

A middle Eocene carbon cycle conundrum

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The Middle Eocene Climatic Optimum (MECO) was an approximately 500,000-year-long episode of widespread ocean-atmosphere warming about 40 million years ago, superimposed on a long-term middle Eocene cooling trend. It was marked by a rise in atmospheric CO₂ concentrations, biotic changes and prolonged carbonate dissolution in the deep ocean. However, based on carbon cycle theory, a rise in atmospheric CO₂ and warming should have enhanced continental weathering on timescales of the MECO. This should have in turn increased ocean carbonate mineral saturation state and carbonate burial in deep-sea sediments, rather than the recorded dissolution. We explore several scenarios using a carbon cycle model in an attempt to reconcile the data with theory, but these simulations confirm the problem. The model only produces critical MECO features when we invoke a sea-level rise, which redistributes carbonate burial from deep oceans to continental shelves and decreases shelf sediment weathering. Sufficient field data to assess this scenario is currently lacking. We call for an integrated approach to unravel Earth system dynamics during carbon cycle variations that are of intermediate timescales (several hundreds of thousands of years), such as the MECO.

The global carbon cycle

The global carbon cycle encompasses the sum of processes that determine the amount of carbon within, and fluxes between, different carbon reservoirs on Earth (Fig. 1). These processes are quantitatively important on a range of timescales and can induce both short-term fluctuations and changes in steady-state conditions^{1–3}. On timescales of up to centuries and thousands of years (kyr), such processes include photosynthesis, respiration and the short-term transfer between surface ocean, atmosphere, biosphere and soils. Annually, these processes transfer ~190 petagrams (1 Pg = 10¹⁵ g) of carbon between the surface reservoirs⁴. On timescales of 10–100 kyr, deep ocean circulation and orbitally paced climate changes (such as glacial–interglacial dynamics) affect global exogenic carbon cycling³. For example, ocean degassing and warming during the last glacial–interglacial transition (~20–10 kyr ago) probably caused a transfer of ~500 Pg of carbon from the ocean to the atmosphere and terrestrial biomass⁵.

Traditionally, variations in the carbon inventory of the ocean–atmosphere system on timescales exceeding 100 kyr have been attributed to changes in the steady-state balance between sources and sinks into and out of the global exogenic carbon cycle (Fig. 1). The dominant inputs are volcanic degassing and weathering of carbonate and organic carbon, and two sinks primarily balance the input of carbon over such timescales^{6,7}. First, carbon fixed in organic matter may be buried as organic carbon in marine and terrestrial sedimentary basins. Second, the weathering of silicates on land⁶ transfers atmospheric CO₂ into dissolved the hydrogen carbonate ion (HCO₃⁻), which is transported to the oceans by rivers. In the ocean, HCO₃⁻ becomes part of the carbonate system and is used together with the carbonate ion (CO₃²⁻) for calcification by marine biota, such as coccolithophores and foraminifers, producing solid calcium carbonate (CaCO₃). Burial of CaCO₃ in marine sediments completes the silicate-weathering process, resulting in a net sink for CO₂.

When biogenic CaCO₃ is exported towards the sea floor, the calcite saturation state ($\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]_{\text{sea water}} / [\text{Ca}^{2+}][\text{CO}_3^{2-}]_{\text{saturation}}$) becomes lower because of increasing pressure and acidity with depth. In open ocean settings, a fraction of the sinking calcite particles will

pass the saturation horizon ($\Omega = 1$), below which dissolution increases significantly so that solid CaCO₃ turns into dissolved HCO₃⁻. Essentially no calcite is preserved below the calcite compensation depth (CCD). In many studies, the CCD operationally represents the horizon at which sediments contain less than 5 or 10 wt% CaCO₃. Much of the sea floor is located above the CCD, so marine biogenic calcite burial is a dominant net carbon sink in the long-term carbon cycle. On geological timescales, the position of the CCD is affected by volcanic degassing of CO₂. An increase in degassing should enhance weathering rates of exposed rocks on land as a result of increased atmospheric pCO₂ and associated warming, thereby increasing ocean alkalinity and deepening the CCD, leading to an increase in carbonate burial rate.

The methane cycle has recently been ascribed a significant role in the global carbon cycle^{8,9}. Some of the strongly ¹³C-depleted methane produced by bacteria in sediments from organic matter is incorporated in hydrates as it diffuses upwards into strata with low temperature and sufficient pressure. In steady state, methane is stored at equal rates as it leaks from the hydrate reservoir. But hydrate reservoirs may build up over time and catastrophically dissociate, releasing carbon into the exogenic cycle on timescales of millennia, followed by gradual recharge of the reservoir over timescales longer than 100 kyr (ref. 8). Multi-million-year variations in the size of the hydrate reservoir may have regulated or modulated the global carbon cycle and related climate trends during certain intervals in Earth's history⁹.

Carbon cycle perturbations in the early Eocene climate

[Au: subheading edited to style (no punctuation). OK?] Rapid perturbations of the carbon cycle occurred during the late Palaeocene and early Eocene (~59–48 Myr ago). The most pronounced is the Palaeocene–Eocene Thermal Maximum¹⁰ (PETM) that occurred about 56 Myr ago, but several other events occurred during the early Eocene, including the Eocene Thermal Maximum 2 about 54 Myr ago¹¹. These events are termed ‘hyperthermals’¹², and were accompanied by global warming and rapid biotic change¹⁰ **[Au: “associated**

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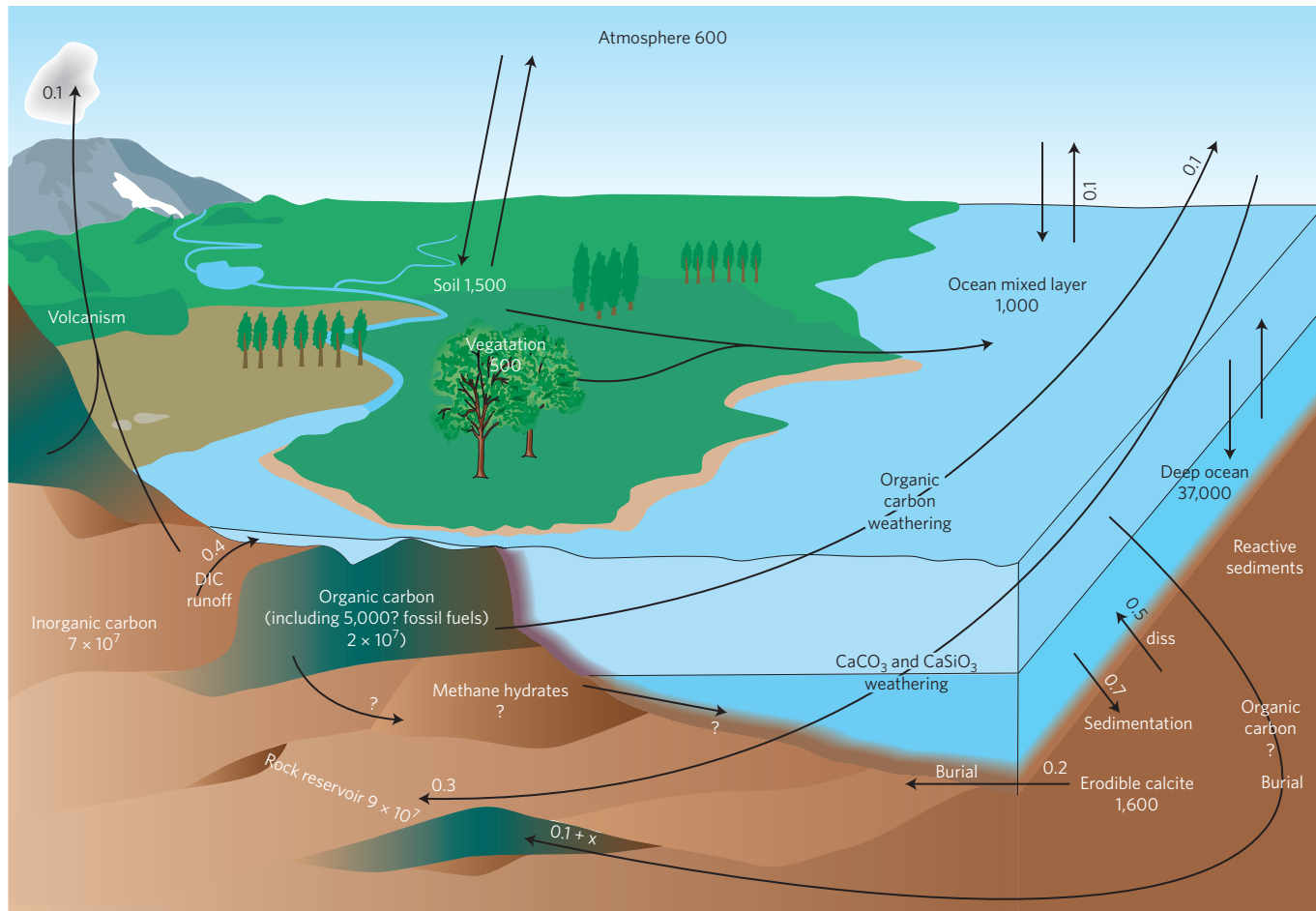


Figure 1 | Fluxes between the carbon reservoirs in the present-day carbon cycle. Rock reservoir is comprised of inorganic carbon (light brown), organic carbon (green) and methane hydrates (dark brown). Fluxes (arrows; note the processes determining the fluxes) are only shown for processes relevant to the timescales discussed in this paper. The ocean–atmosphere–biosphere system is in equilibrium on the considered timescales; the net flux from ocean to atmosphere closes the net long-term balance. The organic carbon burial arrow represents the marine and terrestrial burial flux from the ocean–atmosphere system. Numbers are derived from refs 3,4,40,41. Reservoir sizes are in Pg and fluxes (arrows) in Pg year⁻¹. Question marks indicate uncertain reservoir sizes or fluxes. DIC, dissolved inorganic carbon (includes the chemical weathering product HCO₃⁻; see main text); diss, dissolution of seafloor carbonates.

with” changed to “accompanied by”. OK?]. Stable carbon isotope ($\delta^{13}\text{C}$) records of organic carbon and carbonate on land and in the ocean indicate a pronounced decrease in the $\delta^{13}\text{C}$ of the global exogenic carbon pool¹³. Moreover, massive dissolution of pelagic marine carbonates, as documented by a shoaling of the lysocline and CCD in the major ocean basins^{14,15}, is evidence of acidification of the ocean. These patterns are best explained by the rapid release of several thousand Pg of ^{13}C -depleted carbon into the ocean–atmosphere system¹⁶. The acidification indicates that the input flux of carbon exceeded acid neutralization through weathering of continental rocks. Therefore, most carbon was injected over certainly no more than 20 kyr (ref. 17), but presumably much faster^{18,19}, and the acidification persisted for ~80 kyr in the deep ocean¹⁵. An imbalance between the typical long-term carbon input and output fluxes could not have perturbed the exogenic carbon cycle fast enough to have caused the abrupt rise in ocean–atmosphere carbon concentrations during the PETM.

The negative carbon isotope excursion (CIE) associated with the PETM implies that the injected carbon originated from a ^{13}C -depleted source²⁰, implying organic matter or methane. The magnitude of the CIE of the global exogenic carbon pool^{9,21} and the total mass of injected carbon^{17,22} are still debated, hampering identification of the carbon source. It is also debated if a precursor warming triggered the release of carbon²⁰ or whether the carbon release caused all warming²³. The release of ~2,000 Pg of carbon from methane

hydrates could explain the CIE, but significant warming should have preceded the carbon input to trigger hydrate dissociation²⁰, for which evidence exists²⁴. The release of at least twice this amount of carbon from peat²⁵ or permafrost²⁶ reservoirs must be invoked to explain the CIE by the oxidation of organic matter. This amount may fit better with the recorded magnitude of warming²³, but it has been argued that this should have caused more carbonate dissolution in deep-sea sediments than observed^{19,22}. Hence, although this debate continues, the shoaling of the CCD and a recovery time of ~100 kyr (ref. 15) is consistent with carbon cycle theory¹⁶.

The MECO conundrum

The MECO represents an episode of widespread warming about 4 million years ago^{27,28} (Fig. 2). Proxy records based on carbonate and organic matter suggest that ocean temperatures rose by ~5 °C in mid and high latitudes — but, in contrast to the transient hyperthermals, did so gradually over ~500 kyr (ref. 28). This is also supported by biogeographical patterns, notably an increase in the abundance of cosmopolitan dinoflagellate cyst and calcareous nannofossil species in high-latitude sediments^{29,30}. As suggested by proxy records, the warming was accompanied by an increase in atmospheric CO₂ concentrations³¹. A decrease in deep ocean CaCO₃ mass accumulation rates indicates dissolution and a shoaling of the calcite saturation horizon and CCD (refs 28,32) in the major ocean basins. In the Atlantic Ocean

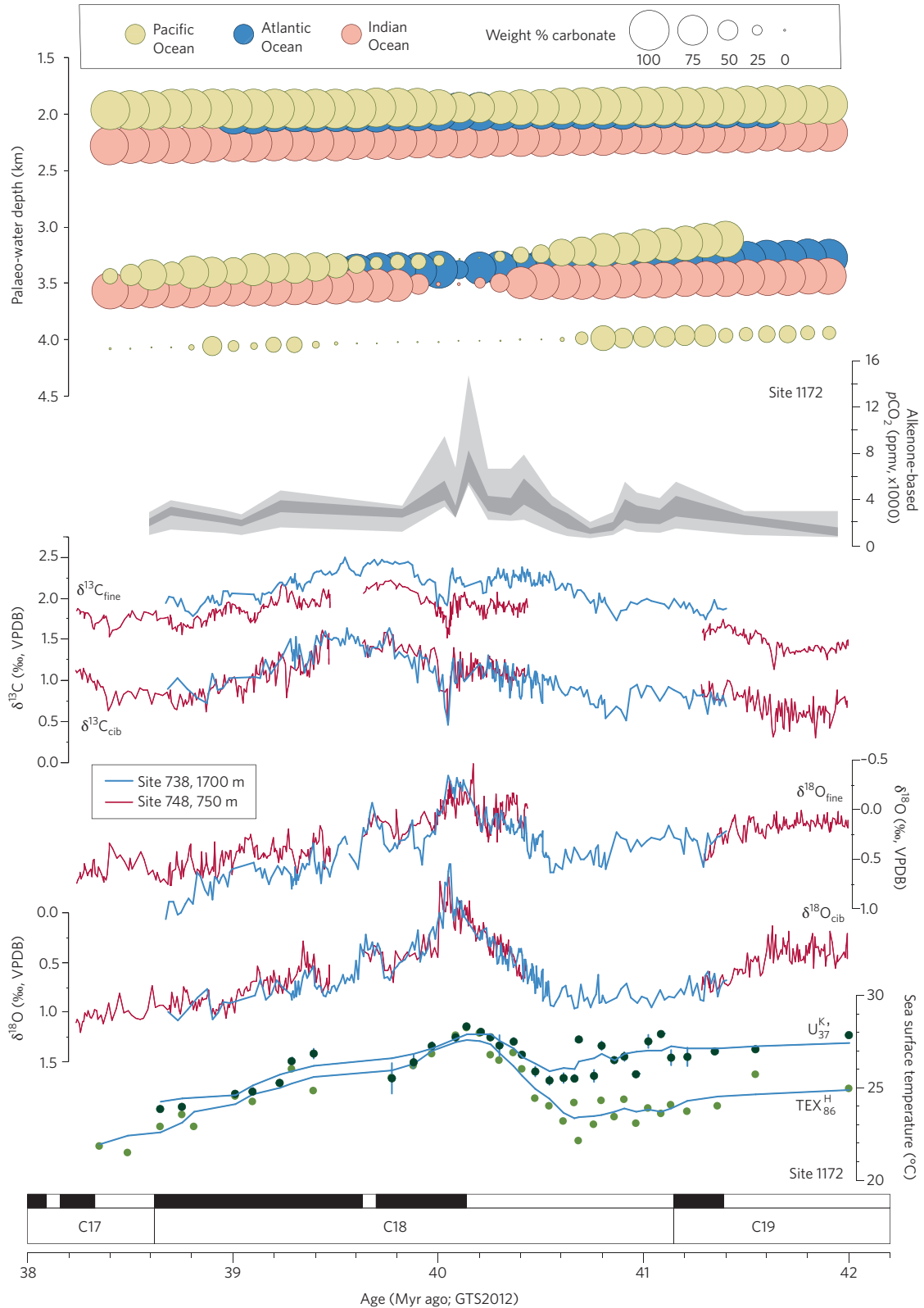


Figure 2 | A compilation of proxy data across the MECO. Deep ocean sediment carbonate wt%, atmospheric pCO_2 (ppmv), sea surface and deep ocean $\delta^{13}C$ and $\delta^{18}O$ records of biogenic carbonate (in ‰ relative to the Vienna Pee Dee Belemnite standard), and $U_{37}^{K'}$ and TEX_{86}^H sea surface temperature data ($^{\circ}C$) [AU: please define $U_{37}^{K'}$ and TEX_{86}^H]. This data, compiled from the literature^{28,31,42,43}, is plotted along the recently published timescale⁴⁴. Atmospheric pCO_2 estimates are based on alkenone stable carbon isotope fractionation factors assuming seawater phosphate concentrations between 0 and 1 mmol l^{-1} (light grey band) and dinoflagellate-cyst-assemblage-based constraints on phosphate concentrations (dark grey band; see ref. 31 for details). The error bars on $U_{37}^{K'}$ and TEX_{86}^H represent analytical error. The data from refs 27,28 [AU: ref. 27 is not cited previously in this caption - but refs 28,31,42,43 are. Is this correct? Please check] are archived in the NOAA Paleoclimate Database, respectively at http://hurricane.ncdc.noaa.gov/pls/paleox/f?p=519:1:1048418619105239:::P1_STUDY_ID:11924 and at http://hurricane.ncdc.noaa.gov/pls/paleox/f?p=519:1:4052202060044267:::P1_STUDY_ID:5948.

Box 1 | Simulating MECO carbon cycling

For a quantitative understanding of climate and carbon cycle changes during the MECO, we carried out various carbon-cycle simulations using the long-term ocean–atmosphere–sediment carbon cycle reservoir model, LOSCAR³⁴. LOSCAR is a carbon-cycle box model coupled to a sediment module⁴⁵. It includes biogeochemical cycles of total carbon, alkalinity, phosphate, oxygen and stable carbon isotopes. Weathering of carbonate and silicate mineral rocks is parameterized in the model as a function of atmospheric CO₂ concentrations¹. Whereas the weathering response to direct effects of higher carbonic acid concentrations in rain-water should be fairly rapid, the weathering response to changes in temperature and hydrology is somewhat delayed. In the current context, however, the timescale is the response time of ocean chemistry and calcite compensation to weathering (5–10 kyr). This should provide sufficient time for the processes described above to respond to changes in pCO₂. Ocean carbonate chemistry routines use algorithms as described in ref. 46 and allow for variations in the Ca and Mg concentration of sea water, which were most probably different from modern values during the Eocene⁴⁷. Global surface temperature changes (Fig. 3) were calculated using predicted atmospheric CO₂ concentrations and a long-term climate sensitivity (Earth system sensitivity) of 5 K per CO₂ doubling.

We aim to produce model results consistent with the MECO target scenario, which includes a rise in atmospheric CO₂, constant or slightly rising δ¹³C of dissolved inorganic carbon (DIC) in the surface and deep ocean, and a shoaling of the CCD over the course

of the simulation period of ~500 kyr (Fig. 2 and Table 1). Although model scenarios 1–4 all result in rising pCO₂, they fail to produce the required CCD shoaling (Table 1). Scenario 4, a reduction of silicate weathering, seems inconsistent with rising temperature and pCO₂, which should enhance weathering. A global increase in the export of biogenic organic and carbonate carbon from the ocean's surface mixed layer (scenario 5) does produce CCD shoaling. This is because a rise in CaCO₃ rain per unit area causes an increase in the CaCO₃ burial flux (output), which must be compensated for by CCD shoaling to balance the input flux from weathering. This scenario predicts an increase in the CaCO₃ flux to sediments, including at shallow and intermediate depths, which is inconsistent with observed CaCO₃ mass accumulation rates in sediments at Site 1209 in the Pacific Ocean²⁸. The same argument holds for scenario 6 (reduction in rain ratio).

Scenario 7 invokes an imbalance in long-term carbon fluxes (Fig. 3). We hypothesize that CaCO₃ shelf deposition increased and CaCO₃ weathering remained constant due to sea-level rise (see main text). Towards the end of the carbon flux imbalance, we propose a pulse of ¹³C-depleted carbon (350 Pg C) into the surface carbon reservoirs, consistent with the observed negative δ¹³C excursion at the termination of the MECO ~40 Myr ago (Figs 2 and 3). We assume a carbon isotope composition of the source carbon of -55‰, consistent with the potential destabilization of oceanic methane hydrates as a result of passing a possible warming threshold at the end of the MECO.

Table 1 | Selection of LOSCAR simulation results compared with MECO target

Scenario	pCO ₂	Deep ocean δ ¹³ C _{DIC}	CCD	Evaluation
0. MECO target (Fig. 2)	↑	Higher or -constant	Shoals↑	—
1. Ocean temperature +5K	↑	-Constant	Deepens ↓	Failure
2. Volcanic degassing +20%	↑	Higher ↑	Deepens ↓	Failure
3. Net C _{org} burial -20%	↑	Lower ↓	Deepens ↓	Failure
4. Silicate weathering -20%*	↑	Higher ↑	Deepens ↓	Failure
5. Biological C _{org} & CaCO ₃ export +20%†	↑	Lower ↓	Shoals↑	Failure
6. Rain ratio (C _{org} /CaCO ₃) -20%‡	↑	-Constant	Shoals↑	Failure§
7. Carbon flux imbalance, small sea-level rise, CaCO ₃ weathering constant and CaCO ₃ shelf deposition increased (see main text).	↑	-Constant	Shoals↑	Success

Parameter variations (as described) were applied as linear changes from zero to the maximum or minimum parameter value over 500 kyr. The net results of these modelled scenarios shown here all yield inconsistencies with the MECO target, except scenario 7. *Inconsistent with warming and rising pCO₂. †Inconsistent with observed CaCO₃ mass accumulation rates in shallow and intermediate-depth sediments. ‡Rain ratio (export production) was reduced by increasing CaCO₃ at constant C_{org}. §Consistent with target variables but inconsistent with other observations (notably †). See Box text for further discussion. DIC, dissolved inorganic carbon; CCD, calcite compensation depth.

(at the Deep Sea Drilling Project Site 523 and Ocean Drilling Program Site 929), dissolution may have occurred during several phases within the MECO (ref. 28). In contrast to the hyperthermals, δ¹³C records across the MECO interval suggest little change or a small increase in the δ¹³C of the global exogenic carbon pool. Towards the end of the event, however, a transient (~50 kyr) negative carbon isotope excursion is recorded, accompanied by invigorated warming, as indicated by the oxygen isotopic composition (δ¹⁸O) of biogenic calcite (Fig. 2). After this spike, an abrupt cooling occurred within ~50 kyr, followed by a longer-term recovery to pre-MECO values over ~100–300 kyr.

These patterns imply that the MECO differs significantly from the hyperthermals. The relatively long duration of this event indicates that the CO₂ rise originated from a long-term imbalance between input and burial of carbon in the system, which reversed long-term middle Eocene cooling and resulted in MECO warming. The absence of a δ¹³C shift shows that this imbalance was not related to organic matter

oxidation or burial, or methane release²⁷ [**Au: sentence change OK?**].

Similarly to the PETM, the shoaling of the CCD was interpreted to reflect ocean acidification following carbon input²⁸. However, this interpretation is problematic for the MECO as the carbon flux imbalance persisted over ~500 kyr. On such timescales, theory^{6,33} suggests that the input of carbon and elevated temperatures should lead to an increase in weathering, enhanced alkalinity supply to the ocean and elevated carbonate saturation state, therefore leading to a deepening of the saturation horizon, lysocline and CCD [**Au: sentence changes OK?**]. Critically, these predictions are in sharp disagreement with the data, which indicate a marked reduction in sediment CaCO₃ concentration at depths below ~3.5 km in the Atlantic, Indian and Pacific oceans across the MECO (Fig. 2). The discrepancy between theory and field data poses a challenge to our understanding of the carbon cycle: how can warming and an increase in atmospheric CO₂ concentrations in the absence of a distinct change in exogenic δ¹³C result in

deep-sea carbonate dissolution on timescales of more than 100 kyr?

To explore the problem from a modelling perspective, we use the established carbon cycle model LOSCAR³⁴, which has previously been applied to carbon cycle perturbations such as the PETM^{22,34} (Box 1). We forced the model with changes in temperature, inorganic versus organic carbon particulate rain ratios, the biological pump, volcanic degassing, and carbonate and silicate weathering (Box 1 Table 1). These simulations indicate that no single mechanism satisfactorily explains the MECO observations. Instead, the model results confirm the predicament that carbon input is difficult to reconcile with sustained CCD shoaling on MECO timescales.

One of the modelled scenarios, which involves a combination of mechanisms, fits the available data relatively well (Fig. 3). We invoke an imbalance in the carbon cycle, which leads to higher atmospheric CO₂ concentrations³¹. This imbalance could be caused by enhanced volcanic outgassing²⁷ which would not necessarily change global exogenic δ¹³C (ref. 35). We also assume a small sea-level rise resulting [AU: resulting 'from'?] thermal expansion, consistent with the 5 °C warming of the ocean, and previous (although speculative) inferences of polar ice-sheet melting³⁶. Sea-level rise causes the weathering of shelf sediments to decrease or, in the case of warming, remain stable and limits the addition of alkalinity to the ocean³³. Moreover, some carbonate burial may be relocated from the deep sea to the shelf^{37,38}, as a small rise in sea level would increase the accommodation space available for shallow-water carbonate deposition. An increase in shelf and reef carbonate deposition resulting from global warming³⁹ would have a similar effect in the model. Finally, at the end of the carbon flux imbalance, we assume a modest release of ¹³C-depleted carbon (for example, methane — similarly to the PETM) to comply with the negative δ¹³C and δ¹⁸O excursions. The combined effects lead to warming and, crucially, a decrease in deep ocean sedimentary CaCO₃ concentration (Fig. 3), consistent with the data.

From a carbon cycle perspective, the simulation presented in Fig. 3 is one plausible scenario that seems consistent with the presently available data. However, several issues remain regarding current data sets and modelling efforts for the MECO event. First, the primary mechanism that caused a sustained imbalance between carbon input and burial (resulting in rising atmospheric CO₂) remains unclear; there is as yet no geological evidence for enhanced volcanism ~40 Myr ago. Second, although two marginal marine sediment sections have been studied³¹, we lack data to assess changes in global sea level and carbon burial in shelf sediments across the MECO to validate our simulation. Third, it remains enigmatic how a long-term imbalance in the carbon cycle leading to higher pCO₂ and temperature during MECO abruptly terminated, coinciding with a transient perturbation.

Outstanding carbon cycle questions

The available data across the MECO pose a true challenge to understanding carbon cycle variations on timescales of several hundreds of thousands of years. Detailed documentation of the precise timing and magnitude of low-to-high latitude temperature change is required. Moreover, variables to assess changes in the carbon cycle, particularly pCO₂, ocean alkalinity and carbonate dissolution patterns, must be documented at high temporal resolution, and site-to-site chronostratigraphic (age) correlations need to be improved. Moreover, although the behaviour of the weathering feedback is relatively well understood for the PETM, estimates of continental weathering rates and response times are required to validate simulated changes in ocean carbonate chemistry for the MECO. High-latitude records are required to determine whether ice sheets existed in the middle Eocene, and to assess the potential for glacioeustatic (ice-sheet) modulation of sea level. Furthermore, sea-level reconstructions in low- and mid-latitude regions must be carried out to assess the potential for decreased carbonate weathering of shelf sediments as well as shelf carbonate burial in low-latitude shallow seas such as the Tethys, as hypothesized in

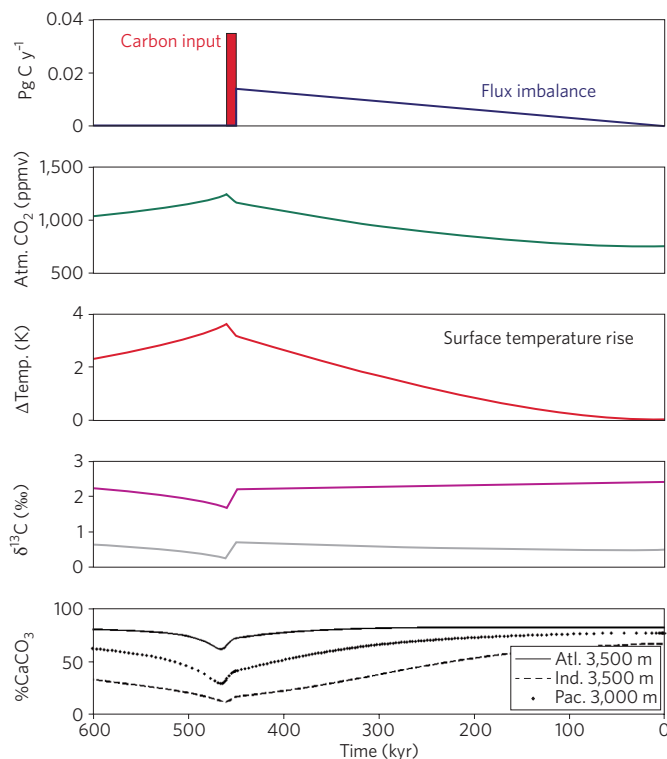


Figure 3 | Results of the LOSCAR model run corresponding to the MECO target. Results of the described model experiment (see main text and scenario 7 in Box 1 Table 1) that approximately correspond to the current MECO records of ocean temperature change, atmospheric pCO₂ and CCD evolution. The two lines represent average surface (purple) and deep (grey) ocean δ¹³C of DIC.

our simulation. Finally, the long-term early-to-middle Eocene evolution of the carbon cycle must be better quantified to assess the cause of its imbalance during the MECO. In particular, alternative mechanisms might be sought in the long-term weathering feedback, as variations in climate and tectonics probably impacted the weatherability³⁸ of rocks on land. If our scenario cannot be validated with data, the MECO stands out as a fundamental problem in our understanding and modelling of the carbon cycle.

Along with the MECO, the multi-million-year swings in ocean δ¹³C of several per mil [AU: please clarify “several per mil”] during the late Palaeocene and early Eocene remain challenging [AU: OK to insert here “to interpret” or something similar?] and will probably provide key information on long-term changes in carbon cycling. Variations in the size of the buried organic matter reservoir on land²⁵ or the methane hydrate reservoir⁹ have been proposed to explain these features. The hyperthermals such as the PETM typically occurred during this long-term trend, which suggests that the long-term carbon cycle and associated long-term changes in climate caused threshold behaviour and transient perturbations in the carbon cycle. However, these questions regarding long-term and superimposed transient carbon cycle changes — on which the research community has been primarily focused for some time — seem notably different from the MECO, which now poses a challenge on intermediate timescales (100–500 kyr).

It could be that the MECO is not unique and that several intervals of CCD shoaling, in both the Cretaceous and Palaeogene periods, are accompanied by CO₂ rise and warming in a similar way. Similar enigmatic CCD variations have been documented in middle Eocene sediments in the equatorial Pacific Ocean³², although they do not seem to have been associated with major temperature changes

and their global nature has yet to be assessed in detail. We propose that such conspicuous time intervals deserve the focused, integrated approach we suggest above for the MECO to better quantify controls and feedbacks in the global carbon cycle, and to gain further insight into mechanisms of Palaeocene climate change.

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Author contributions

A.S. identified the carbon cycle conundrum. R.E.Z. carried out the modelling. P.K.B. and S.M.B. provided ideas and performed the final data compilation. A.S. wrote the paper with input from all authors.

Additional information

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Competing financial interests

The authors declare no competing financial interests.