

Rapid carbon sequestration at the termination of the Palaeocene–Eocene Thermal Maximum

Gabriel J. Bowen^{1*} and James C. Zachos²

The Palaeocene–Eocene Thermal Maximum (PETM), an approximately 170,000-year-long period of global warming about 56 million years ago, has been attributed to the release of thousands of petagrams of reduced carbon into the ocean, atmosphere and biosphere^{1,2}. However, the fate of this excess carbon at the end of the event is poorly constrained: drawdown of atmospheric carbon dioxide has been attributed to an increase in the weathering of silicates or to increased rates of organic carbon burial^{1,3–5}. Here we develop constraints on the rate of carbon drawdown based on rates of carbon isotope change in well-dated marine and terrestrial sediments spanning the event. We find that the rate of recovery is an order of magnitude more rapid than that expected for carbon drawdown by silicate weathering alone. Unless existing estimates of carbon stocks and cycling during this time are widely inaccurate, our results imply that more than 2,000 Pg of carbon were sequestered as organic carbon over 30,000–40,000 years at the end of the PETM. We suggest that the accelerated sequestration of organic carbon could reflect the regrowth of carbon stocks in the biosphere or shallow lithosphere that were released at the onset of the event.

Massive addition of ¹³C-depleted carbon to the Earth-surface (ocean/atmosphere/biosphere) carbon cycle (ESCC) at the initiation of the PETM has been documented in terrestrial and marine carbon isotope records worldwide⁶. The expression of $\delta^{13}\text{C}$ change in individual records is modulated by local biogeochemical, environmental and sedimentological factors^{7,8}, but all records exhibit a relatively abrupt drop in $\delta^{13}\text{C}$ values that has been attributed to the release of >3,000 petagrams (Pg) of reduced carbon to the ESCC (refs 1,2). Reconstruction of the subsequent evolution of $\delta^{13}\text{C}$ values has been complicated by suspected changes in sediment accumulation rates and carbonate preservation throughout the event. Extraterrestrial ³He concentration data now constrain accumulation rate changes for some pelagic marine sites and suggest order-of-magnitude variations in accumulation rates⁹ that are consistent with sedimentological evidence¹⁰. The resulting age models offer a relatively consistent picture of the time evolution of ESCC $\delta^{13}\text{C}$ values as represented in bulk carbonate at Ocean Drilling Program (ODP) site 690 (ref. 11) and an orbitally calibrated¹² pedogenic carbonate record from Polecat Bench, Wyoming¹³ (Fig. 1). Following the initial $\delta^{13}\text{C}$ decrease, values remain low for approximately 100 thousand years (kyr) before beginning a rapid, exponential rise, reaching stable values similar to those preceding the event about 50 kyr later. This pattern is supported by alternative age models for these sites and is replicated in other PETM sections where accumulation rate constraints are available (see Supplementary Information).

Most models for the recovery of the ESCC following the PETM invoke flushing of the excess, isotopically light carbon from the

system, mediated by elevated rates of carbonate carbon burial due to weathering feedbacks^{1,5}. According to this scenario, the recovery of $\delta^{13}\text{C}$ values towards a post-PETM equilibrium state reflects the imbalance of isotopic fluxes associated with burial of new carbonate and weathering of ancient carbonate. As (1) imbalances in the mass fluxes of carbon to and from the ESCC must be small relative to the total mass of carbon within the system, (2) the $\delta^{13}\text{C}$ value of net carbon burial is similar to that of the ESCC as a whole, and (3) the ESCC is well mixed over timescales of many thousands of years¹⁴, flushing of PETM light carbon from the ESCC can be approximated as the exponential decay of an isotopic perturbation (P) with a half-life ($t_{1/2}$) equal to the mean residence time of ESCC carbon (see Supplementary Information).

Data documenting the end-PETM $\delta^{13}\text{C}$ recovery at site 690 and Polecat Bench are fitted well by an exponential decay model (Fig. 2; $R^2 = 0.92$ and 0.91 , respectively), consistent with the expectations of a weathering-dominated recovery. Rate equations for the carbon isotope excursion (CIE) recovery at the two sites differ in the magnitude of the isotopic perturbation at the onset of the CIE recovery by a factor of 2, probably reflecting ecological and climate-driven changes in the isotopic offset between terrestrial and marine carbonates during the PETM (refs 7,15). Both equations, however, indicate very similar values for the half-life of the perturbation (16.7 and 13.9 kyr, respectively). The equivalence of the CIE recovery pattern and rate at these two sites, which reflect the two largest ESCC reservoirs (marine dissolved inorganic C and soil C), suggests that the observed pattern of change reflects the global evolution of $\delta^{13}\text{C}$ values. This result supports the validity of a 1-pool model for this system over the timescale of recovery studied here.

The half-life of carbon in the ESCC is a function of the total mass of carbon (M) and the flux rate through the system. In the absence of carbon redistribution among pools within the ESCC, the flux rate can be considered either in terms of fluxes from the lithosphere (I , volcanism, carbonate weathering and oxidation of fossil organic carbon) or fluxes to the lithosphere (O , carbonate burial and organic carbon burial), which must be approximately equal over timescales exceeding $t_{1/2}$. For the modern carbon cycle the value of M is relatively well known, and is similar to 41,200–42,600 Pg (ref. 16). Estimates of O are more varied, but suggest a net burial flux of organic plus inorganic carbon of 0.22–0.42 Pg yr⁻¹ (refs 14, 17). These values suggest that the half-life of C in the modern ESCC is between 98 and 194 kyr, or approximately an order of magnitude longer than the half-life for the decay of the PETM carbon isotope perturbation.

The anomalously rapid end-PETM $\delta^{13}\text{C}$ recovery implies either that the half-life of Palaeogene ESCC carbon was much shorter than the modern value or that isotopically light carbon was preferentially sequestered from the ESCC during the CIE recovery. Assuming no preferential sequestration of light carbon, values of M and O

¹Earth and Atmospheric Sciences Department and Purdue Climate Change Research Center, Purdue University, West Lafayette, Indiana 47906, USA,

²Earth and Planetary Sciences Department, University of California, Santa Cruz, California 95064, USA. *e-mail: gabe@purdue.edu.

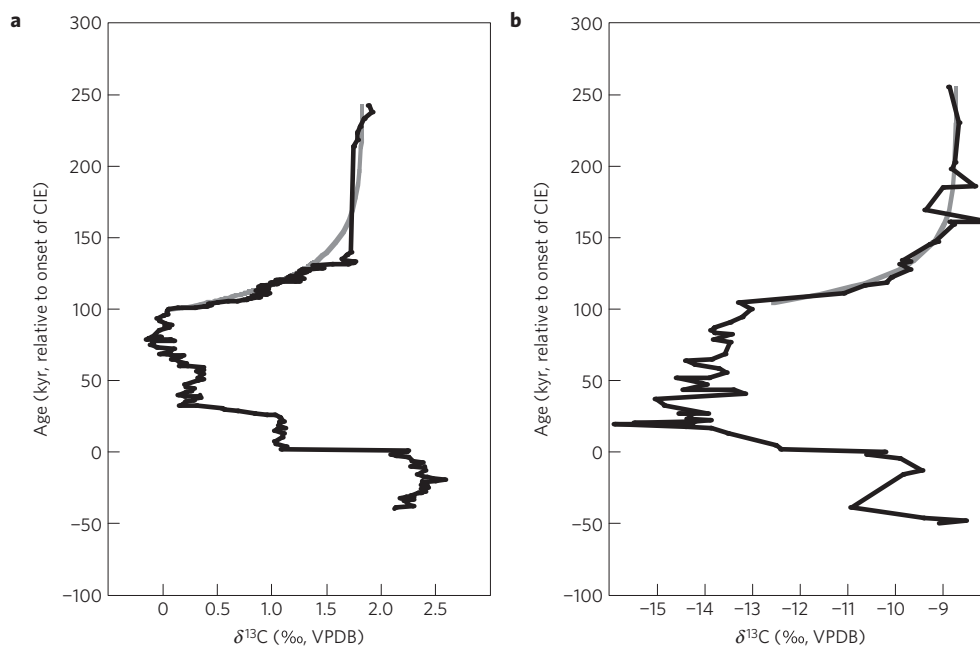


Figure 1 | Carbon isotope records spanning the PETM in marine and terrestrial sediments. a, Bulk carbonate $\delta^{13}\text{C}$ values from ODP site 690 (ref. 11), plotted against relative ages determined by assuming constant rates of extraterrestrial ^3He delivery to the sea floor⁹ (assumptions following scenario I of ref. 6). **b**, Palaeosol carbonate record from Polecat Bench, Wyoming (ref. 13) plotted against cyclostratigraphic age model¹². In both panels, the grey curves show the exponential decay model for recovery from the PETM isotopic perturbation.

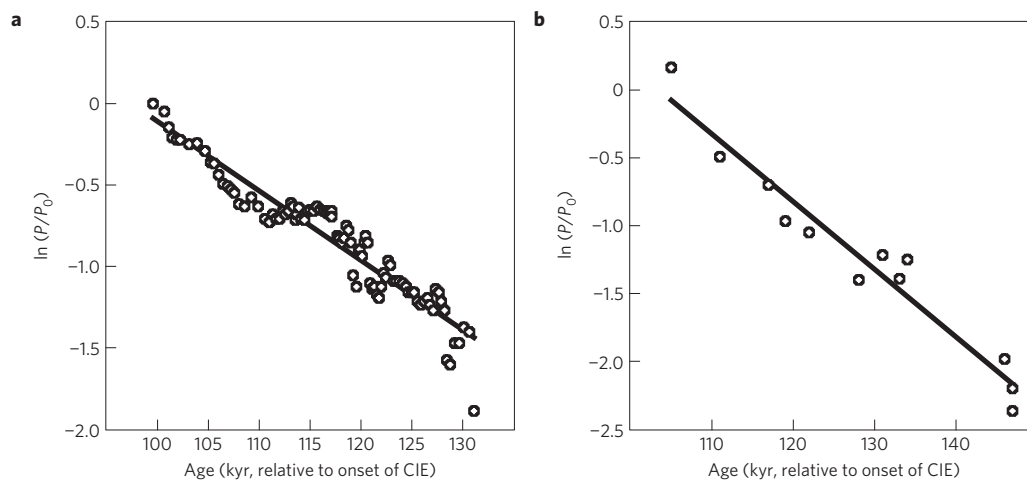


Figure 2 | Model for $\delta^{13}\text{C}$ recovery at the end of the PETM. a,b, Determination of decay rates for PETM isotopic perturbation (P) at ODP site 690 (**a**) and Polecat Bench (**b**). Decay of the initial perturbation (P_0) fits a log/linear model consistent with flushing of a well-mixed ocean/atmosphere/biosphere carbon reservoir. The slope of this function for all samples in the 'recovery' phase of the PETM that exhibit an isotopic perturbation of 0.1‰ or more gives estimates of the half-life of C in the ocean/atmosphere/biosphere carbon reservoir of 16.7 and 13.9 kyr on the basis of data from site 690 and Polecat Bench, respectively.

consistent with the observed half-life can be calculated from the first-order rate law. These values would suggest that the Palaeogene carbon cycle was markedly different from the modern cycle, with a total mass approximately four times smaller or flux rates to/from the lithosphere four times larger than today (Fig. 3).

Mass and flux rate constraints for the Palaeogene carbon cycle can be derived from geochemical data and carbon-cycle models. We estimate that the mass of carbon in Palaeogene marine surface and deep-water dissolved inorganic C pools was not likely to be less than $\sim 75\%$ of the modern value, on the basis of calculations of the carbonate system constrained by marine Ca^{++} concentration estimates from fluid inclusions¹⁸, palaeo-surface-water pH estimates from boron isotopes¹⁹,

and reconstructions of the carbonate compensation depth and deep-water temperatures in the Palaeogene ocean²⁰ (see Supplementary Information). Over million-year timescales, O can be evaluated on the basis of global carbonate accumulation rates, which for the early Palaeogene were probably no greater, and perhaps up to 50% less, than modern values²¹. This does not account for potential short-term changes in weathering and burial fluxes, however, which may have occurred in conjunction with an extreme transient event such as the PETM. Modelling²² suggests the potential for short-term weathering rates as high as ~ 2 times modern values as a result of different palaeogeographic, $p\text{CO}_2$ and climate conditions in the early Palaeogene, and we adopt this as a provisional estimate of the

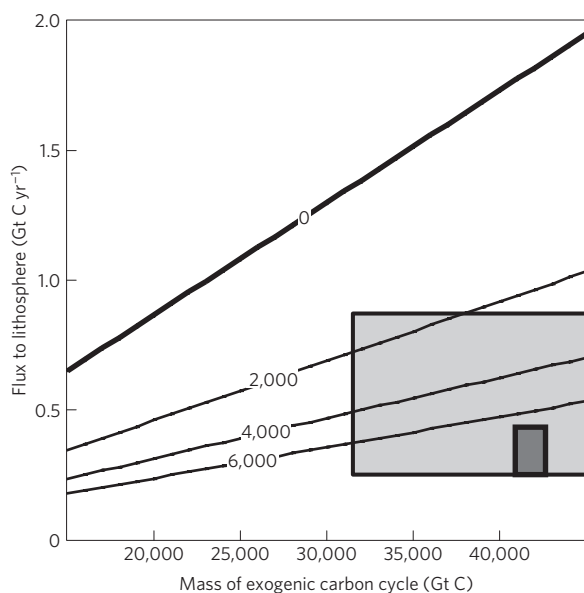


Figure 3 | Carbon-cycle properties consistent with a half-life for the PETM CIE recovery of 16 kyr. Estimates of the mass¹⁶ and burial rate of sedimentary inorganic¹⁴ plus organic carbon¹⁷ in the modern Earth surface carbon cycle are given by the dark grey rectangle, and late Palaeocene/early Eocene constraints on these parameters are shown by the light grey rectangle. Lines show combinations of values required assuming different magnitudes of excess-organic-carbon sequestration during the PETM recovery (values in Pg C).

maximum possible PETM flux rates. Together, these constraints suggest that differences between the mass and flux rates of the PETM and modern ESCCs could partially explain the rapid CIE recovery (Fig. 3).

Alternatively, the preferential sequestration of light carbon, either through burial in the lithosphere or through the growth of ¹³C-depleted ESCC stocks (for example, living biomass, soils and peats), may have enhanced the rate of $\delta^{13}\text{C}$ recovery⁴. As isotopic records indicate that the CIE recovery is well approximated by an exponential decay function, and for mathematical simplicity, we model this feedback as a change in the $\delta^{13}\text{C}$ value of carbon burial that is proportional to the size of the isotopic perturbation (that is, the magnitude of the feedback decays exponentially with the same $t_{1/2}$ as the isotopic perturbation). Assuming that the global magnitude of the CIE at the beginning of the recovery was 3‰ (Fig. 1) and that changes in the $\delta^{13}\text{C}$ values of sequestered carbon resulted from an increase in the sequestration of organic carbon relative to carbonate carbon (with an isotopic difference between these phases of 20‰), the observed rate of CIE recovery could be explained through sequestration of approximately 6,000 Pg of organic carbon from a Palaeogene ESCC with a $t_{1/2}$ equal to the modern value (Fig. 3). Allowing for differences in M , O and $t^{1/2}$ between the modern and PETM carbon cycles, as discussed above, sequestration of approximately 2,000 Pg of organic carbon is required to account for the observed CIE recovery rate.

Our results suggest that although weathering feedbacks may have contributed to the drawdown of isotopically light CO_2 , sequestration of at least $\sim 2,000$ Pg of organic carbon also occurred during termination of the PETM. Given the mass of carbon involved, it is possible that this organic flux could have involved transfer of C to either the lithosphere or biosphere. Previous work has suggested that enhanced lithospheric organic carbon burial was a negative feedback on the PETM carbon-cycle perturbation and demonstrated increased organic carbon burial rates in some environments during the PETM (refs 23–25); however, thus far

there is no evidence for a transient increase in organic burial at the event's termination. Lithospheric sequestration would have required an average increase in global organic carbon burial rates of $\sim 40\%$ (assuming background rates similar to the modern value of 0.16 Pg yr^{-1} ; ref. 17) over the first 16,000 years of the CIE recovery. Alternatively, some or all of this carbon could have been sequestered through the growth or regrowth of biospheric carbon stocks, including standing biomass, soil organic matter and peats, during the event's termination. The mass of carbon sequestration invoked here is similar to the total mass of modern terrestrial biospheric stocks¹⁶, but is probably $\sim 2/3$ or less of the Palaeogene biosphere, given that more ice-free land area, higher atmospheric $p\text{CO}_2$, and a more equable climate probably supported larger terrestrial carbon stocks at the time²⁶.

We suggest that if biospheric sequestration did remove large amounts of carbon from the ocean/atmosphere system at the termination of the PETM, this may be indicative of an active role for the biosphere as a feedback on the carbon cycle throughout the PETM. Carbon-cycle modelling^{1,2} suggests that the mass and carbon isotope composition of carbon released during the PETM are both higher than expected for a pure methane hydrate source^{5,27}, implying that some amount of this carbon may have been derived from other reduced pools such as living and dead biomass. We suggest that biospheric stocks may have fed back on PETM global change, being oxidized in response to factors such as extremely high tropical temperatures²⁸ and seasonal aridity within the continental interiors²⁹ and releasing substantial quantities of C to the ocean/atmosphere system. Data demonstrating temporary cessation of organic-rich sedimentary deposition in continental environments²⁹, large increases in physical erosion from the continents²³, and tropical floral extinctions³⁰ are consistent with a disruption of the terrestrial biosphere during the PETM. Regrowth of these depleted stocks during the recovery phase of the event would have sequestered ¹³C-depleted carbon, contributing to the rapid CIE recovery and climate stabilization. A secondary effect of this rapid and permanent removal of CO_2 would have been an increase in ocean pH throughout the PETM, thereby contributing to supersaturation of ocean waters with respect to CaCO_3 and massive carbonate deposition observed in seafloor records^{9,15}.

The model presented here involving rapid sequestration of ¹³C-depleted carbon in lithospheric and/or dynamic biospheric reservoirs can explain the rapid recovery of global ESCC $\delta^{13}\text{C}$ values, and potentially global climate, at the termination of the PETM. Left unresolved, however, is the question of what triggered the abrupt onset of light-carbon sequestration some 100 kyr after the beginning of the PETM (Fig. 1). Both external forcings (for example, orbital thresholds, changes in volcanic emissions) and internal feedbacks (for example, depletion of C stocks sustaining fluxes to the ESCC, re-establishment of marine carbonate burial fluxes) could be involved. Identification of the mechanisms triggering rapid carbon sequestration during the PETM recovery will be essential to understanding the resiliency of the coupled carbon-cycle/climate system to major perturbations such as that marking the Palaeocene/Eocene boundary.

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Author contributions

G.J.B. conceived and carried out the study. J.C.Z. advised on age models for marine records. Both authors wrote the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to G.J.B.