Understanding long-term carbon cycle trends: The late Paleocene through the early Eocene

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The late Paleocene to the early Eocene (58–52 Ma) was marked by significant changes in global climate and carbon cycling. The evidence for these changes includes stable isotope records that reveal prominent decreases in δ18O and δ13C, suggesting a rise in Earth’s surface temperature (~4°C) and a drop in net carbon output from the ocean and atmosphere. Concurrently, deep-sea carbonate records at several sites indicate a deepening of the calcite compensation depth (CCD). Here we investigate possible causes (e.g., increased volcanic degassing or decreased net organic burial) for these observations, but from a new perspective. The basic model employed is a modified version of GEOCARB III. However, we have coupled this well-known geochemical model to LOSCAR (Long-term Ocean-atmosphere Sediment CARbon cycle Reservoir model), which enables simulation of seawater carbonate chemistry, the CCD, and ocean δ13C. We have also added a capacitor, in this case represented by gas hydrates, that can store and release 13C-depleted carbon to and from the shallow geosphere over millions of years. We further consider accurate input data (e.g., δ13C of carbonate) on a currently accepted timescale that spans an interval much longer than the perturbation. Several different scenarios are investigated with the goal of consistency amongst inferred changes in temperature, the CCD, and surface ocean and deep ocean δ13C. The results strongly suggest that a decrease in net organic carbon burial drove carbon cycle changes during the late Paleocene and early Eocene, although an increase in volcanic activity might have contributed. Importantly, a drop in net organic carbon burial may represent increased oxidation of previously deposited organic carbon, such as stored in peat or gas hydrates. The model successfully recreates trends in Earth surface warming, as inferred from δ18O records, the CCD, and δ13C. At the moment, however, our coupled modeling effort cannot reproduce the magnitude of change in all these records collectively. Similar problems have arisen in simulations of short-term hyperthermal events during the early Paleogene (Paleocene-Eocene Thermal Maximum), suggesting one or more basic issues with data interpretation or geochemical modeling remain.


1. Introduction

Prominent decreases in the δ18O and δ13C of marine carbonate occurred over the late Paleocene and early Eocene (LPEE; Figure 1) [Shackleton, 1986; Zachos et al., 2001; Cramer et al., 2009; Zachos et al., 2010]. The drop in δ18O indicates a long-term warming trend, whereby Earth’s surface at high latitudes and the deep ocean warmed by ~4°C [Zachos et al., 2001; Bijl et al., 2009; Westerhold et al., 2011; Hollis et al., 2012]. Almost concurrently, planktic and benthic stable carbon isotope ratios gradually dropped by about 2%, while deep-sea carbonate records at several sites indicate a deepening of the calcite compensation depth (CCD) [Hancock et al., 2007; Leon-Rodriguez and Dickens, 2010]. The precise magnitude of CCD deepening is uncertain but was probably several hundred meters. Absolute ages surrounding the LPEE also remain uncertain; throughout this work, we assume the “Option-1” time scale presented by Westerhold et al. [2008] is close to being correct, such that the LPEE δ13C drop occurred from ~58.0 to 52.5 Ma (Figure 1).
This interval of the Cenozoic is also characterized by a series of short-lived hyperthermals, or transient episodes of warming. The Paleocene-Eocene Thermal Maximum (PETM), which occurred around 55.5 Ma, was the most prominent hyperthermal; however, at least two additional and significant warming events followed (ETM-2 or H-1 circa 53.7 Ma and K/X circa 52.5 Ma; Figure 1b) [Lourens et al., 2005; Nicolo et al., 2007; Stap et al., 2009; Zachos et al., 2010; Leon-Rodriguez and Dickens, 2010]. Each of the hyperthermals exhibits a negative carbon isotope excursion as well as a carbonate dissolution horizon in deep-sea sediments (above references). These events have been associated with rapid ($\sim$10$^4$ years) and massive inputs of $^{13}$C-depleted carbon to the ocean-atmosphere system [Dickens et al., 1997; above references; McInerney and Wing, 2011]. For the PETM, several thousand petagrams of carbon (1 Pg = 10$^{15}$ g) represents a minimum estimate.

The present study uses a combination of data analysis and numerical modeling to constrain the cause of several trends in records spanning the LPEE—in a broad sense, the large changes in background conditions surrounding the hyperthermals. These include the prominent drops in the $\delta^{13}$C of surface and deep ocean, the temperature rise, and the deepening of the CCD. Such modeling should allow better understanding of long-term carbon cycling and possible relationships with the superimposed, transient hyperthermals.

We assess the problem from two different perspectives. First, we focus on two mechanisms within the context of conventional views for the global carbon cycle (Figure 2). We examine whether an increase in volcanic degassing or, alternatively, a decrease in the net burial of organic carbon might have caused the long-term carbon cycle and climatic variations during the LPEE. Note that, from a modeling perspective, we cannot distinguish between decreased burial of organic carbon, increased oxidation of organic carbon, or some combination of both. We therefore refer to the sum of these processes as “net organic carbon burial” throughout this work. Second, we examine a mechanism that lies outside of conventional views for the global carbon cycle. Specifically, we added a dynamic capacitor that can store and release very large quantities of $^{13}$C-depleted carbon in the shallow geosphere over time. For this study, we focused on a gas hydrate capacitor, because this possibility has been suggested [Dickens, 2003, 2011]. In order to quantify the effects of these mechanisms, we first performed simple mass and isotope balance calculations and followed these by a more sophisticated analysis employing numerical modeling.
rather than the modern values of \([Ca^{2+}] = 10\ \text{mmol kg}^{-1}\) and \([Mg^{2+}] = 53\ \text{mmol kg}^{-1}\) as inferred from fluid inclusions in marine halites, the model accounts for the effects of evolving temperature. In our simulations we used \([Ca^{2+}] = 20\ \text{mmol kg}^{-1}\) and \([Mg^{2+}] = 30\ \text{mmol kg}^{-1}\) as inferred from fluid inclusions in marine halites.\([7]\) LOSCAR includes the distribution of various biogeochemical tracers, such as total carbon (TCO\(_2\)), total alkalinity (TA), dissolved phosphate (PO\(_4\)), dissolved oxygen (O\(_2\)), and stable carbon isotopes (\(\delta^{13}C\)) of surface, intermediate and deep water and bulk sediments. Parameters such as [CO\(_2\)], [CO\(_2^+\)], pH, and calcite saturation state are then computed from predicted TCO\(_2\) and TA using chemistry routines explained by Zeebe and Wolf-Gladrow [2001].

In our simulations we used \([Ca^{2+}] = 20\ \text{mmol kg}^{-1}\) and \([Mg^{2+}] = 30\ \text{mmol kg}^{-1}\) as inferred from fluid inclusions in marine halites [Lowenstein et al., 2001; Horita et al., 2002], rather than the modern values of \([Ca^{2+}] = 10\ \text{mmol kg}^{-1}\) and \([Mg^{2+}] = 53\ \text{mmol kg}^{-1}\) [Tyrrell and Zeebe, 2004]. Warmer surface and bottom water temperatures in the late Paleocene and early Eocene have an impact on solubility and equilibrium constants. Bottom water temperatures are prescribed at 8\(^\circ\)C for the late Paleocene (circa 58 Ma) and the model accounts for the effects of evolving temperature. Specifically, temperature changes as a function of CO\(_2\), and this impacts equilibrium constants for reactions involving dissolved \([Ca^{2+}]\) and \([Mg^{2+}]\). The model also uses ocean basin volumes based on a Paleocene/Eocene topography by Bice and Marotzke [2002]. LOSCAR’s architecture, main components, and variables as well as process parameterization are described in detail by Zeebe [2012].

[8] GEOCARB III is a model developed by Berner and Kothavala [2001] to explain long-term variations in the exogenic carbon cycle. More specifically, it considers carbon exchange processes between geologic (crustal rocks and deeply buried sediments) and surficial (atmosphere and oceans) reservoirs (equation (1)). The balance of carbon fluxes between different reservoirs ultimately determines the atmospheric CO\(_2\) concentration [Ridgwell and Zeebe, 2005].

The two fundamental steady state equations embedded in GEOCARB III are

\[
F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg}
\]

(1)

\[
\delta F_{wc} + \delta F_{mc} + \delta F_{bg} = \delta F_{bc} + (\delta F_{bg} - \epsilon g F_{bg})
\]

(2)

where parameters are described in Table 1. These two equations, or their time-dependent form, also lie at the core of other geochemical models [e.g., Kump and Arthur, 1999].

[9] The model assumes that during each 1 Myr period (the time step of GEOCARB III), the rate of burial of carbon as carbonates in sediments (\(F_{bc}\)) is equal to the rate of weathering of carbon from silicates (\(F_{wc}\)) and carbonates (\(F_{wc}^\prime\)). Therefore, \(F_{wsi} = F_{bc} - F_{wc}^\prime\). This assumption is approximately true on a million year timescale because carbon in the ocean-atmosphere system has a relatively rapid turnover, which is a result of its very small carbon storage capacity compared to fluxes from and to the geologic reservoir. A more detailed explanation of the GEOCARB III model parameterization, its architecture, and processes can be found in Berner and Kothavala [2001].

[10] It is important to recognize that input data used in GEOCARB III modeling have a linearly interpolated (\(\geq 10\) Myr resolution. Hence, the original GEOCARB III model cannot be used directly for investigating carbon cycling during the LPEE, because the input data are too coarse. Knowing the average values of bulk sediment \(\delta^{13}C\) (\(\delta_{bc}\)) between 58 Ma and 52 Ma is critical because sediment burial rates of carbonate and organic carbon are calculated using the carbon isotopic data of ancient seawater. Therefore, it was necessary to modify GEOCARB III in order to capture the processes of the long-term carbon cycle during the LPEE more realistically. This modified version is referred to as the GEOCARB module.

[11] Unlike GEOCARB III, which implements a smoothed fit to \(\delta^{13}C\) data presented by Veizer et al. [1999] (over 10 million years time intervals), the GEOCARB module uses a much higher temporal resolution of the \(\delta^{13}C\). We use \(\delta^{13}C\) records at Deep Sea Drilling Project (DSDP) Sites 527 and 577 (Figure 1b), which recently have been placed onto a common and current timescale [Dickens and Backman, 2013]. For the purposes of this study, the data were smoothed using a local linear kernel estimator with a constant bandwidth of 1 Ma (Figure 1b, solid lines). For more information on the statistical technique used here, see Samworth and Poore [2005] and Poore et al. [2006]. This approach eliminates aberrant model variations (caused by rapid fluctuations in the \(\delta^{13}C\) associated with the PETM and other hyperthermal events), while still capturing the

Figure 2. A box model of the long-term carbon cycle. Each box represents a reservoir, and arrows represent fluxes of carbon between the reservoirs. Dashed frame includes the standard carbon cycle [e.g. Berner, 1999], whereas the fluxes and reservoir outside of the frame illustrate a hypothetical organic capacitor (e.g. methane hydrates). Fdp - bicarbonate flux, Fmeth - methanogenesis, Faom - anaerobic oxidation of methane [Dickens, 2011]. For flux and mass values refer to Table 1.
The long-term trend of the δ\textsuperscript{13}C over this time interval. This is justified by the fact that we are only investigating long-term carbon cycle behavior, rather than short-term fluctuations.

Because the isotopic fractionation between organic carbon and carbonates (ε\textsubscript{g}) is approximately equal to the difference between the δ\textsuperscript{13}C of sedimentary carbonates (δ\textsubscript{bc}) and δ\textsuperscript{13}C of total organic carbon (δ\textsubscript{TOC}) [Hayes et al., 1999], the ε\textsubscript{g} also had to be recalculated:

\[
ε_g = \left[ \frac{δ_{bc} + 1000}{δ_{TOC} + 1000} - 1 \right] \times 10^3
\]

Values of δ\textsubscript{TOC} can be found for the late Paleocene [Erdman and Schorno, 1979; Macko and Pereira, 1990] and for the early Eocene [Erdman and Schorno, 1978a, 1978b, 1978c]. This adjustment leads to a decrease in ε\textsubscript{g} of about 1.0‰ between 58 Ma and 52 Ma (from ~31.0‰ to ~30.0‰). Interestingly, one might predict an increase in carbon isotope fractionation between dissolved inorganic carbon (DIC) and organic carbon during the LPEE due to rising pCO\textsubscript{2} [e.g., Freeman and Hayes, 1992]. The discrepancy may reflect a poor and incomplete record of δ\textsubscript{TOC} across this time interval. However, other than discontinuous records of organic δ\textsuperscript{13}C from the central Arctic Ocean [Stein et al., 2006; Sluijs and Dickens, 2012], an unusual location, the above references seemingly provide the only pertinent data available in the literature.

### 2.2. Coupling

GEOCARB does not include ocean chemistry or sediments and hence cannot predict the position of the CCD and its variation over time. In order to successfully reconcile and simulate the multihundred million year trends observed during the late Paleocene and early Eocene, the computation of the CCD and its evolution throughout the studied time period is vital. Therefore, it was necessary to couple GEOCARB with the LOSCAR model (Figure 3). More precisely, the GEOCARB module has been implemented as a function that is called from within LOSCAR. Once LOSCAR is initiated, it uses the GEOCARB module to obtain the fluxes (F\textsubscript{wc}, F\textsubscript{mc}, F\textsubscript{bg}, and F\textsubscript{mg}) across the LPEE (58 to 52 Ma). LOSCAR then runs forward in time (starting at 58 Ma) calling the GEOCARB module at prescribed time increments. We set these increments to 1000 years and note that lower values will give smoother results. In turn, LOSCAR sends information to GEOCARB, such that fluxes are updated for LOSCAR every 1000 years. Using these fluxes and biogeochemical tracer distributions (TCO\textsubscript{2}, TA, PO\textsubscript{4}, O\textsubscript{2}, δ\textsuperscript{13}C, and wt%CaCO\textsubscript{3} in sediments), different parameters were calculated, including atmospheric CO\textsubscript{2}, ocean pH, calcite and aragonite saturation state, and calcite compensation depth (see Figure 3).

### 3. Results and Discussion

#### 3.1. Decoupled Mass Balance Experiments

We first determined long-term responses of the ocean-atmosphere system to increased volcanic degassing and decreased net organic carbon burial using a “decoupled” mass balance approach (see supporting information). Examined responses were the evolution of δ\textsuperscript{13}C, atmospheric

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Initial Value</th>
<th>Initial Value Sim 2 (58 Ma)</th>
<th>Initial Value Sim 3 (62 Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c, g</td>
<td>These subscripts refer to carbonate and organic carbon, respectively.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{wc}, F\textsubscript{mg}</td>
<td>Rate of release of carbon to the ocean-atmosphere-biosphere system via the weathering.</td>
<td>F\textsubscript{wc} = 16.0</td>
<td>F\textsubscript{wc} = 16.37</td>
<td>F\textsubscript{wc} = 18.76</td>
</tr>
<tr>
<td>F\textsubscript{mc}, F\textsubscript{bg}</td>
<td>Rate of release of carbon to the ocean-atmosphere-biosphere system via the metamorphic/volcanic breakdown.</td>
<td>F\textsubscript{mc} = 6.0</td>
<td>F\textsubscript{mc} = 6.04</td>
<td>F\textsubscript{mc} = 5.89</td>
</tr>
<tr>
<td>F\textsubscript{bg}, F\textsubscript{mg}</td>
<td>Burial rate of carbon.</td>
<td>F\textsubscript{bg} = F\textsubscript{mc} + F\textsubscript{wc}</td>
<td>F\textsubscript{mg} = 21.12</td>
<td>F\textsubscript{mg} = 24.3</td>
</tr>
<tr>
<td>F\textsubscript{bg}, F\textsubscript{mc}</td>
<td>Rate of uptake of atmospheric CO\textsubscript{2} via the weathering of Ca and Mg silicates followed by precipitation of the Ca and Mg as carbonates.</td>
<td>F\textsubscript{mc} = 10.0</td>
<td>F\textsubscript{mg} = 6.31</td>
<td>F\textsubscript{mc} = 5.34</td>
</tr>
<tr>
<td>F\textsubscript{mc}, F\textsubscript{bg}</td>
<td>Methanogenesis and its isotopic value.</td>
<td>F\textsubscript{nath} = 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M\textsubscript{OC}</td>
<td>Mass of the ocean cap.</td>
<td>3000 Pg C,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M\textsubscript{OC, atm}</td>
<td>Mass of ocean + atmosphere.</td>
<td>irrelevant</td>
<td>27,139 Pg C</td>
<td>34,290 Pg C</td>
</tr>
</tbody>
</table>

*Fluxes: 10\textsuperscript{15} mol yr\textsuperscript{-1}.*
Figure 3. LOSCAR-GEOCARB coupling schematics (see text for description of variables).

Table 2. Summary of All Experiments and Simulations Performed in This Study

<table>
<thead>
<tr>
<th>Explanation</th>
<th>Figure Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>A + N Experiment 1</td>
<td>Mass balance + LOSCAR CCD calculation: increased volcanic degassing scenario</td>
</tr>
<tr>
<td>A + N Experiment 2</td>
<td>Mass balance + LOSCAR CCD calculation: decreased organic burial scenario</td>
</tr>
<tr>
<td>Simulation 1</td>
<td>LOSCAR + GEOCARB module (standard parameters: $\Delta T = 0.09^\circ C^{-1}$, $\Delta T_{x2} = 2.3^\circ C$)</td>
</tr>
<tr>
<td>Simulation 2</td>
<td>LOSCAR + GEOCARB module (ACT = 0.05$^\circ C^{-1}$, $\Delta T_{x2} = 3^\circ C$)</td>
</tr>
<tr>
<td>Simulations 3 and 4</td>
<td>LOSCAR, methane hydrate capacitor (Simulation 3, DIC:TA = 1:0, $\Delta T_{x2} = 3^\circ C$) (Simulation 4, DIC:TA = 1:1, $\Delta T_{x2} = 3^\circ C$)</td>
</tr>
</tbody>
</table>
fractionation (see supporting information), the “per carbon mol” effects of volcanic degassing and net organic burial upon surface ocean δ13C and the CCD are substantially different (Figures S1 and S2 and Table S1). The difference is due to the fact that carbon emissions from volcanoes are much less depleted in δ13C (δ13C ~ -4 to -5‰) than organic carbon buried in sediments (δ13C ~ -30‰) [Lasaga et al., 1985; Kump and Arthur, 1999]. Hence, an increase in carbon emissions from volcanoes (either from the mantle or metamorphism of upper crust) has a much smaller effect on ocean δ13C but a much greater impact on the CCD than a decrease in net burial of organic carbon. In other words, for the same δ13C excursion, the CCD change is much greater if the carbon originates from mantle. This is best illustrated by calculating the per mole effects of volcanic degassing and net organic carbon burial on the δ13C and the CCD (Table S1). To first order, if increased volcanic degassing was the sole cause for the observed drop in δ13C of the surface ocean during the LPEE, the CCD should have deepened three times (∆δ13C/∆Fbg > 3 × ∆δ13C/∆Fws) as much as if decreased organic carbon burial was the sole cause.

[20] According to the results presented above, it is very unlikely that increased volcanic degassing was the main cause of carbon cycle changes during the LPEE, because this would have pushed the CCD far deeper than allowed by observations (Figure S1). However, excess volcanism might have contributed to overall climate change across the time interval. From a conventional view of the global carbon cycle, we agree with Kurtz et al. [2003]: A decrease in the net burial of organic carbon seems the most plausible explanation for the observed drop in δ13C from the late Paleocene through the early Eocene.

3.2. Coupled LOSCAR and GEOCARB Modeling

[21] We next simulated the evolution of the exogenic carbon cycle during the LPEE using the coupled GEOCARB-LOSCAR model (Simulation 1; Table 2). This simulation (Figure 4) uses new input data (e.g., δec and εg), but most GEOCARB parameters and variables were set to standard values described by Berner and Kothavala [2001]. GEOCARB predicts a 6% increase in volcanic degassing between 58 and 52 Ma, which partly governs the increase in pCO2 (Figure 4a). The outcome of the experiment (Figure 4) is predominantly a result of new input data (δec and εg, see above), which are the main drivers of the model. However, in reality, the δ13C of the surface ocean is set by carbon input and output fluxes, not the other way around.

[22] The trends are mainly driven by a decrease in net burial of organic carbon predicted by the GEOCARB module. The initial and final organic carbon burial fluxes are 6.3 × 1018 mol Myr−1 at 58 Ma and ~4.4×1018 mol Myr−1 at 53 Ma, respectively. These values agree reasonably well with independent estimates made from the abundance of organic carbon in various types of sedimentary rocks [Berner and Canfield, 1989]. The results presented by Berner and Canfield [1989], just like GEOCARB III, have a 10 Myr temporal resolution. Despite this low resolution, they suggest organic burial rates around 6.7×1018 mol Myr−1 at 60 Ma (the Cenozoic maxima), which then decrease slightly throughout the Cenozoic.

![Figure 4. LOSCAR + GEOCARB module simulation results. The response of the ocean-atmosphere system due to changes of fluxes predicted by the GEOCARB module (new input data); (a) CO2; (b) silicate weathering (Fws), carbonate weathering (Fwc), organic carbon burial (Fbg), organic carbon weathering (Fwg); (c) δ13C of both surface and deep ocean; and (d) calcite compensation depth. LA: low-latitude surface Atlantic, LP: low-latitude surface Pacific, DA: deep Atlantic.](image)

[23] Other modeling studies [Kurtz et al., 2003; Hilting et al., 2008] have identified the latest Paleocene and early Eocene as a time interval marked by decreasing burial of organic carbon, although with approaches somewhat different from the ones implemented in this study. Between 57 and 52 Ma, Kurtz et al. [2003] and Hilting et al. [2008] suggested decreases in Fbg from ~5.8 to ~4.1×1018 mol Myr−1 and from ~8.5 to ~7.5×1018 mol Myr−1, respectively. However, Kurtz et al. [2003] did not address the evolution of atmospheric pCO2, carbonate chemistry of seawater, or the CCD. Basically, their carbon cycle consists of a single reservoir with one input (weathering) and two outputs (organic and carbonate carbon burial). While Hilting et al. [2008] included estimates for pCO2 and seawater chemistry, the CCD was omitted. Note also that some stable isotope records used in previous modeling exercises were on incorrect timescales, such that inflections in δ13C at some sites were offset by 0.5 Myr or more [Dickens and Backman, 2013].

[24] The decrease in net organic carbon burial calculated by the GEOCARB module does not necessarily imply decreased burial of organic carbon into marine or terrestrial sediments. From a standard carbon cycle perspective...
DIC remains constant over time, so will the
2008\]. This implies that as long as the ratio of nutrients and
is probably larger than allowed from sediment records.
1150 m in the Atlantic during the LPEE (Figure 4d), which
LPEE \[\text{(Figure 1b)}\]. Because bulk sediment comprises
mostly calcareous nannofossils, which lived in surface
water, this would suggest minimal change in the surface to
dep \(\delta^{13}C\) gradient. Unlike the model employed by Hilting
et al. [2008], the coupled GEOCARB-LOSCAR approach
does not use the deep ocean \(\delta^{13}C\) record as input data, but
rather predicts this curve. This allows a detailed examination
of various mechanisms (e.g., biological pump, biological
productivity, rain ratio, etc.) and their effect on the surface
to deep gradient of \(\delta^{13}C\), which might allow us to better
constrain the model.

3.3. Earth System Sensitivity and Biological Pumping

[25] Due to the predicted \(pCO_2\) and temperature rises, carbonate and silicate weathering fluxes accelerate across
the LPEE. In turn, this increases the carbonate ion supply
to the ocean and thus, the concentration of \(CO_2^+\). The position of the carbonate compensation depth (CCD) is ulti-
mately controlled on long time frames by the requirement
that riverine carbon input fluxes need to balance carbonate
burial output fluxes. Hence, the enhanced weathering
causes a deepening of the CCD from about 57 Ma to 52 Ma,
as inferred from carbonate accumulation records at sev-
eral locations [Hancock et al., 2007; Leon-Rodriguez and
Dickens, 2010]. Again, there is a problem. According to
Simulation 1, the CCD deepens by 1260 m in the Pacific and
1150 m in the Atlantic during the LPEE (Figure 4d), which
is probably larger than allowed from sediment records.

[26] Carbon fluxes in GEOCARB are calculated by
supplying the model with the \(\delta^{13}C\) data of the bulk carbonate
\(\beta_{bc}\) in equation (2). On the other hand, the \(\delta^{13}C\) of the bulk carbonate in LOSCAR is controlled by carbon inputs
and outputs and their respective isotopic values, which are
supplied by GEOCARB. In theory, this means that the
~2.0\%o decrease of surface ocean \(\delta^{13}C\) between 58 and
~52 Ma prescribed by GEOCARB should be the same in
LOSCAR, which is the case. The \(\delta^{13}C\) of the surface
\(\delta^{13}C_{surf}\) in LOSCAR is then calculated using an offset from
the bulk sediment stable isotope value of 0.5\%. The offset
was inferred based on the difference between bulk carbonate
\(\delta^{13}C\) record and planktonic foraminifera \(\delta^{13}C\) during the
LPEE [Shackleton et al., 1984].

[27] Unlike surface ocean \(\delta^{13}C\), which is independent
of internal oceanic processes, at least on long timescales,
dep deep ocean \(\delta^{13}C\) (and therefore the vertical gradient) is
also controlled by the biological pump and vertical mixing
[Kump, 1991]. The maximum value of the gradient primar-
ily depends on the ratio of nutrients to DIC [Hilting et al.,
2008]. This implies that as long as the ratio of nutrients and
DIC remains constant over time, so will the \(\delta^{13}C\) gradient
between the surface and deep ocean. In LOSCAR, biologi-
cal uptake is parameterized using phosphate concentrations,
which are prescribed and constant over time in the present
simulations. On the other hand, due to increased \(pCO_2\)
and enhanced weathering between 58 and 52 Ma, DIC of the
ocean increases. Therefore, the modeled phosphate/DIC ratio
decreases through time, and the surface to deep \(\delta^{13}C\) gradient diminishes (Figure 4c). This result is consistent
with one set of observations, namely the difference between
planktonic foraminifera \(\delta^{13}C\) and benthic foraminifera \(\delta^{13}C\),
which lessened by about 1\%o at multiple sites during the
LPEE [Hilting et al., 2008]. However, bulk sediment \(\delta^{13}C\)
approximately paralleled benthic foraminifera \(\delta^{13}C\) during
the LPEE (Figure 1b).
A decrease in planktonic foraminifera $\delta^{13}C$ across the LPEE faithfully represents a past decrease in surface to deep water $\delta^{13}C$, a possible mechanism to reconcile the inferred temperature change would be through a decrease in the efficiency of the biological pump [Hilting et al., 2008]. However, a weaker biological pump would lead to a deeper CCD; everything else being constant. This is due to the fact that a weaker biological pump decreases CaCO$_3$ production and raises the CaCO$_3$ saturation state of the ocean. Basically, the deep-sea carbonate ion concentration increases, so the CCD deepens, which instigates more precipitation to counteract the higher saturation state (i.e., a stabilizing feedback) [Zeebe and Westbroek, 2003].  

3.4. Inclusion of an Organic Capacitor and Release of Methane From the Seafloor as a Specific Example

The above scenarios for the long-term carbon cycle changes are mostly “divorced” from the hyperthermals. That is, while they might be offered as potential explanations for the broad decrease in $\delta^{13}C$ spanning the LPEE, they offer no insight to the well-known series of rapid and massive injections of $^{13}C$-depleted carbon that occurred within the time interval (Figure 1). Examination of the GEOCARB module (Figure 2) shows the reason: There is no means to store massive amounts of $^{13}C$-depleted carbon and return it to the ocean or atmosphere quickly.
during the LPEE can be linked, at least from a modeling perspective, by adding a large and dynamic organic carbon capacitor to the exogenic carbon cycle [Berner, 1987; Dickens, 2003; Kurtz et al., 2003]. Effectively, there would be some reservoir in the shallow geosphere that could store massive amounts of $^{13}$C-depleted carbon over time and release such carbon to the ocean and atmosphere at variable rates depending on environmental change. Suggested possibilities have included methane in marine sediment and peat on land [Dickens, 2003; Kurtz et al., 2003].

[37] We next consider the LPEE as representing slow release of $^{13}$C-depleted carbon from a large, dynamic organic capacitor and choose seafloor methane as a specific case. This requires two basic modifications to our modeling framework. First, the timescale of interest needs expansion. The drop in $\delta^{13}$C across the LPEE goes from the absolute high to the near low in carbon isotope records covering the entire Cenozoic. This suggests that at ~58 Ma, the ocean-atmosphere system was far outside of multimillion year quasi steady state conditions. More specifically, 58 Ma would be a time when the organic capacitor had already stored large amounts of carbon. We therefore started the modeling at the point where $\delta^{13}$C is about average for the Cenozoic (62 Ma). Second, the GEOCARB model needs modification to include the additional box, which lies outside of the traditional exogenic reservoirs (Figure 2). Following Dickens [2003] and Dickens [2011], we connect gas hydrate systems to the ocean and atmosphere through some basic fluxes: (1) a small fraction of conventional organic carbon burial ($F_{bg}$) goes through methanogenesis; (2) methanogenesis produces $^{13}$C-rich bicarbonate that returns to the ocean ($F_{dp}$) and $^{13}$C-depleted methane that can remain in sediment ($F_{meth}$); and (3) methane returns to the ocean through anaerobic oxidation of methane (AOM) and production of bicarbonate ($F_{AOM}$). The latter reaction can be expressed as [Reeburgh, 1976]

$$\text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}. \quad (4)$$

Importantly, addition of such a capacitor changes the mathematical expressions (equations (1) and (2)), because they need to include the new fluxes:

$$F_{wc} + F_{mg} + F_{mg} + F_{AOM} + F_{dp} = F_{bg} + F_{bg} + F_{dp} + F_{AOM} \quad (5)$$

$$\delta F_{wc} + \delta F_{mc} + \delta F_{mg} + \delta F_{AOM} = \delta F_{AOM} \quad (6)$$

[38] The initial conditions at 62 Ma (e.g., masses, volcanic degassing flux, carbonate and silicate weathering rates, etc.) for these simulations were similar to those in the original GEOCARB module but with modifications to account for the small steady state inputs from the capacitor (Figure 1b). As a starting point, we use the quasi steady state fluxes suggested in previous work [Dickens, 2011]. Unlike in our previous simulations, however, most parameters in GEOCARB (e.g., organic carbon burial, isoation fractionation, and volcanic degassing) are assumed to be constant over time. This means, after 62 Ma ($t > 0$), responses in the global carbon cycle become independent of the GEOCARB module; they are calculated by LOSCAR with the forcing achieved by changing the balance between inputs ($F_{meth}$) and outputs ($F_{AOM}$) to the gas hydrate capacitor. Crucially, surface ocean $\delta^{13}$C is now predicted rather than prescribed, and the ocean-atmosphere system evolves in response to variations in the total mass of carbon within the capacitor, in this case seafloor methane.

[39] To vary the total mass of seafloor methane, we changed the flux of AOM to achieve reasonable agreement with the $\delta^{13}$C of bulk sediment (Figures 6 and 7). This AOM forcing is as follows: from 1.0 to 0.6 x 10^{12} mol yr^{-1} over the first 4 Myr (62 to 58 Ma), from 0.6 to 1.5 x 10^{12} mol yr^{-1} over the next 5 Myr (58 to 53 Ma), from 1.5 x 10^{12} mol yr^{-1} to 1.0 x 10^{12} mol yr^{-1} over 2.5 Myr (53 to 50.5 Ma), and constant at 1.0 x 10^{12} mol yr^{-1} until 48 Ma (Figures 6a and 7a). The underlying rationale for this approach is that the long-term flux of carbon through AOM should relate to the mass of gas hydrate in marine sediment, which should be dictated mainly by deep ocean temperature [Dickens, 2001a, 2001b, 2003]. It also should be stressed that these AOM fluxes are not hugely different than those (~0.6 x 10^{12} mol yr^{-1}) assumed in previous modeling exercises devoted to understanding the short-term negative $\delta^{13}$C excursion across the PETM.

![Figure 6. LOSCAR carbon capacitor simulation results.](image-url)

The response of the ocean-atmosphere system due to the prescribed $F_{AOM}$ changes from the carbon capacitor; (a) $F_{AOM}$ forcing and reservoirs’ masses over time; (b) $\text{CO}_2$; (c) silicate weathering ($F_{ws}$), carbonate weathering ($F_{wc}$), organic carbon burial ($F_{bg}$), and organic carbon weathering ($F_{mg}$); (d) $\delta^{13}$C of surface and deep ocean and bulk sediment; and (e) calcite compensation depth. LA: low Atlantic, LP: low Pacific, DA: deep Pacific. No alkalinity contribution from AOM (DIC:TA = 1.0).
the PETM (55.53 Ma on the timescale of the bulk ı
(3000 Pg C) at 62 Ma to a peak mass of about 1.49
alkalinity (TA). For CO2, the DIC to TA ratio is 1:0; for
however, these outputs of DIC should have different total
occur at about the time of maximum seafloor methane mass.

The fraction of organic carbon entering sediment and form-
ditions that would allow a methane hydrate capacitor to grow
through AOM is decreasing but still above that of quasi
steady state conditions. Should the long-term drop in
δ13C across the LPEE relate to diminishing fluxes from a large
and dynamic gas hydrate capacitor, one that grew through
the middle to late Paleocene, the PETM necessarily had to
occur at about the time of maximum seafloor methane mass.

[42] The capacitor simulations also give intriguing results
regarding the δ13C gradient and the CCD deepening during
the LPEE (Figures 6 and 7). Namely, the δ13C gradient
and the CCD deepening produced in the capacitor simu-
lations are more consistent with the observations (Figures 6e
and 7e), which is due to smaller carbon fluxes (explained
below). Comparison of the capacitor simulations (Simula-
tions 3 and 4) shows that the increased alkalinity scenario
damps the CCD and pCO2 variations. This is due to an
increased buffer capacity of the ocean as a consequence of
the higher alkalinity.

[45] At this point, a methane hydrate capacitor seems a
plausible cause for both the short-term and the long-term
carbon cycle trends across the LPEE. However, for this
explanation to be fully compatible with observations, it
requires different perspectives on Earth system sensitivity
and gas hydrate masses.

[44] Because CH4 in gas hydrate is typically very depleted
in ı3C (probably δ13C <70‰ in the early Paleogene)
[Dickens, 2003], the amounts and fluxes of carbon neces-
sary to drive the observed δ13C trends are much smaller
than those required by burial of organic carbon. This is reflec-
ted by the predicted modest temperature rise (0.8 to 1.6°C)
between 58 and 52 Ma (Figures 6 and 7), assuming an Earth
system sensitivity of 3°C per doubling of pCO2. Either Earth
system sensitivity has to be more than twice the canonical
value of 3°C, or a good fraction of the warming during the
LPEE (as well as the preceding cooling) was unrelated to
changes in carbon cycling represented by δ13C and CCD
records. We note the latter is consistent with the temporal
lag between δ18O and δ13C (Figure 1b), as well as an ex-
planation involving gas hydrates, because changes in carbon
fluxes would result from warming (and cooling) rather than
the other way around [Dickens et al., 1997; Dickens, 2011].
This same issue—Earth surface warming leading massive
carbon addition—has been emphasized in papers regarding
the short-term hyperthermal events of the early Paleogene
[e.g., Sluijs et al., 2012; Zeebe et al., 2009].

[45] The global mass of gas hydrates in marine sediment
and the rates to and from this reservoir remain uncertain
for any time in Earth’s history, including the present day.
Various studies have suggested that gas hydrates on mod-
ern continental slopes store between 1000 and 22,000 Pg C
[Kvenvolden, 1993; Dickens, 2001b; Milkov, 2004; Archer,
2007; Burwicz et al., 2010]. As pointed out by Dick-
ens [2011], the lower estimates do not conform to basic
field data, and we accept 5000–10,000 Pg C as reasonable
for the present day. In our model simulations, the masses
of the gas hydrate capacitor at initial steady state condi-
tions (62 Ma) are smaller than this value. However, during
the late Paleocene, the mass grows much larger. Benthic
foraminifera δ18O records suggest an ~4 Myr interval of
bottom water cooling that preceded the LPEE (Figure 1a).
In theory, this 3–4° cooling would nearly double the vol-
ume of the methane capacitor by thickening the gas hydrate
stability zone in marine sediment [Dickens, 2001a, 2001b].
The fraction of organic carbon entering sediment and form-
ing methane in the past also may have been significantly
greater than today because of lower dissolved O2, lower dis-
solved SO2, and faster methanogenesis [Gu et al., 2011;
Dickens, 2011]. Is it possible that these factors created con-
tions that would allow a methane hydrate capacitor to grow

Figure 7. Same as Figure 6, except DIC:TA input from
AOM = 1:1.

Dickens, 2003]. The weathering feedback used here is
weaker compared to that in standard GEOCARB modeling,
but the same as that used in Simulation 2.

[40] We considered two cases for simulation, one in which
carbon exchange from seafloor methane to the ocean occurs
as CO2 (Simulation 3) and one in which such exchange
occurs as HCO– (Simulation 4). The reason for this is that
dissolved inorganic carbon (DIC) can escape seafloor gas
hydrate systems as CO2 (through aerobic oxidation of CH4
in the water column) or as HCO– (through CH4 generation
in sediment, through anaerobic oxidation of CH4 in sediment,
and subsequent diffusion of both) [Dickens, 2003, 2011];
however, these outputs of DIC should have different total
alkalinity (TA). For CO2, the DIC to TA ratio is 1:0; for
HCO–, the DIC to TA ratio is 1:1.

[41] According to our simulations (Figures 6 and 7), the
capacitor grows from an initial mass 0.25 × 1018 mol C
(3000 Pg C) at 62 Ma to a peak mass of about 1.49×
1018 mol C (~17,900 Pg C) around 55.8 Ma, or just before
the PETM (55.53 Ma on the timescale of the bulk δ13C
record used for modeling). From then, the capacitor steadily
discharges, until it is almost completely empty by 50 Ma.
Note that the peak mass occurs about 2.5 Myr after the peak
in surface water δ13C. This is because the flux of carbon
through AOM is decreasing but still above that of quasi
steady state conditions. Should the long-term drop in δ13C
across the LPEE relate to diminishing fluxes from a large
and dynamic gas hydrate capacitor, one that grew through
the middle to late Paleocene, the PETM necessarily had to
occur at about the time of maximum seafloor methane mass.
sufficiently large such that its collapse drove the carbon cycle changes during the LPEE? We acknowledge that a peak mass of ~18,000 Pg C, as required in our simulations, does seem high for Paleocene conditions.

[46] Other organic carbon capacitors can be suggested and simulated with a coupled LOSCAR-GEOCARB model, notably peat or permafrost carbon [Kurtz et al., 2003]. However, we emphasize that such modeling will lead to basic issues concerning the mass balance and the CCD. The δ13C of terrestrial carbon in the early Paleogene was nominally −30% [Jaramillo et al., 2010; Samanta et al., 2013]. Consequently, relative to methane, a much greater mass of carbon is required to drive the long-term changes in δ13C. For example, initial modeling by Kurtz et al. [2003] led to a buildup of 60,000 Pg C in terrestrial carbon pools during the latest Paleocene, compared to the ~1000 Pg C in peat [Page et al., 2011] or ~1600 Pg C in Arctic permafrost [Tarnocai et al., 2009] at present day. The oxidation of this peat would also cause drops in the CCD more than observed (Figures 5 and 6).

4. Conclusions and Outlook

[47] An interval of the early Paleogene (62 to 48 Ma) was characterized by major perturbations in the global carbon cycle. These include both long-term (>1 Myr) and short-term (<200 kyr) variations in the δ13C of carbon-bearing phases as well as variations in the CCD [e.g., Leon-Rodriguez and Dickens, 2010; McInerney and Wing, 2011; Westerhold et al., 2011; Pälike et al., 2012]. Carbon cycle changes across the hyperthermals have received considerable attention [e.g., Lourens et al., 2005; Stap et al., 2009; Zachos et al., 2010; McInerney and Wing, 2011; Westerhold et al., 2011], while those across the broader time frame (i.e., the background variations) largely have been ignored. Notably, this includes the LPEE (58–52 Ma), when δ13C of marine carbonate decreased by 1.5–2.5‰, and the CCD deepened by several hundreds of meters.

[48] The present study shows that long-term changes in carbon cycling during the LPEE were likely due to a net decrease in organic matter burial. An increase in volcanic degassing seems highly unlikely as the primary cause, although it might have contributed to some degree. This conclusion is based upon a coupled GEOCARB-LOSCAR model and is consistent with previous modeling studies [Kurtz et al., 2003; Hilting et al., 2008]. However, this is the first study to also consider the evolution of the CCD, as well as complete ocean carbonate chemistry, and prognostic surface to deep δ13C gradients. We show that these are essential additional components for constraining possible causes for carbon cycle changes during the studied period.

[49] A fundamental concept to recognize is that a decrease in net organic carbon burial leads to multiple possibilities, especially including increased fluxes from an organic matter reservoir. Given previous work, the two obvious cases are greater oxidation of terrestrial organic matter [Kurtz et al., 2003], and greater fluxes of CH4 from the seafloor, which would have been rapidly oxidized in the ocean or atmosphere [Dickens, 2003]. In theory, these different causes for the drop in δ13C across the LPEE can be distinguished from the record of carbonate accumulation on the seafloor (Figures 4–7). This is because the δ13C of terrestrial organic carbon (~−30‰) is very different than that of methane in marine sediment (~−70‰), so that changes in δ13C of the exogenic carbon cycle would relate to much different fluxes of carbon.

[50] Unfortunately, the position of the CCD across the Paleocene and early Eocene remains somewhat unconstrained. Between 58 and 52 Ma, it most probably did not deepen by more than 500 to 1000 m [Van Andel, 1975; Hancock et al., 2007; Leon-Rodriguez and Dickens, 2010]. This almost assuredly excludes mantle carbon inputs as a primary cause for prominent carbon cycle changes during the LPEE but leaves discussions on plausible organic carbon sources open to debate. Future modeling studies regarding early Paleogene carbon cycling would greatly benefit from an increased number and spread of early Paleogene CCD records.

[51] Despite the limited CCD records for the LPEE, the modeling used in this study leads to simulations that reproduce observed long-term trends in temperature, carbonate δ13C, and the CCD. The problem is that our modeling is unable to reproduce all these trends quantitatively and collectively. The surface to deep ocean gradient in δ13C can only be reproduced if bulk carbonate records rather than mixed layer planktonic foraminifera records are assumed to reflect surface water changes in δ13C. The predicted temperature rise resulting from carbon cycle changes is much lower than the temperature rise reconstructed from proxies. To some degree, we are not surprised, these same issues have arisen in modeling studies of the short-term hyperthermal events [Zeebe et al., 2009]. Clearly, there are still one or more data-model problems confronting a full understanding of early Paleogene carbon cycle and climate variance.

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