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Ocean chemistry and atmospheric CO_2 sensitivity to carbon perturbations throughout the Cenozoic

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[1] We assess the response of atmospheric CO_2 (pCO_2) and ocean chemistry to carbon perturbations, placing modern carbon-cycle sensitivity in the context of the Cenozoic. We use the carbon-cycle model LOSCAR to study the effect of perturbations over the past 67 Ma. Our results indicate that atmospheric CO_2 and surface ocean pH were slightly more sensitive to carbon perturbations during the Miocene (~15 Ma ago) compared to modern conditions and less sensitive during the earlier part of the Cenozoic. We find that the sensitivity to carbon input at the Paleocene-Eocene boundary (~56 Ma ago) was most likely lower compared to modern conditions. Further, we show that the Cenozoic evolution of steady state pCO_2 and seawater Mg/Ca ratios is critical for the system's sensitivity to a carbon release. **Citation:** Stuecker, M. F., and R. E. Zeebe (2010), Ocean chemistry and atmospheric CO_2 sensitivity to carbon perturbations throughout the Cenozoic, *Geophys. Res. Lett.*, *37*, L03609, doi:10.1029/2009GL041436.

1. Introduction

[2] From 1751 to 2006, mankind has released ~329 Pg carbon (C) into the atmosphere due to fossil fuel combustion and cement production [*Boden et al.*, 2009], with an average rate of ~5 Pg C y^{-1} in the period from 1954–2004 [*Boden et al.*, 2009]. A 3000 Pg C release during a 500 year period would lead to a drop of surface ocean pH by ~0.5 units [*Zeebe et al.*, 2008]. A recovery of the carbonate system to the initial state will only occur on timescales of tens of thousands of years and increased weathering due to elevated pCO_2 levels will also only have a significant effect on millennial timescales [*Uchikawa and Zeebe*, 2008]. The strength and mode of atmospheric and oceanic feedbacks to a carbon perturbation depends largely on the ocean's chemistry. This response might have differed substantially from today in earlier times of the Cenozoic [*Zachos et al.*, 2008; *Goodwin et al.*, 2009]. The purpose of the present study is to investigate the effect of a carbon perturbation on atmospheric CO_2 and ocean chemistry for different seawater chemistry and bathymetry configurations. The findings will allow us to interpret the sensitivity of the modern ocean to a massive carbon release in the context of the entire Cenozoic.

2. Model Description and Parameterization

[3] For the present study, we used the LOSCAR (Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir) model (for details, see *Zeebe and Zachos* [2007], *Uchikawa and Zeebe* [2008], and *Zeebe et al.* [2009]). We investigated the effect of ocean basin temperature, initial atmospheric pCO_2, calcite compensation depth (CCD), magnesium (Mg^{2+}) and calcium (Ca^{2+}) ion concentrations, as well as different bathymetries and ocean circulation pattern on the marine carbonate system for two different perturbation scenarios.

[4] The ocean basin temperature was varied by introducing a parameter Θ [°C], the offset relative to the modern basin temperature. We first calculated the pre-perturbation steady state solutions for different parameter values (for details, see auxiliary material), then simulated the carbon input using two different release scenarios.[2] (1) A slow rate of 3,000 Pg C over 5,000 years (0.6 Pg C y^{-1}), resembling a scenario similar to the Paleocene-Eocene boundary event, and (2) a fast rate of 3,000 Pg C over 500 years (6 Pg C y^{-1}), resembling a scenario similar to the present anthropogenic perturbation.

[5] Three response variables were used to quantify the effects of the carbon release in a given parameter space. (1) ΔpH, the maximum decline of the pH in the Atlantic surface box. (2) $\Delta\Omega_{\text{calcite}}$, the maximum decline of the calcite saturation state in the Atlantic surface box (the pH and saturation state decreases are very similar in all surface boxes). (3) ΔT [°C], the global surface temperature increase caused by the rise in atmospheric CO_2:

$$\Delta \mathrm{T} = \mathrm{T}_{x2} \times \ln\left(\frac{pCO_2^{\max}}{pCO_2^{\text{initial}}}\right) / \ln 2, \qquad (1)$$

where T_{x2} [°C] denotes the equilibrium climate sensitivity, i.e. the increase in global surface temperature caused by a doubling of pCO_2. Unless stated otherwise, T_{x2} is assumed to be 3°C throughout the experiments, which is used as a reference climate sensitivity in the range from 1.5 to 4.5°C [*Intergovernmental Panel on Climate Change*, 2007].

[6] The model was integrated for 20,000 years in total to insure that the peak values of the response variables were captured during the integration. The basin paleotemperatures were estimated using oxygen-isotope data ($\delta^{18}O$) from deep-sea benthic foraminifera [*Zachos et al.*, 2008] and Shackleton's linear paleo-temperature equation (Figure 1a) [see *Bemis et al.*, 1998]. To account for the ice volume effect, an offset of the seawater $\delta^{18}O$ value was used for the times when the northern (~3 Ma) and southern hemisphere ice sheets (~34 Ma) mostly formed [*Zachos et al.*, 2008]. We used a seawater $\delta^{18}O$ correction of −0.2‰ for the modern data to account for the older standard used by

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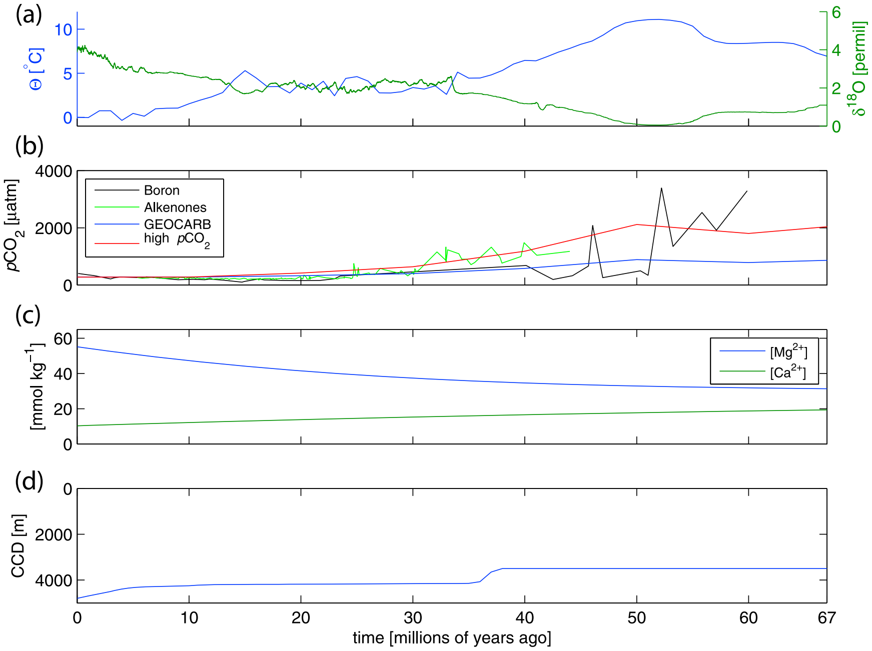

Figure 1. Proxy data used in the present study. (a) Oxygen isotope (δ^{18}O) data [*Zachos et al.*, 2008] and paleo-temperature estimates. Θ denotes the temperature offset compared to the modern basin temperature. (b) Atmospheric CO_2 reconstructions [*Berner and Kothavala*, 2001; *Pearson and Palmer*, 2000; *Pagani et al.*, 2005]. (c) Magnesium and calcium ion concentrations derived from proxy data [*Tyrrell and Zeebe*, 2004]. (d) History of the calcite compensation depth (CCD) [*Tyrrell and Zeebe*, 2004].

Shackleton [see *Bemis et al.*, 1998]. A linear decrease of seawater δ^{18}O from −0.2‰ (2 Ma) to −1.0‰ (4 Ma) was assumed. For times prior to the formation of the Antarctic ice sheet, seawater δ^{18}O was set to −1.2‰. The paleo-atmospheric CO_2 concentrations were based on the GEOCARB pCO_2 model output [*Berner and Kothavala*, 2001], which indicates values that are lower than those based on boron isotopes and alkenones [*Pearson and Palmer*, 2000; *Pagani et al.*, 2005] (Figure 1b). In addition, a high pCO_2 scenario was generated, which offsets the GEOCARB output to a range closer to the proxy data. We used $R(t) = R_G(0) + 3 \times [R_G(t) - R_G(0)]$, where $R(t)$ is the ratio of pCO_2 at time t relative to modern; G = GEOCARB. The [Mg^{2+}], [Ca^{2+}] and CCD proxy data were obtained from *Tyrrell and Zeebe* [2004] (Figures 1c and 1d).

[7] For the Late Paleocene (~56 Ma) and the Late Maastrichtian (~67 Ma), published bathymetries were used to reconstruct the basin sizes and depth profiles [*Bice et al.*, 1998; *Sewall et al.*, 2007]. Basin sizes for the Middle Miocene (~15 Ma) were reconstructed from the data by *Herold et al.* [2008]. However, their depth gradient reconstruction is too simplified to allow for a reasonable adjustment of the CCD position [*Stuecker*, 2009]. Hence, a discrete reconstruction in 5 Ma steps between the published bathymetries was performed for the whole Cenozoic by linear interpolation.

3. Results

[8] We first investigated the effect of two individual ocean parameters at a time on the system's sensitivity, while all other parameters were kept constant at their respective modern values (Figure 2). Initial conditions with increased Θ resulted in increased sensitivity of ΔpH and ΔT to carbon perturbations. In contrast, initial conditions with increased pCO_2 resulted in decreased sensitivity of these response variables to perturbations (Figures 2a and 2b). The warmer water temperatures lead to a lower CO_2 solubility, causing a higher fraction of the released carbon to stay in the gas phase [*Zeebe and Wolf-Gladrow*, 2001]. Steady states with elevated temperature and constant deep-sea carbonate ion concentrations [CO_3^{2-}] are therefore characterized by lower dissolved inorganic carbon (DIC) and total alkalinity (TA). In contrast, steady states with elevated initial pCO_2 and constant deep-sea [CO_3^{2-}] have higher DIC and TA.

[9] Observations indicate that the seawater Mg/Ca ratio was lower in the past than today (for a summary, see *Tyrrell and Zeebe* [2004]), which causes an increase of ΔpH and ΔT (Figures 2c and 2d). Earlier in the Cenozoic, [Ca^{2+}] was higher compared to modern conditions, while the saturation state Ω was approximately the same. Because Ω is defined by the product of [Ca^{2+}] and [CO_3^{2-}], higher [Ca^{2+}] in the past was compensated for by lower [CO_3^{2-}] [*Tyrrell and Zeebe*, 2004]. With pCO_2 being constant in this experiment, a decrease of [CO_3^{2-}] results in a decrease of DIC and TA, therefore lowering the carbonate buffering capacity and increasing the system's sensitivity to the perturbation. Further, we observe a deepening of the CCD from the early Cenozoic to the present (Figures 2e and 2f). The favored explanation for this is a shift of $CaCO_3$ production from the shelves in the past to increased open ocean production in the modern, and thus enhanced export of $CaCO_3$ to the deep ocean [*Ridgwell*, 2005]. Therefore, a shallower CCD and lower deep-water [CO_3^{2-}] in the early Cenozoic compared to modern conditions resulted in an increase of ΔpH and ΔT.

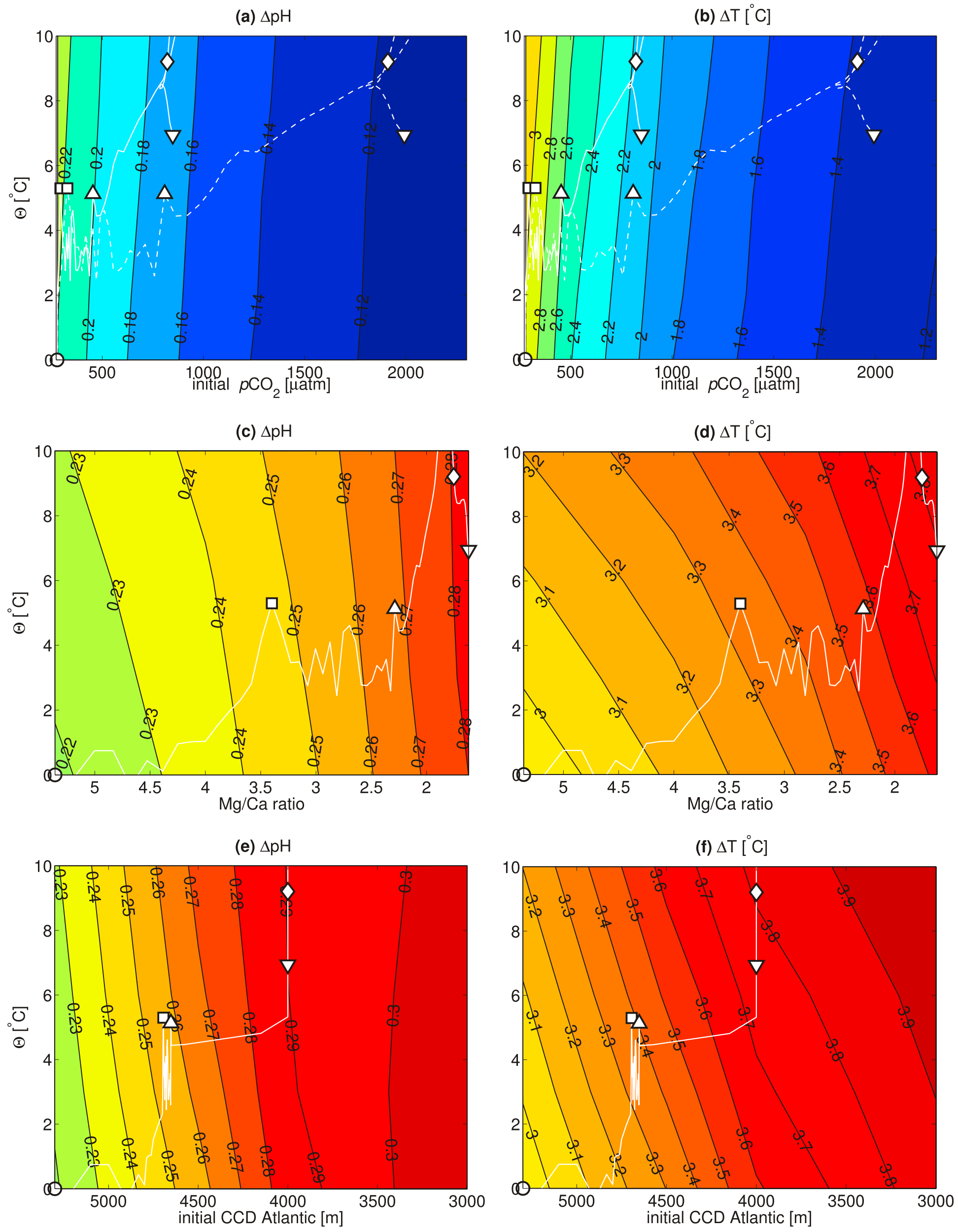

Figure 2. Effect of individual parameter variations on the sensitivity to the carbon perturbation. Each location in the plot refers to a model ocean in which the parameters displayed on the x- and y-axis have the respective values; all other parameters are constant at their modern value. Contour lines show the response to the slow emission scenario. The white lines are based on the proxy data (Figure 1). Time slices are marked as follows: Modern, circle; Middle Miocene, square; Late Eocene, upward facing triangle; Late Paleocene, diamond; and Late Maastrichtian, downward facing triangle. ΔT was calculated with equilibrium climate sensitivity T_{x2} = 3.0°C. (a) ΔpH for GEOCARB $p\mathrm{CO}_2$ (solid line) and high $p\mathrm{CO}_2$ (dashed line) scenario; (b) ΔT for GEOCARB $p\mathrm{CO}_2$ (solid line) and high $p\mathrm{CO}_2$ (dashed line) scenario; (c, e) ΔpH in the past; and (d, f) ΔT in the past.

[10] We further reconstructed steady states in which all parameters were changed according to their respective proxy values for the whole Cenozoic and applied the carbon perturbation at each time point, once with modern bathymetry (Figures 3a and 3b) and once with changing bathymetry (Figures 3a and 3c–3f). The experiment was conducted for both the GEOCARB $p\mathrm{CO}_2$ (blue lines) and the high $p\mathrm{CO}_2$ scenario (red lines). Because the Mg/Ca ratio has a significant effect on the results (Figures 2c and 2d), we used one scenario with variable Mg/Ca ratio (solid lines) and one with constant, modern Mg/Ca ratio (dash-dot lines) for the modern bathymetry experiment (Figures 3a and 3b).

[11] We find that initial $p\mathrm{CO}_2$ has the largest influence on the response variables. Assuming the fast release scenario (Figure 3e), the surface ocean pH decline ΔpH is ~0.32 units for the GEOCARB $p\mathrm{CO}_2$ scenario during the early Cenozoic (modern ΔpH = 0.48) while assuming the high $p\mathrm{CO}_2$ scenario, ΔpH is only ~0.19 units. We observe a similarly strong effect on ΔT (Figure 3f). ΔpH is ~0.23 units for the early Cenozoic assuming the slow rate GEOCARB

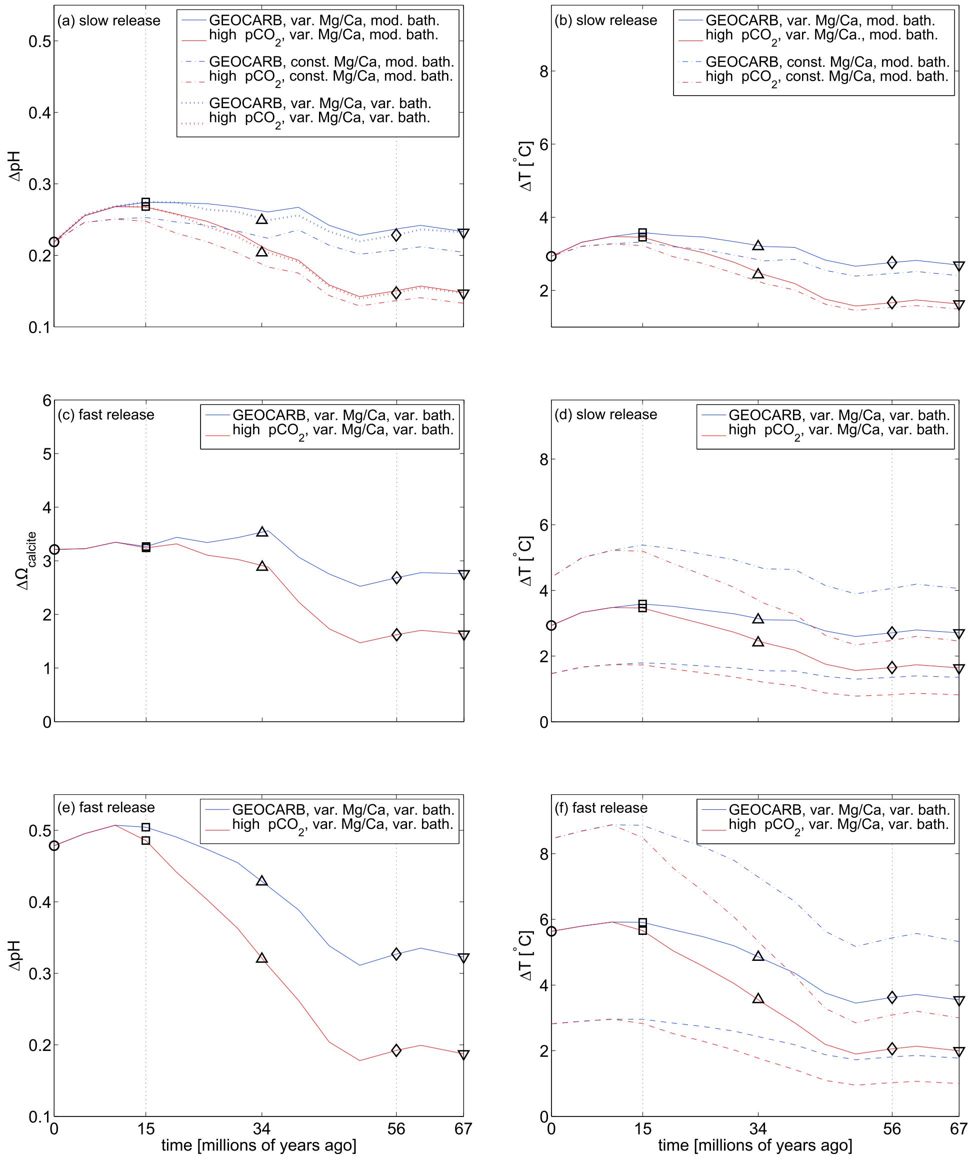

Figure 3. Sensitivity of ΔpH and ΔT to the carbon perturbation throughout the Cenozoic. Blue lines, GEOCARB $p\mathrm{CO}_2$; and red lines, high $p\mathrm{CO}_2$ scenario. Symbols are used to mark the same time slices as in Figure 2. Vertical dotted lines represent published bathymetry reconstructions. (a) ΔpH response over time. (b) ΔT response over time (T_{x2} = 3.0°C). (c) $\Delta\Omega_{\mathrm{calcite}}$ response over time. (d, f) ΔT response over time for different equilibrium climate sensitivities: T_{x2} = 1.5°C (dashed lines), T_{x2} = 3.0°C (solid lines) and T_{x2} = 4.5°C (dash-dotted lines). (e) ΔpH response over time.

scenario with varying Mg/Ca, while it is ~0.20 units for the slow rate GEOCARB $p\mathrm{CO}_2$ scenario with constant Mg/Ca ratio (Figure 3a, modern bathymetry). The effect of the Mg/Ca ratio on ΔT is similar (Figure 3b). In contrast, the effect of bathymetry and ocean circulation is very small (Figure 3a). The response of $\Delta\Omega_{\mathrm{calcite}}$ (Figure 3c) is qualitatively similar to the response of ΔpH (Figure 3e) when comparing the modern ocean and the early Cenozoic. However, we observe little variation of $\Delta\Omega_{\mathrm{calcite}}$ over the last 34 Ma.

4. Discussions and Conclusions

[12] We find a small increase of ΔpH and ΔT at the Middle Miocene compared to modern conditions (Figures 3a–3f). However, the response of $\Delta\Omega_{\mathrm{calcite}}$ shows little change. The Middle Miocene was ~5°C warmer, had a considerably lower seawater Mg/Ca ratio (~3.4) and the basin averaged CCD was ~600 m shallower than during modern times. These changes result in an increase of the sensitivity to the carbon release. In contrast, the increase in steady state $p\mathrm{CO}_2$ is small compared to modern times (~14 μatm) and hence not able to compensate for the antagonistic (sensitivity increasing) effect of the other parameters. Note that the difference in ΔpH and ΔT between modern times and the Middle Miocene might have been slightly smaller, considering uncertainties in the Mg/Ca proxy data (Figures 3a and 3b) (see discussion by *Tyrrell and Zeebe* [2004]). Further, note that if future research reveals $p\mathrm{CO}_2$ values much higher than ~300 μatm for the Middle Miocene, it is possible that the modern response and the response during the Middle Miocene of ΔpH and ΔT also turn out to be similar.

[13] In general, we find a long-term increasing trend in the sensitivity of the response variables to carbon perturbations from the early Cenozoic to modern times. Assuming a fast release rate similar to the present anthropogenic perturbation, we observe a significantly lower response during the early Cenozoic compared to modern conditions, for both the GEOCARB and the high $p\mathrm{CO}_2$ scenarios (Figures 3e and 3f). Assuming a slow release rate (Figures 3a and 3d), only the high $p\mathrm{CO}_2$ scenario results in significantly different responses during the early Cenozoic. This is explained by the effect of the ocean's DIC on the sensitivity at different release rates (high DIC during early Cenozoic vs. low in the modern ocean). Slow negative feedback mechanisms such as sediment calcium carbonate dissolution and increased weathering are only effective in the slow release scenario. In contrast, in the fast release scenario, mostly seawater carbonate buffering dominates, making the response highly dependent on the system's DIC.

[14] The low sensitivity to carbon perturbations during the Late Paleocene and the Late Maastrichtian is caused by profoundly different environmental conditions. The temperature proxy data indicate a 7–9°C warmer average basin temperature, an average CCD position of 3500 m and a Mg/Ca ratio of 1.6–1.7. Despite the strong effect of these parameters on the system's sensitivity, the high atmospheric CO_2 steady state concentrations at this time are able to overcompensate and cause a decrease in sensitivity compared to modern conditions. While there is no alkenone data available for times earlier than 44 Ma, the boron data [*Pearson and Palmer*, 2000] indicate very high $p\mathrm{CO}_2$ for the Late Paleocene. The large uncertainty of the $p\mathrm{CO}_2$ reconstructions translates into the broad range of possible responses to the carbon perturbation scenarios as shown. Nevertheless, the sensitivity response was most likely smaller during the Late Paleocene than in modern times, especially when considering release rates closer to the modern anthropogenic perturbation.

[15] The findings of the present study for the Late Paleocene are consistent with the results of *Zeebe et al.* [2009]. For the Late Paleocene, we find an increase of ΔT from 1.4–4.1°C for the GEOCARB $p\mathrm{CO}_2$ scenario and of 0.8–2.5°C for the high $p\mathrm{CO}_2$ scenario (Figure 3d).

[16] *Goodwin et al.* [2009] have also analyzed the effect of changes in ocean chemistry on the carbon-cycle response in carbon perturbation scenarios, using a different approach however (a biogeochemical box model by *Ridgwell* [2005] and the GENIE-1 Earth system model by *Ridgwell et al.* [2007]). The box model does not take $[\mathrm{Mg}^{2+}]$ and basin temperature changes into account and the GENIE-1 model assumes a modern climatology and continental configuration. A major advance of the present study is the quantitative investigation of these parameters, where the Mg/Ca ratio turned out to have a significant effect on the overall sensitivity.

[17] The main finding of *Goodwin et al.* [2009] is that the radiative forcing of the climate system is more sensitive to carbon perturbations now than it has been over much of the preceding 400 million years. This conclusion is consistent with our long-term results for the earlier part of the Cenozoic. However, we find that initial steady state $p\mathrm{CO}_2$, the Mg/Ca ratio, and the release rate are essential to determine the magnitude of global temperature change and surface ocean acidification. *Goodwin et al.* [2009] further concluded that the Paleocene-Eocene Thermal Maximum (PETM) provides a useful analogy for the present-day scenario, because the buffered carbonate inventory was similar to that of the pre-industrial ocean. Yet, we expect much more severe effects in the near future than during the PETM because of the likely higher anthropogenic release rate (even at the same total carbon input).

[18] Improvement of the Mg/Ca and $p\mathrm{CO}_2$ proxy data would be of great value because these parameters turned out to have a strong effect on the system's sensitivity to carbon perturbations. It would enable more precise reconstructions of ocean acidification and global temperature changes as a result of past carbon injections. A better understanding of the geologic past provides a useful framework to forecast the effects of our current carbon perturbation, especially regarding further feedback mechanisms that might enhance climate change.

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