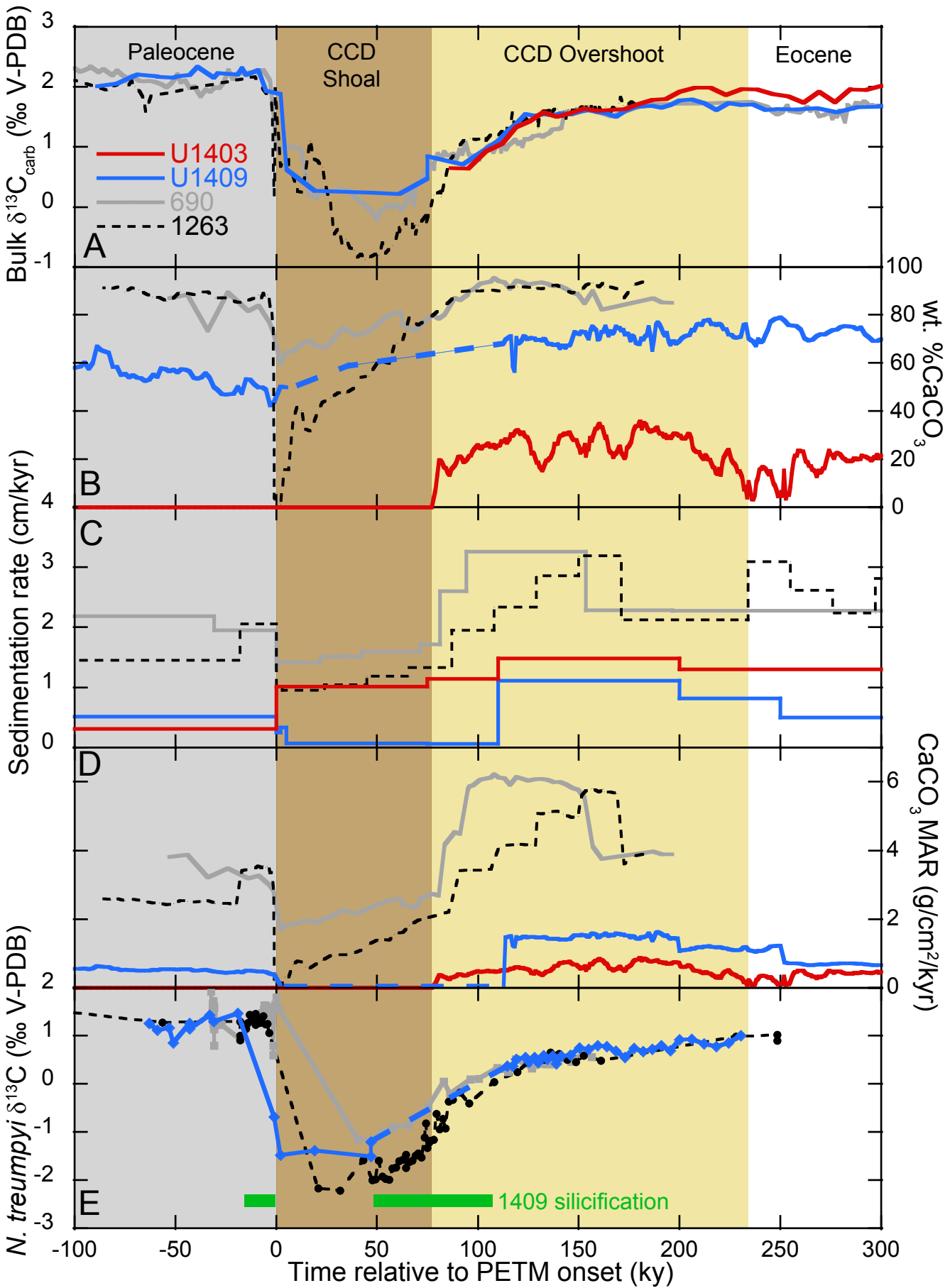
This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/pure/about/ebr-terms>

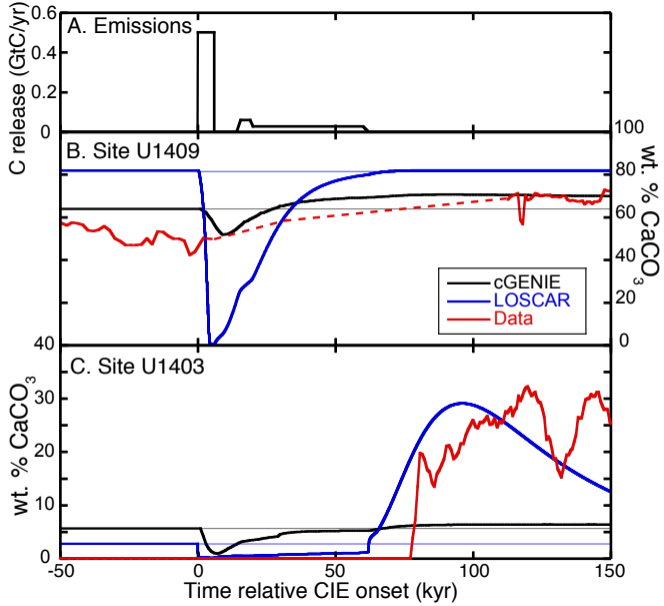
1 A carbonate compensation depth overshoot in the aftermath of the
2 Paleocene-Eocene Thermal Maximum

3
4 Donald E. Penman
5 Sandra Kirtland Turner
6 Philip Sexton
7 Richard Norris
8 Alexander J. Dickson
9 Slah Boulila
10 Andy Ridgwell
11 Richard E. Zeebe
12 James Zachos
13 Adele Cameron
14 Thomas Westerhold
15 Ursula Röhl
16 IODP Expedition 342 Scientists
17
18

19 **During the Paleocene-Eocene Thermal Maximum (PETM, ~56Ma), thousands of**
20 **petagrams of carbon were released into the atmosphere and oceans in just a few**
21 **thousand years (kyr), followed by gradual sequestration over ~200 kyr. Theory and**
22 **carbon cycle models predict that if silicate weathering is one of the key negative**
23 **feedbacks responsible for the removal of this carbon, a period of calcium carbonate**
24 **oversaturation (relative to pre-event levels) should have occurred during the event's**
25 **recovery. This could be reflected in the marine geological record as an over-**
26 **deepening of the calcite compensation depth (CCD). However, despite previous**
27 **evidence for enhanced calcium carbonate accumulation at shallow depths following**
28 **the PETM, no direct observations of this hypothesized CCD over-deepening have**
29 **yet been made. Here we present evidence from two new North Atlantic sections that**
30 **test this hypothesis. Consistent with existing records, we find higher calcite**
31 **accumulation during the PETM recovery phase compared to pre-event**
32 **accumulation at a mid-abyssal site (U1409), demonstrating intensified post-PETM**







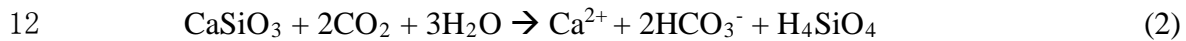
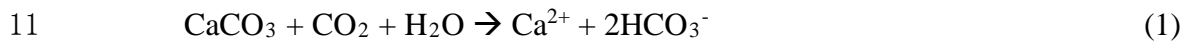
1 **calcite preservation above the CCD. However, at a second, deeper (lower abyssal)**
2 **site (U1403) that comprises calcite-barren clay prior to the PETM, we observe a**
3 **transition to calcite-rich during the PETM recovery, providing the first**
4 **observational evidence of the posited post-PETM CCD over-deepening. We also find**
5 **an ~70 kyr lag between the PETM onset and CCD overshoot that is best explained**
6 **in our Earth system model experiments by prolonged low-level PETM carbon**
7 **emissions following a large initial carbon release. Our findings indicate that PETM**
8 **carbon sequestration was accomplished by both globally enhanced calcite burial**
9 **above the CCD and by an over-deepening of the CCD (at least in the North**
10 **Atlantic), advancing our understanding of how the Earth system recovers from**
11 **major carbon cycle perturbations.**

12 The Paleocene-Eocene Thermal Maximum (PETM; ~56 Ma) represents one of the
13 largest and most abrupt greenhouse warming events in Earth history. Marine and
14 terrestrial records document a global >2.5‰ negative carbon isotope excursion (CIE)¹⁻³
15 coincident with global mean surface ocean warming of >4°C⁴ and geochemical and
16 sedimentological evidence for ocean acidification^{5,6}. Collectively, these lines of evidence
17 suggest a rapid (10³-10⁴ years) and massive (~3,000-10,000 PgC) release of ¹³C-depleted
18 carbon into the ocean-atmosphere system⁷⁻⁹. The PETM thus offers the opportunity to
19 examine the response and recovery of the global carbon cycle and seawater carbonate
20 chemistry to an ancient CO₂ release similar in magnitude to ongoing anthropogenic fossil
21 fuel combustion¹⁰.

22 Current understanding of long-term carbon cycle processes suggests that large-
23 scale carbon injection into the ocean-atmosphere should induce a two-phase response in

1 ocean carbonate saturation. Initially, rapid invasion of CO₂ into the ocean lowers pH and
2 carbonate saturation state (Ω) in tandem^{6,11,12}, resulting in dissolution of both newly
3 deposited and pre-existing carbonate sediments⁵. The result is a dramatic reduction in
4 CaCO₃ burial in marine sediments globally and, in places, evidence for a shoaling of the
5 calcite compensation depth (CCD, the depth below which no calcium carbonate, in the
6 form of calcite, is preserved).^{5,13,14}.

7 A second phase of carbonate saturation and burial response arises from elevated
8 atmospheric pCO₂ and increased global temperatures that are thought to drive an increase
9 in the rate of terrestrial carbonate and silicate rock chemical weathering^{15,16}, which can be
10 generalized:



13 Accelerating these reactions increases the delivery of Ca²⁺ (and thus total alkalinity) and
14 dissolved inorganic carbon (DIC) to the oceans, elevating Ω . An intensification of
15 continental weathering during the PETM is supported by a pronounced increase in the
16 ¹⁸⁷Os/¹⁸⁸Os of seawater^{17,18} and an increase in kaolinite in marine sediments¹⁹. However,
17 although the silicate weathering rate responds quickly to increased temperature/CO₂, the
18 rate of CO₂ drawdown from global weathering (~ 0.1 PgC/yr¹¹) is small in comparison to
19 estimates of initial carbon release (thousands of PgC)⁷⁻⁹, meaning that this feedback
20 should take >10⁴ years to gradually overcome the undersaturation associated with the
21 initial acidification phase²⁰⁻²². On longer timescales (>10⁵ years)²², this increased
22 weathering-derived flux of TA and DIC to the oceans must be balanced by carbonate
23 production and burial to balance the ocean's alkalinity budget:

1 regarding the magnitude of carbon release and the processes involved in the recovery
2 from an abrupt carbon cycle perturbation.

3 A carbonate burial overshoot is a predicted consequence of the silicate weathering
4 feedback. Indeed, the existence of a CCD over-deepening is predicted by several carbon
5 cycle model simulations of the PETM that include such a feedback^{9,20}. Yet no records
6 exist from deep sites below the pre-PETM CCD with which to detect possible CCD over-
7 deepening. Deep-sea sedimentary records from above the CCD (Southern Ocean Site 690
8 ²⁴⁻²⁷ at ~1900m paleodepth and South Atlantic Sites 1263^{5,26,27} at ~1500m paleodepth and
9 1266^{5,28} at ~2500m paleodepth) show increases in CaCO₃ content and accumulation rate
10 during and after the PETM recovery²⁵⁻²⁷. These records are consistent with weathering
11 feedbacks prompting increased carbonate burial during the PETM recovery. These supra-
12 CCD records are important constraints because the long-term requirement to balance the
13 elevated weathering flux only requires carbonate burial to increase globally (not
14 necessarily buried at deeper depths), and it is theoretically possible to accommodate such
15 elevated global carbonate burial without substantial deepening of the CCD²⁹.
16 Nonetheless, some models^{9,10,20} predict that a testable facet of the recovery process from
17 massive carbon cycle perturbation involves an over-deepening of the CCD, and the
18 location of these sites above the pre-PETM CCD means that they cannot directly test for
19 this predicted CCD over-deepening. Direct observational evidence sites deep enough to
20 test for a post-PETM CCD overshoot has thus far remained elusive.

21 Here we present lithology, CaCO₃ content, and carbon isotope ($\delta^{13}\text{C}$) records
22 from recently recovered sediment cores in the North Atlantic (IODP Sites U1403, PETM
23 paleodepth ~4374m and U1409, paleodepth ~2913m³⁰) that provide important constraints

1 on the evolution of the CCD through the PETM, including the first evidence for CCD
2 over-deepening during the PETM recovery. To explore the broader implications of these
3 records for PETM carbon emissions scenarios, we present new carbon release
4 experiments using two carbon cycle models – LOSCAR^{9,31} and cGENIE^{32,33} and discuss
5 uncertainties in the representation of geological carbon cycling in current models.

6 At Site U1409, the PETM CIE occurs in an interval of variously silicified
7 sediments (siliceous claystones, siliceous limestones and cherts) at 178.9-179.2 mcd
8 (Figure 1A), contrasting with the nannofossil chalk that characterizes much of the
9 Paleogene at this site³⁰. Although likely somewhat condensed, the $\delta^{13}\text{C}_{\text{carb}}$ record bears
10 the typical²⁷ PETM CIE pattern of an abrupt decrease (here of $\sim 2\text{‰}$) followed by a
11 plateau of low values and then gradual recovery (Fig. 1). Bulk $\delta^{13}\text{C}_{\text{carb}}$ over the PETM
12 CIE interval sampled a heterogeneous mixture of lithology (clay, carbonate-rich burrows
13 within that clay, and siliceous sediments), with all three lithologies revealing significantly
14 lower $\delta^{13}\text{C}$ within the CIE than pre-event values. The integrity of the bulk $\delta^{13}\text{C}_{\text{carb}}$ record
15 is also supported by the close structural similarity between it and the equivalent bulk
16 $\delta^{13}\text{C}_{\text{carb}}$ records from the Southern Ocean and Walvis Ridge (Fig. 1, 2A). The Site U1409
17 $\delta^{13}\text{C}$ record from benthic foraminifera is discontinuous owing to silicification across the
18 onset and initial recovery, but minimum values within the CIE show a large ($\sim 3\text{‰}$)
19 excursion, similar to that seen in benthic records from the Southern Ocean³⁴ and South
20 Atlantic³⁵. Below the CIE, carbonate content is between 60-70 wt%, decreases to a
21 minimum of ~ 40 wt% at the CIE onset, and rebounds to $\sim 70\%$ following the CIE. This
22 pattern is similar to other pelagic PETM sections¹⁴ and implies that the local CCD was
23 always deeper than the paleodepth of Site U1409, while the decrease in carbonate during

1 the PETM can be interpreted as a transient decrease in the calcite saturation state, Ω ,
2 consistent with shoaling of the CCD. The absence of near-0 wt% CaCO_3 sediment at Site
3 U1409 contrasts with records from the South Atlantic Ocean⁵ where cores even shallower
4 than U1409 are barren of carbonate within the CIE. Although this observation could
5 imply that CCD shoaling in the North Atlantic was less dramatic than that in the South
6 Atlantic, hiatuses, bioturbation by burrowing, or incomplete recovery of this silicified
7 interval could have obscured or resulted in the loss of the interval containing the lowest
8 wt% CaCO_3 values. Regardless, carbonate content and accumulation rate at Site U1409
9 were higher during the PETM recovery than before the event, similar to other sites at
10 mid-ocean depths or shallower^{5,24-26,28}, thus providing support for elevated saturation
11 states and increased carbonate burial above the CCD during the recovery phase.

12 Lower abyssal Site U1403 features a prominent transition (over ~5 cm) from
13 carbonate-poor (<0.5 wt%) claystone in the Upper Paleocene (extending from the P-E
14 boundary to at least ~61 Ma³⁰) to carbonate-bearing (~20-30 wt%) nannofossil claystone
15 in the lower Eocene (Figure 1B). This carbonate-rich interval contains calcareous
16 nannofossils of zone NP9B, including PETM excursion taxa *Discoaster araneus* and
17 *Rhomboaster* spp³⁰. Bulk $\delta^{13}\text{C}_{\text{org}}$ reveals a negative CIE between 200.7 and 201.5 mcd
18 that is superimposed on comparatively high amplitude orbital timescale variability in the
19 late Paleocene. The $\delta^{13}\text{C}_{\text{carb}}$ record necessarily begins at the onset of carbonate
20 sedimentation with low values of ~0.6‰, followed by a gradual 1.4‰ increase over the
21 next ~1.6 m, parallel to the recovery in $\delta^{13}\text{C}_{\text{org}}$. Given the simultaneous trends to higher
22 values in both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ within zone NP9B, this $\delta^{13}\text{C}$ increase can be
23 unambiguously assigned to the PETM CIE recovery. The magnitude of the $\delta^{13}\text{C}_{\text{carb}}$

1 increase (1.4‰) is close to the full amplitude of the PETM CIE recovery observed in
2 bulk carbonates globally²⁷ and at Site U1409 (Figure 2A), so we confidently assign the
3 onset of carbonate sedimentation at Site U1403 to early in the PETM recovery phase.

4 We construct age models by correlating the $\delta^{13}\text{C}_{\text{carb}}$ records to a compilation of
5 bulk and fine-fraction $\delta^{13}\text{C}_{\text{carb}}$ on an orbitally calibrated age model²⁷ (Figure 2A and 2C).
6 This age model, based on several PETM sites, produces a shorter duration of the PETM
7 CIE than extraterrestrial ^3He -based estimates,^{24,28} so durations here may represent
8 minima. On this timescale, carbonate sedimentation begins at Site U1403 ~70kyr after
9 the PETM onset and is followed by a period of elevated (20-40) wt% CaCO_3 that persists
10 for a further ~150kyr. Fluctuations between 5 and 25 wt% CaCO_3 continue throughout
11 the lower Eocene. Although the CIE onset at Site U1403 as defined by the somewhat
12 noisy $\delta^{13}\text{C}_{\text{org}}$ record introduces some uncertainty around the placement of the P-E
13 boundary, this does not affect the relative timing of the initial appearance of carbonate at
14 this lower abyssal site, which is unambiguously assigned to the PETM recovery interval
15 based on $\delta^{13}\text{C}_{\text{carb}}$ and the occurrence of PETM excursion-interval calcareous
16 nannofossils.

17 The pattern of carbonate sedimentation at Site U1403 (carbonate-barren in the
18 Paleocene with carbonate appearing during the PETM recovery) has not previously been
19 observed in sediments spanning the PETM. The absence of carbonate in the Upper
20 Paleocene and into the earliest Eocene indicates the CCD lay shallower than Site U1403
21 before the PETM and through the CIE onset and body. The onset of carbonate
22 sedimentation ~70kyr after the PETM onset indicates that the CCD over-deepened to
23 below the ~4400 m lower abyssal paleo-water depth of Site U1403 during the early phase

1 of PETM recovery – direct evidence for a post-PETM CCD overshoot. The ~150kyr
2 period of elevated carbonate deposition at Site U1403 represents the main phase of the
3 CCD over-deepening, and is coeval with enhanced carbonate accumulation and
4 preservation at shallower paleodepths documented here at Site U1409 and
5 elsewhere^{5,25,26,28} (Figure 2D). These observations strongly implicate elevated whole-
6 ocean saturation state as the cause of enhanced carbonate burial at all water depths and
7 from the North Atlantic to the Southern Ocean.

8 To explore the implications of a CCD overshoot and its timing, and the CCD
9 over-deepening at U1403 in particular, we tested a variety of PETM carbon emissions
10 scenarios using the models LOSCAR and cGENIE. Rather than carry out an extensive
11 sweep of all combinations of plausible size and duration of carbon release, our emissions
12 scenarios are based on ref. ⁹, characterized by an initial C input ($\delta^{13}\text{C} = -50\text{‰}$) of 3000
13 PgC over 5 kyr, followed by 1480 PgC over 50 kyr, and originally developed to best
14 match records of carbonate dissolution (particularly in the South Atlantic⁵). However, we
15 explored a number of variations on this basic emissions trajectory (Figs. S4-S15) such as
16 doubling the total mass with half the isotopic composition ($\delta^{13}\text{C} = -25\text{‰}$). In order to
17 isolate the response of carbonate burial dynamics from circulation effects that might
18 diverge in the two models, we ran cGENIE with radiative forcing (and thus ocean
19 circulation) fixed, and for direct comparison with cGENIE (Figure 3) we omitted the
20 prescribed circulation changes of ref. 9 in LOSCAR. We tracked the evolution of global
21 sedimentary wt% CaCO_3 preserved, and simulated the expected marine sediment record
22 in modeled ‘cores’ at North Atlantic depths approximating Sites U1409 and U1403.

1 The configurations of both LOSCAR and cGENIE models used here include a
2 CO₂-dependent silicate weathering feedback (see methods). Both models simulate a
3 global CCD and wt% CaCO₃ overshoot which occurs between 20 and 45 kyr after the
4 onset of carbon emissions and peaks between 65 and 97 kyr after the onset, depending on
5 the emissions schedule and model (Figure 3 and Figure S3)^{9,20}. The carbonate overshoot
6 begins earlier when the carbon pulse occurs over a shorter interval of time (Figures S6,
7 S12). The long delay (~70kyr) in the onset of carbonate sedimentation at Site U1403 that
8 we infer from our age model is hence difficult to reconcile with only a short “spike” of
9 carbon released at the onset of the PETM. Rather, the delay is better explained by a
10 sustained release of carbon lasting many tens of kyr after an initial spike (Figure 3, S1),
11 consistent with the conclusions of refs. ⁹ and ⁶. Such sustained carbon release might arise
12 as a feedback response to initial warming^{36,37} or represent prolonged North Atlantic
13 volcanism. Our experiments also demonstrate that the timing of the overshoot is not
14 particularly sensitive to the mass of carbon released – doubling the mass of carbon results
15 in < 2 kyr delay in overshoot timing (e.g. Figure S4 vs. Figure S5).

16 While both models generate a whole-ocean carbonate burial overshoot during the
17 recovery interval, the spatial distribution of CaCO₃ content in sediments shows
18 differences both between the models and in comparison to Sites U1403 and U1409
19 (Figure 3). Because LOSCAR has much coarser spatial resolution (e.g. it represents the
20 deep Atlantic as a single box), regional patterns need to be interpreted with greater
21 caution. Nevertheless, LOSCAR generates a deep (4500m) %CaCO₃ overshoot
22 comparable to that seen at Site U1403, but in shallow sediments (3000m) generates a
23 larger %CaCO₃ decrease (to near-zero) and smaller overshoot than seen at Site U1409. In

1 contrast, cGENIE closely matches the Site U1409 record, but at 5000m, sediments
2 overshoot their pre-event %CaCO₃ levels by only ~1%, in conflict with the Site U1403
3 record. It appears that in response to enhanced weathering-driven elevated saturation
4 states, LOSCAR accommodates greater global carbonate burial with higher %CaCO₃ in
5 deep sediments (an over-deepening of the CCD), whereas cGENIE accommodates greater
6 global carbonate burial predominantly within and above the lysocline. Observational
7 evidence (in the form of new and previous carbonate accumulation rate records) suggest
8 that in the real world (at least in the case of the PETM), both of these processes may
9 operate.

10 The differences between the models' predictions for the locus of intensified
11 carbonate burial result from of how the models represent sedimentary processes. In
12 cGENIE, the respiration of organic carbon in sediments reduces porewater saturation
13 state and dissolves CaCO₃ even in shallow sediments well above the carbonate saturation
14 horizon. Because of this, those shallow sediments have greater potential to accommodate
15 an increase in CaCO₃ content in response to higher bottom water saturation state such as
16 that seen in the aftermath of the PETM. cGENIE thus balances enhanced weathering flux
17 via elevated carbonate burial mostly in shallow sediments (within and above the
18 lysocline)²⁹. Conversely, %CaCO₃ in sediments above the lysocline in LOSCAR is set by
19 the ratio of clay to CaCO₃ in the sediment rain (81% CaCO₃ in the present
20 configuration)³¹, so when saturation state increases those shallow sediments cannot
21 accommodate higher CaCO₃ contents (they are already at a maximum). Hence, LOSCAR
22 balances an increase in weathering flux via enhanced carbonate burial within the
23 lysocline and below the (pre-event) CCD.

1 A notable aspect of the Site U1403 carbonate record is that following the main
2 phase of the CCD over-deepening featuring the highest carbonate contents, wt% CaCO₃
3 does not return to 0% (its pre-event level) before the next major hyperthermal (ETM-2,
4 ~2Myr later³⁰) (Fig. 1, 2). Hence, the North Atlantic CCD did not return to its pre-PETM
5 state. Two possible explanations exist for this observation. First, negative feedbacks on
6 carbonate undersaturation could have been very slow to re-establish equilibrium. This is
7 unlikely, given that all other records of environmental and carbon-cycle perturbation
8 during the PETM (such as temperature⁴, pH³⁸, and the CIE²⁷) recovered in hundreds of
9 thousands of years, not millions. Second, the carbon cycle might have transitioned to a
10 new equilibrium state featuring a deeper CCD. Several mechanisms may help explain a
11 deeper post-PETM equilibrium CCD in the North Atlantic. First, the PETM CCD
12 evolution may have been superimposed on a long-term (multi-million year) global CCD
13 deepening trend³⁹⁻⁴². Increasing $p\text{CO}_2$ on multi-million year timescales across the Late
14 Paleocene-Early Eocene from greater volcanic CO₂ release or an imbalance between
15 terrestrial C_{org} oxidation and marine C_{org} burial could have strengthened weathering rates,
16 thus increasing seawater carbonate saturation and driving a gradual CCD deepening from
17 ~58 to ~52Ma, independently of the PETM³⁹. Indeed, LOSCAR simulations of carbon
18 release superimposed on gradual long-term CCD deepening (Figure S2) agree well with
19 observations from Site U1403, including the persistence of the overshoot.

20 A second possibility is that changing ocean circulation or regional carbonate
21 export across the PETM affected the regional North Atlantic CCD (i.e. the observed CCD
22 over-deepening was not necessarily global). Weakened North Atlantic-sourced
23 overturning during the acidification phase followed by strengthened overturning during

1 the oversaturation phase could have produced the initial large CCD shoal documented at
2 Walvis Ridge⁵ (South Atlantic) and the later CCD over-deepening at Site U1403 (North
3 Atlantic). If such circulation changes persisted for several Myr, they could have produced
4 a persistently deeper post-PETM North Atlantic CCD. Spatial benthic $\delta^{13}\text{C}$ gradients can
5 shed light on circulation changes³⁴, because the accumulation of respired C_{org} reduces the
6 $\delta^{13}\text{C}$ of deep water DIC as it ages. Owing to its location in the lower abyss, Site U1403 is
7 unfortunately nearly barren of benthic foraminifera throughout the PETM and its
8 recovery. However, Site U1409 benthic $\delta^{13}\text{C}$ values overlap with those of South
9 Atlantic³⁵ and Southern Ocean³⁴ during intervals immediately prior to the PETM and
10 during the later stages of the recovery, including the time interval (>110kyr after the
11 event) during which Site U1403 documents a CCD overshoot (Figure 2). Benthic
12 gradients between the South and North Atlantic therefore do not show any evidence for
13 large-scale changes in Atlantic overturning circulation during the PETM recovery that
14 could have contributed to a localized CCD over-deepening.

15 It is also possible that the CCD over-deepening was influenced by other carbon
16 sequestration processes operating during the PETM recovery that removed carbon from
17 the ocean/atmosphere and increased seawater pH and saturation state (in a sense, the
18 opposite of the PETM acidification phase), and hence influence the CCD. In particular,
19 studies have suggested that the pace of the CIE recovery, which is complete within
20 ~150kyr^{24,28}, is too rapid to be explained by enhanced weathering and carbonate burial
21 alone. Instead, the preferential removal of ^{12}C via enhanced burial of organic carbon
22 (C_{org}) has been proposed to explain the CIE recovery timing⁴³. This is consistent with
23 evidence of increased marine productivity during the PETM from elevated biogenic

1 barium accumulation rates^{44,45} and coccolith Sr/Ca⁴⁶. Our model experiments focus on the
2 long-term inorganic carbon cycle and silicate weathering and hence cannot exclude a role
3 for enhanced organic carbon burial.

4 In summary: our finding of a post-PETM CCD overshoot in the North Atlantic
5 Ocean constitutes the first evidence for post-PETM variations in carbonate burial from
6 sediments deeper than the pre-PETM CCD. It thus represents an important constraint on
7 the vertical extent of the CCD's response to carbon release during the PETM and
8 consequently, the processes responsible for restoring the carbon cycle to steady state. It is
9 tempting to use this constraint to directly calculate the mass of carbon released during the
10 PETM because the excess carbonate burial should scale with the mass of carbon released.
11 However, we recognize that one site does not fully constrain the global extent of the
12 overshoot, nor its absolute magnitude. Further constraints on the CCD over-deepening
13 from even deeper water depths and additional ocean basins are therefore an essential
14 target for future scientific drilling. Additionally, uncertainty in the parameterization and
15 strength of the silicate weathering feedback (Figure S2)⁴⁷ as well as the potential
16 influences of initial carbon cycle conditions, circulation changes, C_{org} burial, and
17 changing clay flux preclude explicit calculation of the total carbon release¹⁰. Indeed, the
18 differing responses of the two different global carbon cycle models we have tested
19 against the observations underscore the lack of consensus on how the marine carbonate
20 carbon sink responds in detail (and particularly in the depth distribution of CaCO₃ burial)
21 to perturbation. Multiple combinations of mass and rate of carbon release, weathering
22 feedback strength, and C_{org} burial are consistent with the new observations described
23 here. Our findings nevertheless provide an important constraint on how carbon was

1 sequestered in the aftermath of the PETM, an event that continues to guide our
2 understanding of Earth system processes and feedbacks during large-scale carbon cycle
3 perturbations.

4

5 **Author Contributions:** DP, SKT, PS, RN, and SB conceived the study and participated
6 in IODP Expedition 342 that recovered and described the sediments used here. DP
7 generated carbonate stable isotope analyses in the lab of JZ, and AD generated organic
8 carbon stable isotope and Coulomat %CaCO₃ analyses. XRF records were generated by
9 SKT at Scripps, and AC, PS, TW, and UR at MARUM. DP and SKT performed the
10 carbon cycle modeling with guidance from RZ and AR. DP drafted the manuscript, SKT
11 contributed cGENIE modeling text, and all authors edited the manuscript.

12

13 **Acknowledgements:** We thank the scientists and crew of IODP Expedition 342 and the
14 Bremen Core Repository. The comments of two anonymous reviewers greatly improved
15 the manuscript. This work was supported by NSF OCE-1220615 to JZ and RZ.

16

17 **METHODS**

18 **Geochemical analyses**

19 During IODP Expedition 342, drilling operations penetrated the P-E boundary at
20 Sites U1403 (39°56.5997N, 51°48.1998W, 4946m depth) and U1409 (41°17.7501N,
21 49°13.9996W, 3502m depth). Shipboard investigation described lithology, identified the
22 approximate positions of the P-E boundary by nannofossil biostratigraphy, and provided
23 coarse-resolution records of wt% CaCO₃. The surface of core archive halves spanning the

1 PETM were scanned at 1-2 cm-resolution at the MARUM – Center for Marine
2 Environmental Sciences, University of Bremen and at Scripps Institution of
3 Oceanography using Avaatech X-ray fluorescence (XRF) core scanners. Estimates of the
4 total abundance of calcium (Ca) and iron (Fe) were obtained by scanning cores at an
5 energy level of 10kV, current of 500 uA, count time of 20 sec, and measurement area of
6 10 x 12 mm. Estimated wt% CaCO₃ records were generated by regressing shipboard wt%
7 CaCO₃ measurements³⁰ against the natural logarithm of XRF-derived Ca/Fe ratios. For
8 stable isotope analyses, samples were collected at ~5cm resolution from Site U1409 and
9 10cm resolution from Site U1403, freeze dried, homogenized with mortar and pestle, and
10 analyzed for $\delta^{13}\text{C}_{\text{carb}}$ on a ThermoFisher MAT 253 stable isotope mass spectrometer
11 coupled to a Kiel IV carbonate device using standard dual-inlet techniques. In addition,
12 samples from Site U1409 were washed and sieved, and specimens of the benthic
13 foraminifera *Nuttalides truempyi* were picked from the 150-200 and 212-300 μm size
14 fraction. Where possible, 3-8 of these specimens from each sample were run using the
15 $\delta^{13}\text{C}_{\text{carb}}$ methods described above. For $\delta^{13}\text{C}_{\text{org}}$ analysis of Site U1403, homogenized
16 sample powders were de-carbonated in 1M HCL and washed in de-ionized water. $\delta^{13}\text{C}_{\text{org}}$
17 was measured using a Thermo-Finnegan MAT 253 mass spectrometer coupled to a
18 Thermo Scientific 2000 HT elemental analyzer via a Conflo IV interface optimized for
19 the measurement of samples with low organic carbon abundances. Analytical
20 reproducibility was monitored using analyses of IAEA CH-6 sucrose and was $< \pm 0.1\text{‰}$
21 (1 S.D). All $\delta^{13}\text{C}$ data are expressed relative to V-PDB. Additional Site U1403 wt. %
22 CaCO₃ was measured using a Strohlein Coulomat.

23 **Carbon cycle modeling**

1 LOSCAR is a numerically-efficient geochemical box model of the marine carbon
2 cycle with realistic interaction with sediments, capable of multi-million year simulations
3 of carbon cycle processes including CCD depth. All runs use Paleogene LOSCAR
4 setup³¹. cGENIE is an intermediate-complexity Earth system model including a 3-D
5 dynamic ocean model with biogeochemical cycling of key elements and isotopes and a
6 spatially resolved sediment model capable of generating virtual sediment cores –
7 synthetic stacks of deep-sea sediments^{32,33,48}. We use the late Paleocene/early Eocene
8 configuration of ref. ¹². For this study, we evaluate virtual sediment core results from a
9 depth transect in the North Atlantic ranging from 5000-3000 m water depth and at
10 locations corresponding to Expedition 342 sites.

11 Both models include carbonate and silicate weathering feedbacks. In LOSCAR,
12 weathering is parameterized as $F_w = F_{eq} * ([CO_2]_{atm} / [CO_2]_{eq})^{N_{Si}}$, where F_{eq} and
13 $[CO_2]_{eq}$ are equilibrium weathering flux and atmospheric pCO_2 at which volcanic carbon
14 emissions are perfectly balanced by silicate weathering and carbonate burial³¹. N_{Si} sets
15 the strength of the silicate weathering feedback (default $N_{Si} = 0.2$). We implement the
16 same formulation for a CO_2 -dependent carbonate and silicate weathering feedback in
17 cGENIE using a model for terrestrial rock weathering⁴⁹. Following ref. ⁵⁰, we assume
18 carbonate weathering proportional to the square root of $[CO_2]_{atm} / [CO_2]_{eq}$ and silicate
19 weathering proportional to $[CO_2]_{atm} / [CO_2]_{eq}$ raised to the power of 0.3. We assume a
20 50:50 split between carbonate and silicate weathering in order to match total carbonate
21 burial, and balance silicate weathering with volcanic outgassing. We utilize the cGENIE
22 and LOSCAR models in this study in order to qualitatively demonstrate what

1 mechanisms are consistent with the new data, not in an attempt to reconstruct exactly a
2 PETM scenario.

3 **FIGURE CAPTIONS**

4 **Figure 1:** Lithology and $\delta^{13}\text{C}$ over the PETM at Sites U1409 (top) and U1403 (bottom)
5 plotted against composite depth (mcd). Each panel shows core photo (Site U1403
6 vertically compressed), lithologic description, calcareous nannofossil biostratigraphy, wt.
7 $\% \text{CaCO}_3$ estimated by XRF (black line), and bulk $\delta^{13}\text{C}_{\text{carb}}$ (blue line). Bulk $\delta^{13}\text{C}_{\text{org}}$
8 (green line) and wt. $\% \text{CaCO}_3$ measured with a Coulomat device (black X's) are also
9 shown for Site U1403, and benthic foraminifer *Nuttalides truempyi* $\delta^{13}\text{C}$ (red squares) is
10 shown for Site U1409. Depth intervals representing the Paleocene, CIE, Recovery, and
11 post-PETM based on $\delta^{13}\text{C}$ stratigraphy are highlighted with grey, red, orange, and white
12 shaded bars, respectively. PETM phases nomenclature from ref. 32.

13

14 **Figure 2:** A: Bulk $\delta^{13}\text{C}_{\text{carb}}$ records from Sites 690²⁵, 1263²⁷, U1403, and U1409 plotted
15 on the age model used in this study. B: Weight $\% \text{CaCO}_3$ of Sites U1403 and U1409 (this
16 study), 690²⁵, and 1263⁵. C: Linear sedimentation rates used in age models constructed by
17 this study for Sites U1403 and U1409, and Sites 690 and 1263 from Röhl, et al. ²⁷ D:
18 Carbonate mass accumulation rate calculated from dry bulk density, sedimentation rates
19 (C), wt. $\% \text{CaCO}_3$ (B). E: Comparison of benthic foraminifer $\delta^{13}\text{C}$ from South Atlantic
20 Site 1263,³⁵ Southern Ocean Site 690,³⁴ and U1409 demonstrating small and constant
21 North-South aging gradient during the CCD overshoot. Green bars indicate silicified
22 intervals at Site U1409 which precluded measurement of benthic foraminifers. In (B), (D)
23 and (E), the silicified interval of U1409 is marked with a dashed line to reflect potential

1 hiatuses or incomplete recovery which may have resulted in an incomplete %CaCO₃
2 record (see text).

3

4 **Figure 3:** Comparison of LOSCAR and cGENIE C release experiments using the
5 Emissions scenario of ref. 9 with radiative forcing (and thus circulation) fixed in
6 cGENIE, and no circulation changes in LOSCAR. Top panel: Emissions scenario. Middle
7 panel: modeled 3000m sediment core-top %CaCO₃ compared with Site U1409 %CaCO₃
8 record. Bottom panel: modeled 4500m (LOSCAR) and 5000m (cGENIE) sediment core-
9 top %CaCO₃ compared with Site U1403 %CaCO₃ record. In middle and bottom panels,
10 thin, opaque traces mark pre-event %CaCO₃ for cGENIE and LOSCAR.

11

12 **Figure S1:** LOSCAR modeling of the CCD overshoot. A: Carbon emissions forcing for
13 spike (0.6PgC/yr for 5kyr) and spike + leak (0.11PgC/yr for an additional 65kyr)
14 scenarios. B: Evolution of the modeled Atlantic CCD in response to spike and spike +
15 leak scenarios. Without a sustained leak, the CCD overshoots within ~15kyr, in contrast
16 to the Site U1403 record C: Large sensitivity of the CCD overshoot magnitude, timing,
17 and duration to the strength of the weathering feedback, which is poorly constrained.
18 Weathering flux is parameterized in LOSCAR as $F_w = F_{eq} * ([CO_2]_{atm} / [CO_2]_{eq})^{N_{Si}}$,
19 where F_{eq} and $[CO_2]_{eq}$ are equilibrium weathering flux and atmospheric pCO₂ at which
20 volcanic carbon emissions are perfectly balanced by silicate weathering and carbonate
21 burial³¹. N_{Si} is a free parameter in the model which sets the strength of the silicate
22 weathering feedback (default $N_{Si} = 0.2$). All scenarios are spike only.

1 **Figure S2:** Atlantic CCD evolution of a single 6 kyr 3000 GtC pulse superimposed on a
2 long-term CCD deepening trend forced by increasing volcanic carbon flux by 15% over
3 3Ma.

4
5 **Figure S3:** Comparison of LOSCAR and cGENIE C release experiments using double
6 the emissions scenario of Zeebe et al., 2009. LOSCAR includes the circulation switch of
7 Zeebe et al., 2009, while cGENIE is run with radiative forcing (and thus circulation)
8 fixed. Top panel: Emissions scenario. Middle panel: modeled 3000m sediment %CaCO₃
9 compared with Site U1409 %CaCO₃ record. Bottom panel: modeled 4500m(LOSCAR)
10 and 5000m (cGENIE) sediment %CaCO₃ compared with Site U1403 %CaCO₃ record.
11 Modeled cGENIE wt% CaCO₃ decreases appear to slightly precede emissions (Figs. 3 &
12 S3) as a result of the effects of mixing, sediment rain input, and dissolution on carbonate
13 age, which can thus deviate from current model time.

14
15 **Figures S4-S9:** cGENIE model output of various mass and timing of C release, with
16 radiative forcing (and hence circulation) held constant (top panels) and radiative forcing
17 responding to pCO₂ (bottom panel). Plotted are virtual sediment cores from 5000 and
18 3000m depth with %CaCO₃ and carbonate δ¹³C plotted against sediment age, global
19 mean sediment wt% CaCO₃, and C emissions forcing plotted against model time.

20 **S4:** Emissions scenario of Zeebe et al., 2009

21 **S5:** Double the emissions scenario of Zeebe et al., 2009 and input δ¹³C = -25‰

22 **S6:** The total mass of Zeebe et al., 2009 injected in one 10 kyr pulse

23 **S7:** Double the total mass of Zeebe et al., 2009 injected in one 10kyr pulse

1 **S8:** The total mass of Zeebe et al., 2009 injected in one 20 kyr pulse
2 **S9:** Double the total mass of Zeebe et al., 2009 injected in one 20kyr pulse
3 **Figures S10-S15:** LOSCAR model output of various mass and timing of C release.
4 Plotted are $\delta^{13}\text{C}$ of the surface Atlantic, atmospheric pCO_2 , CCD depth of each ocean
5 basin, and globally averaged, 3000m Atlantic, and 4500m Atlantic $\% \text{CaCO}_3$ versus
6 model time.
7 **S10:** Emissions scenario of Zeebe et al., 2009
8 **S11:** Double the emissions scenario of Zeebe et al., 2009 and input $\delta^{13}\text{C} = 25\text{‰}$
9 **S12:** The total mass of Zeebe et al., 2009 injected in one 10 kyr pulse
10 **S13:** Double the total mass of Zeebe et al., 2009 injected in one 10kyr pulse
11 **S14:** The total mass of Zeebe et al., 2009 injected in one 20 kyr pulse
12 **S15:** Double the total mass of Zeebe et al., 2009 injected in one 20kyr pulse
13 **Figure S16:** Bulk carbonate and organic carbon isotope data and raw XRF intensity data
14 from Site U1403 plotted against composite depth (mcd).
15 **Figure S17:** Bulk carbonate carbon isotope data and raw XRF intensity data from Site
16 U1409 plotted against composite depth (mcd).
17 **Table S1:** Age model tie points for Sites U1403 and U1409, based on correlation of the
18 bulk carbon isotope records at both sites to the compilation of ref. 32.

19
20
21

References

- 22 1 Koch, P. L., Zachos, J. C. & Gingerich, P. D. Correlation Between Isotope
23 Records in Marine and Continental Carbon Reservoirs Near the Palaeocene
24 Eocene Boundary. *Nature* **358**, 319-322 (1992).
25 2 Kennett, J. P. & Stott, L. D. Abrupt Deep-Sea Warming, Palaeoceanographic
26 Changes and Benthic Extinctions At the End of the Palaeocene. *Nature* **353**, 225-
27 229 (1991).

- 1 3 McInerney, F. A. & Wing, S. The Paleocene-Eocene Thermal Maximum: A
2 Perturbation of Carbon Cycle, Climate, and Biosphere with Implications for the
3 future. *Annual Review of Earth & Planetary Sciences* **39**, 489-516 (2011).
- 4 4 Dunkley-Jones, T. *et al.* Climate model and proxy data constraints on ocean
5 warming across the Paleocene-Eocene Thermal Maximum. *Earth-Science*
6 *Reviews* **125**, 123-145 (2013).
- 7 5 Zachos, J. C. *et al.* Rapid acidification of the ocean during the Paleocene-Eocene
8 thermal maximum. *Science* **308**, 1611-1615 (2005).
- 9 6 Penman, D. E., Hönisch, B., Zeebe, R. E., Thomas, E. & Zachos, J. C. Rapid and
10 sustained surface ocean acidification during the Paleocene - Eocene Thermal
11 Maximum. *Paleoceanography* (2014).
- 12 7 Dickens, G. R., Oneil, J. R., Rea, D. K. & Owen, R. M. Dissociation of Oceanic
13 Methane Hydrate As a Cause of the Carbon Isotope Excursion At the End of the
14 Paleocene. *Paleoceanography* **10**, 965-971 (1995).
- 15 8 Panchuk, K., Ridgwell, A. & Kump, L. R. Sedimentary response to Paleocene-
16 Eocene Thermal Maximum carbon release: A model-data comparison. *Geology*
17 **36**, 315-318 (2008).
- 18 9 Zeebe, R. E., Zachos, J. C. & Dickens, G. R. Carbon dioxide forcing alone
19 insufficient to explain Palaeocene-Eocene Thermal Maximum warming. *Nature*
20 *Geoscience* **2**, 576-580, doi:10.1038/ngeo578 (2009).
- 21 10 Zeebe, R. & Zachos, J. Long-term legacy of massive carbon input to the Earth
22 system: Anthropocene vs. Eocene. *Philosophical Transactions of the Royal*
23 *Society*, 1-22 (2012).
- 24 11 Hönisch, B. *et al.* The Geological Record of Ocean Acidification. *Science* **335**,
25 1058-1063 (2012).
- 26 12 Ridgwell, A. & Schmidt, D. N. Past Constraints on the vulnerability of marine
27 calcifiers to massive carbon dioxide release. *Nature Geoscience* **3**, 196-200
28 (2010).
- 29 13 Sluijs, A., Zachos, J. C. & Zeebe, R. E. Constraints on hyperthermals. *Nature*
30 *Geosci* **5**, 231-231 (2012).
- 31 14 Zeebe, R. E. & Zachos, J. C. Reversed deep-sea carbonate ion basin gradient
32 during Paleocene-Eocene thermal maximum. *Paleoceanography* **22**, - (2007).
- 33 15 Walker, J. C. G., Hays, P. B. & Kasting, J. F. A Negative Feedback Mechanism for
34 the Long-Term Stabilization of Earths Surface-Temperature. *J Geophys Res-Oc*
35 *Atm* **86**, 9776-9782 (1981).
- 36 16 Berner, R. A., Lasaga, A. C. & Garrels, R. M. The carbonate-silicate geochemical
37 cycle and its effects on atmospheric carbon dioxide over the past 100 million
38 years. *American Journal of Science* **283**, 641-683 (1983).
- 39 17 Dickson, A. J. *et al.* Evidence for weathering and volcanism during the PETM
40 from Arctic Ocean and Peri-Tethys osmium isotope records. *Palaeogeography*
41 *Palaeoclimatology Palaeoecology* (in press).
- 42 18 Ravizza, G., Norris, R. N., Blusztajn, J. & Aubry, M. P. An osmium isotope
43 excursion associated with the late Paleocene thermal maximum: Evidence of
44 intensified chemical weathering. *Paleoceanography* **16**, 155-163 (2001).

- 1 19 Robert, C. & Kennett, J. P. Antarctic Subtropical Humid Episode At the
2 Paleocene-Eocene Boundary - Clay-Mineral Evidence. *Geology* **22**, 211-214
3 (1994).
- 4 20 Dickens, G. R., Castillo, M. M. & Walker, J. C. G. A blast of gas in the latest
5 Paleocene: Simulating first-order effects of massive dissociation of oceanic
6 methane hydrate. *Geology* **25**, 259-262 (1997).
- 7 21 Goodwin, P. & Ridgwell, A. Ocean - atmosphere partitioning of anthropogenic
8 carbon dioxide on multimillennial timescales. *Global Biogeochemical Cycles* **24**
9 (2010).
- 10 22 Lord, N., Ridgwell, A., Thorne, M. & Lunt, D. An impulse response function for
11 the “long tail” of excess atmospheric CO₂ in an Earth system model. *Global*
12 *Biogeochemical Cycles* (2015).
- 13 23 Palike, H., Lyle, M., Nishi, H. & al., e. A Cenozoic record of the equatorial Pacific
14 carbonate compensation depth. *Nature* **488**, 609-614 (2012).
- 15 24 Farley, K. A. & Eltgroth, S. F. An alternative age model for the Paleocene-Eocene
16 thermal maximum using extraterrestrial He-3. *Earth and Planetary Science*
17 *Letters* **208**, 135-148 (2003).
- 18 25 Kelly, D. C., Zachos, J. C., Bralower, T. J. & Schellenberg, S. A. Enhanced
19 terrestrial weathering/runoff and surface ocean carbonate production during the
20 recovery stages of the Paleocene-Eocene thermal maximum. *Paleoceanography*
21 **20**, - (2005).
- 22 26 Kelly, D. C., Nielsen, T. M. J., McCarren, H. K., Zachos, J. C. & Rohl, U.
23 Spatiotemporal patterns of carbonate sedimentation in the South Atlantic:
24 Implications for carbon cycling during the Paleocene-Eocene thermal maximum.
25 *Palaeogeography Palaeoclimatology Palaeoecology* **293**, 30-40 (2010).
- 26 27 Röhl, U., Westerhold, T., Bralower, T. J. & Zachos, J. C. On the duration of the
27 Paleocene-Eocene thermal maximum (PETM). *Geochemistry Geophysics*
28 *Geosystems* **8**, - (2007).
- 29 28 Murphy, B. H., Farley, K. A. & Zachos, J. C. An extraterrestrial He-3-based
30 timescale for the Paleocene-Eocene thermal maximum (PETM) from Walvis
31 Ridge, IODP Site 1266. *Geochimica Et Cosmochimica Acta* **74**, 5098-5108
32 (2010).
- 33 29 Greene, S. *et al.* in *2014 AGU Fall Meeting Abstracts*. PP41C-1407.
- 34 30 Norris, R. *et al.* Paleogene Newfoundland sediment drifts. *Integrated Ocean*
35 *Drilling Program: Preliminary Reports*, 1-263 (2012).
- 36 31 Zeebe, R. LOSCAR: Long-term ocean-atmosphere-sediment carbon cycle
37 reservoir model v2. 0.4. *Geoscientific Model Development* **5**, 149-166 (2012).
- 38 32 Ridgwell, A. & Hargreaves, J. Regulation of atmospheric CO₂ by deep - sea
39 sediments in an Earth system model. *Global Biogeochemical Cycles* **21** (2007).
- 40 33 Ridgwell, A. Interpreting transient carbonate compensation depth changes by
41 marine sediment core modeling. *Paleoceanography* **22** (2007).
- 42 34 Nunes, F. & Norris, R. D. Abrupt reversal in ocean overturning during the
43 Palaeocene/Eocene warm period. *Nature* **439**, 60-63 (2006).
- 44 35 McCarren, H., Thomas, E., Röhl, U. & Zachos, J. C. The Paleocene-Eocene
45 Carbon Isotope Excursion: Insights from the benthic record (ODP Leg 208,
46 Walvis Ridge). *Geophysics, Geosystems, Geochemistry* (2008).

- 1 36 Zeebe, R. E. What caused the long duration of the Paleocene - Eocene Thermal
2 Maximum? *Paleoceanography* **26**, 1-13 (2013).
- 3 37 Bowen, G. J. Up in smoke: A role for organic carbon feedbacks in Paleogene
4 hyperthermals. *Global and Planetary Change* **109**, 18-29 (2013).
- 5 38 Penman, D. E., Hönisch, B., Zeebe, R. E., Thomas, E. & Zachos, J. C. Rapid and
6 sustained surface ocean acidification during the Paleocene - Eocene Thermal
7 Maximum. *Paleoceanography* **29**, 357-369 (2014).
- 8 39 Komar, N., Zeebe, R. & Dickens, G. Understanding long - term carbon cycle
9 trends: The late Paleocene through the early Eocene. *Paleoceanography* **28**, 650-
10 662 (2013).
- 11 40 Leon-Rodriguez, L. & Dickens, G. R. Constraints on ocean acidification
12 associated with rapid and massive carbon injections: The early Paleogene record
13 at ocean drilling program site 1215, equatorial Pacific Ocean. *Palaeogeography,*
14 *Palaeoclimatology, Palaeoecology* **298**, 409-420 (2010).
- 15 41 Hancock, H. J., Dickens, G. R., Thomas, E. & Blake, K. L. Reappraisal of early
16 Paleogene CCD curves: foraminiferal assemblages and stable carbon isotopes
17 across the carbonate facies of Perth Abyssal Plain. *International Journal of Earth*
18 *Sciences* **96**, 925-946 (2007).
- 19 42 Slotnick, B. *et al.* Early Paleogene variations in the calcite compensation depth:
20 new constraints using old boreholes across Ninetyeast Ridge in the Indian Ocean.
21 *Climate of the Past Discussions* **10**, 3163-3221 (2014).
- 22 43 Bowen, G. J. & Zachos, J. C. Rapid carbon sequestration at the termination of the
23 Palaeocene-Eocene Thermal Maximum. *Nature Geoscience* **3**, 866-869 (2010).
- 24 44 Bains, S., Norris, R. D., Corfield, R. M. & Faul, K. L. Termination of global
25 warmth at the Palaeocene/Eocene boundary through productivity feedback.
26 *Nature* **407**, 171-174 (2000).
- 27 45 Ma, Z. *et al.* Carbon sequestration during the Palaeocene-Eocene Thermal
28 Maximum by an efficient biological pump. *Nature Geoscience* (2014).
- 29 46 Stoll, H. M. & Bains, S. Coccolith Sr/Ca records of productivity during the
30 Paleocene-Eocene thermal maximum from the Weddell Sea. *Paleoceanography*
31 **18** (2003).
- 32 47 Uchikawa, J. & Zeebe, R. E. Influence of terrestrial weathering on ocean
33 acidification and the next glacial inception. *Geophysical Research Letters* **35**
34 (2008).
- 35 48 Ridgwell, A. Application of sediment core modelling to interpreting the glacial-
36 interglacial record of Southern Ocean silica cycling. *Clim Past* **3**, 387-396 (2007).
- 37 49 Colbourn, G., Ridgwell, A. & Lenton, T. The Rock Geochemical Model
38 (RokGeM) v0. 9. *Geoscientific Model Development* **6**, 1543-1573 (2013).
- 39 50 Walker, J. C. G. & Kasting, J. F. Effects of fuel and forest conservation on future
40 levels of atmospheric carbon dioxide. *Palaeogeogr., Palaeoclimatol., Palaeoecol.*
41 **97**, 151-189 (1992).
- 42