



Examining possible effects of seawater pH decline on foraminiferal stable isotopes during the Paleocene-Eocene Thermal Maximum

Joji Uchikawa¹ and Richard E. Zeebe¹

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[1] A large body of paleoceanographic data for the Paleocene-Eocene Thermal Maximum (PETM) is based on foraminiferal stable carbon and oxygen isotope composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). However, the proxy records could be biased due to a “pH effect” on stable isotopes during times when the ocean became more acidic, as has been demonstrated for modern planktonic foraminifera. In this paper, we calculate the possible ranges of the pH effect on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the PETM based on the relative pH decline (ΔpH) from the preperturbation steady state simulated by a carbon cycle model and the empirical relationships obtained from culture experiments with planktonic foraminifera. The model is configured with Eocene paleogeography and simulates ΔpH for surface, intermediate, and deep water in the major ocean basins in response to various carbon input scenarios (2000 to 5000 Pg C). For an array of scenarios, the modeled ΔpH of the surface ocean ranges from 0.1 to 0.28 units. This suggests that $\delta^{13}\text{C}$ of planktonic foraminifera may be increased by up to 2.1‰ and $\delta^{18}\text{O}$ may be increased by up to 0.7‰ (corresponding to over 3°C error in paleotemperature estimate). Under conditions in which the model best simulates the global CaCO_3 dissolution pattern, we find marked differences in the deep-sea ΔpH between the Atlantic (−0.4) and Pacific oceans (−0.1). This would imply that the magnitude of the negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ excursions of benthic foraminifera in the Atlantic Ocean was dampened by up to 2.8‰ and 0.9‰ at maximum, respectively, relative to a constant pH scenario.

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1. Introduction

[2] A series of culture experiments with live planktonic foraminifera demonstrated that seawater $[\text{CO}_3^{2-}]$ and hence pH has a marked effect on foraminiferal stable carbon and oxygen isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) [Spero *et al.*, 1997; Bijma *et al.*, 1998, 1999]. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of foraminiferal shells become isotopically heavier as seawater pH decreases, which is referred to as the “pH effect” hereafter. This raises a concern that paleoceanographic information derived from foraminiferal stable isotopes can be significantly biased for past time windows during which seawater pH was notably different from the modern condition or varied rapidly. For example, Spero *et al.* [1997, 1999] and Lea *et al.* [1999] argued that the foraminiferal stable isotope records for the last glacial maximum are perhaps biased due to much different seawater carbonate chemistry. Similarly Zeebe [2001] suggested that sea surface temperatures of the mid-Cretaceous can be higher by 2°C to 3.5°C than previously thought if the pH effect on foraminiferal $\delta^{18}\text{O}$ is taken into consideration.

[3] Another time interval to consider regarding this issue is the Paleocene-Eocene Thermal Maximum (PETM) (~55 million years ago). This relatively short-lived yet

highly extraordinary climatic aberration is often considered as the closest paleoanalog for future climate changes associated with the anthropogenic carbon emissions [Bowen *et al.*, 2006; Pagani *et al.*, 2006a; Zachos *et al.*, 2008]. The PETM is marked by the prominent negative carbon isotope excursion (CIE) in contemporaneously deposited carbon-bearing phases [Kennett and Stott, 1991; Bains *et al.*, 1999; Zachos *et al.*, 2001; Thomas *et al.*, 2002]. This CIE indicates presumably massive and fairly rapid introduction of isotopically depleted carbon into the ocean-atmosphere system [Dickens, 2000; Dickens *et al.*, 1995, 1997]. Independent paleotemperature proxies ($\delta^{18}\text{O}$ and Mg/Ca ratios of foraminiferal calcite tests, and TEX_{86}) consistently suggest consequential global warming during the PETM [Bains *et al.*, 1999; Zachos *et al.*, 2003, 2006; Tripati and Elderfield, 2004; Shuijs *et al.*, 2006, 2007]. Concomitant paleontological indications such as poleward expansion of warm-water oceanic plankton as well as large-scale floral changes in the terrestrial realm are also consistent with the inferred global warming [Crouch *et al.*, 2001; Kelly, 2002; Wing *et al.*, 2005; Bowen *et al.*, 2006]. Furthermore, the massive carbon input at the onset of the PETM simultaneously caused a significant perturbation to the global carbon cycle as well as seawater carbonate chemistry. Widespread dissolution of sedimentary CaCO_3 across the Paleocene-Eocene boundary indicates notable shoaling of the CaCO_3 compensation depth, which in turn suggests ocean acidification [Zachos *et al.*, 2005; Zeebe and Zachos, 2007; Zeebe *et al.*, 2009]. Hence $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of preserved foraminiferal

¹Department of Oceanography, SOEST, University of Hawai‘i at Mānoa, Honolulu, Hawaii, USA.

shells from the PETM strata can potentially provide misleading paleoceanographic information. Although this issue has been previously acknowledged [Zachos *et al.*, 2003; Bowen *et al.*, 2004; Pagani *et al.*, 2006b], the possibility of the pH effect is commonly overlooked in the interpretation of the PETM foraminiferal stable isotope records [e.g., Tripathi and Elderfield, 2004].

[4] Assessing the magnitude of the pH effect on foraminiferal stable isotopes for the PETM is nontrivial because one needs to know the extent of ocean acidification in terms of the changes in seawater pH. Since proxy-based constraints of the seawater carbonate chemistry (i.e., the use of foraminiferal boron isotopes) for the PETM are still lacking, such attempts need to rely on modeling approaches. Carbon cycle models have become an important tool to predict the geochemical fate of carbon cycle perturbations and to evaluate the importance of feedback mechanisms [e.g., Archer *et al.*, 1998; Zeebe *et al.*, 2008; Uchikawa and Zeebe, 2008]. These models are also useful in studying the carbon cycle dynamics during the PETM if applied with reasonable boundary conditions [e.g., Zeebe *et al.*, 2009]. The exact value of the simulated results (such as absolute seawater pH values during the PETM) may be different from the actual values as they rely heavily on the assumed initial steady state, which is hitherto poorly characterized. Nevertheless, the simulated changes in the carbonate system relative to the initial steady state (such as the relative pH change from the pre-PETM level) in response to manipulated perturbations should provide valuable information.

[5] The remaining prerequisite to simulate the carbon cycle perturbations during the PETM is the mass of carbon release during the event. Dickens *et al.* [1995, 1997] suggested a total release of 1200 to 2500 Pg C (Pg = 10^{15} g) possibly from thermal dissociation of oceanic methane hydrates. Zachos *et al.* [2005] argued that the release of over 4500 Pg C is more consistent with paleotemperature records as well as stratigraphic evidence. Using an Earth system model, Panchuk *et al.* [2008] even suggested that the carbon release was larger than 6800 Pg C. In contrast, a recent model study by Zeebe *et al.* [2009] argued that an input of 3000 Pg C is most consistent with the global carbonate dissolution pattern (see below). Such apparent variations in the estimated amount are partially due to the fact that the ultimate source(s) and mechanism(s) of the carbon release are still debated [Dickens *et al.*, 1995, 1997; Kurtz *et al.*, 2003; Svensen *et al.*, 2004; Higgins and Schrag, 2006; Pagani *et al.*, 2006a; Storey *et al.*, 2007]. Since the mass of carbon release is a key variable to determine the extent of the carbon cycle perturbations, such inconsistency in the estimates results in significant uncertainties in simulating the relative changes in seawater pH during the PETM.

[6] In this study, we examine the potential magnitude of the pH effect on foraminiferal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the PETM. We used a carbon cycle model configured with early Eocene paleotopography to simulate relative changes in seawater pH during the PETM. In order to cover the uncertainty in the estimated amount of the carbon release during the event, we forced the model with a series of

carbon input scenarios ranging from a total input of 2000 Pg to 5000 Pg C. The model results (simulated relative seawater pH decline from the initial steady state) were then used to calculate the ranges of the correction for the pH effect on foraminiferal stable isotopes based on the empirical relationships obtained from the culture experiments with planktonic foraminifera by Spero *et al.* [1997].

2. Model Descriptions and Methods

[7] We assess the possible range of seawater pH changes during the PETM in response to an array of carbon input scenarios using the Long-term Ocean-Atmosphere-Sediment Carbon cycle Reservoir (LOSCAR) model [Uchikawa and Zeebe, 2008; Zeebe *et al.*, 2008, 2009]. The LOSCAR model is a carbon cycle reservoir model (modified from Walker and Kasting [1992]) coupled to a sediment module [Zeebe and Zachos, 2007]. The model includes biogeochemical cycles of ΣCO_2 , total alkalinity, phosphate, oxygen and $\delta^{13}\text{C}$. Weathering of continental carbonate and silicate rocks, which is particularly important for the carbon cycling on millennial timescales and beyond [Uchikawa and Zeebe, 2008], is parameterized as a function of atmospheric CO_2 . Parameters of the ocean carbonate chemistry such as $[\text{CO}_3^{2-}]$, pH and CaCO_3 saturation state are calculated from total CO_2 and total alkalinity using the algorithms of Zeebe and Wolf-Gladrow [2001]. For this study, model runs were performed with a configuration of Eocene topography based on a $2^\circ \times 2^\circ$ paleogeography reconstruction by Bice and Marotzke [2002]. The ocean reservoirs consisting of the Atlantic, Indian, Pacific and Tethys oceans are subdivided into surface (0–100 m depth), intermediate (100–900 m depth) and deep ocean (below 900 m) components. For the pre-PETM initial steady state, an atmospheric CO_2 level of 1000 ppmv was assumed. Steady state seawater pH values were constrained from the prescribed atmospheric CO_2 level and CaCO_3 compensation depths in major ocean basins inferred from stratigraphic evidence [see Zeebe *et al.*, 2009]. The average surface seawater pH value at the initial steady state was about 7.6, whereas the typical pH values for the intermediate and deep ocean boxes of the Atlantic and Pacific were in the vicinity of 7.2.

[8] The specific tunings of the LOSCAR model for PETM simulations were essentially kept the same as the settings used by Zeebe *et al.* [2009]. To simulate the notable differences in the shoaling of the Atlantic and Pacific CaCO_3 compensation depth [e.g., Colosimo *et al.*, 2005; Zachos *et al.*, 2005; Zeebe and Zachos, 2007], the formation of North Pacific Deep Water was turned on (in addition to Southern Ocean deep water sources) during the PETM [Bice and Marotzke, 2002]. Furthermore, in the simulations presented by Zeebe *et al.* [2009], 60% of the carbon input was added to the atmosphere, whereas the remaining 40% was directly introduced into the deep Atlantic Ocean. Since this assumption appears to be broadly consistent with lithological and chemical interpretations [Katz *et al.*, 1999; Dickens, 2000], we adopted this setting for most of the simulations presented in this paper. However, we also conducted additional simulations by changing the fraction of the partial

carbon injection into the deep Atlantic Ocean from 0% to 50% in order to determine if our final estimates are influenced by this parameterization.

[9] In order to reproduce the reconstructed duration of the CIE (roughly 70 kyr) during the main phase of the PETM, the carbon input ($\delta^{13}\text{C} = -50\text{‰}$) is separated into an initial injection at the onset of the PETM and an additional continuous source of 1480 Pg C. In this study, the amount and duration of the initial carbon injection was manipulated to investigate the carbon cycle perturbations in response to different estimates for the carbon release during the PETM. The amount of carbon input was varied from 2000 to 5000 Pg C in increments of 500 Pg C. The magnitude of the carbon cycle perturbation such as the decrease in seawater pH depends also on the duration of carbon release, which is referred to as the release time [Uchikawa and Zeebe, 2008; Zeebe et al., 2008]. A detailed chronology of the PETM stable isotope records by Röhl et al. [2000] suggests that the carbon released over a 20 kyr period at the beginning of the PETM. However, most of the release occurred as two short pulses (each lasted less than 1 kyr). In the model simulations by Dickens et al. [1997] and Dickens [2000], carbon was released over 10 kyr. In this study, the release time of the initial injection was varied from 0.5 to 10 kyr. The model was run for the duration of 200 kyr. Temperatures of all ocean boxes were evenly increased by 4°C for the first 70 kyr of the simulation (duration of the CIE). But this warming poses an insignificant control on the seawater carbonate chemistry. When the simulations with and without this temperature forcing are compared, the differences in the simulated seawater pH are less than 0.03 units.

3. The pH Effect on Foraminiferal Stable Isotopes

[10] Culture experiments by Spero et al. [1997] demonstrated that decreasing $[\text{CO}_3^{2-}]$ caused an increase in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of planktonic foraminifera *Orbulina universa* and *Globigerina bulloides*. In successive culture experiments, two other planktonic species, *Globigerinoides ruber* and *Globigerinoides sacculifer*, were found to have a similar response to changing seawater carbonate chemistry [Bijma et al., 1998, 1999; Spero et al., 1999]. Furthermore, the findings from several field studies seem to support the influence of seawater carbonate chemistry on shell stable isotopes of planktonic foraminifera *G. bulloides*, *G. ruber*, *Pulleniatina obliquiloculata*, *Neogloboquadrina pachyderma* and *Globorotalia inflata* under in situ conditions [Russell and Spero, 2000; Peeters et al., 2002; Bauch et al., 2002; Wilke et al., 2006]. Naturally, $[\text{CO}_3^{2-}]$ and pH covary in seawater. Thus it is difficult to unequivocally conclude whether $[\text{CO}_3^{2-}]$ or pH is the controlling variable for the foraminiferal stable isotopes. From a thermodynamic perspective, however, pH appears to be the controlling variable because what ultimately determines the relative abundance of the dissolved inorganic carbon (DIC) species is pH, and not $[\text{CO}_3^{2-}]$ itself. In a series of culture experiments by Bijma et al. [1999] in which $[\text{CO}_3^{2-}]$ was varied over a wide range (from 100 to 800 $\mu\text{mol/kg}$) while pH was held constant, $\delta^{18}\text{O}$ of

O. universa remained virtually unaffected. This experimental evidence is also consistent with the notion that pH is the ultimate controlling variable.

[11] The pH effect on $\delta^{18}\text{O}$ appears to be thermodynamically controlled. Zeebe [1999] suggested that the increase in foraminiferal $\delta^{18}\text{O}$ in response to pH decline reflects the rise in the overall $\delta^{18}\text{O}$ fractionation between H_2O and the sum of the DIC as the $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ ratio becomes larger (Figure 1). This is due to the fact that HCO_3^- ions are more enriched in ^{18}O relative to CO_3^{2-} ions because of the thermodynamic isotope effects, if the system is in isotopic equilibrium. Therefore one may compute the correction for foraminiferal $\delta^{18}\text{O}$ in response to a given pH change based on theoretical calculations [e.g., Zeebe, 2001, 2007]. In this paper, however, we instead rely on the empirical $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ (and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$) relationships obtained from culture experiments for several reasons.

[12] First, the aforementioned thermodynamic theory by Zeebe [1999] cannot simultaneously provide an explanation for the pH effect on foraminiferal $\delta^{13}\text{C}$. Presumably alteration of the carbonate chemistry within the microenvironment near calcification sites as well as vital effects and some additional kinetic isotope effects play an important role for the coupling between pH and $\delta^{13}\text{C}$ [Zeebe, 1999; Zeebe et al., 1999]. Second, the observation of the pH effect based on culture experiments has been limited to the pH range between roughly 7.7 and 8.9 [Spero et al., 1997; Bijma et al., 1998, 1999]. Therefore, it is still unknown if the pH effect in fact follows the trajectory predicted by the thermodynamic theory below pH 7 (comparable to the PETM condition), where large changes in $\delta^{18}\text{O}$ of the sum of the DIC per unit pH is expected (Figure 1). Thus, if the responses by foraminifera below pH 7 agree with the thermodynamic calculations, our assumption can potentially underestimate the magnitude of the pH effect on $\delta^{18}\text{O}$. And lastly, as mentioned above, modeled absolute pH values depend largely on the assumed initial steady state prior to the PETM. However, what is more relevant from our model simulations is “ ΔpH ,” the relative change in seawater pH from the initial steady state value. Accordingly the most practical approach to apply corrections for the pH effect on foraminiferal stable isotopes from the PETM strata is to apply the empirical $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ relationships obtained from culture experiments.

[13] In Figure 2, data from the culture experiments with planktonic foraminifera *O. universa* and *G. bulloides* by Spero et al. [1997] are compiled. Although these two are both planktonic species, *O. universa* hosts algal symbionts while *G. bulloides* does not. Therefore, *O. universa* might be a good representative species for surface planktonic foraminifera, whereas *G. bulloides* might be particularly relevant to thermocline dwellers as well as benthic species. Since the pH range covered in the culture experiments was relatively limited, these data are fitted with linear regression in order to obtain the $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ relationships. The slopes of the linear regressions ($\Delta\delta^{18}\text{O}/\Delta\text{pH}$ and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$) as well as r^2 values are summarized in Table 1. The values for $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ can then be used to calculate the potential bias

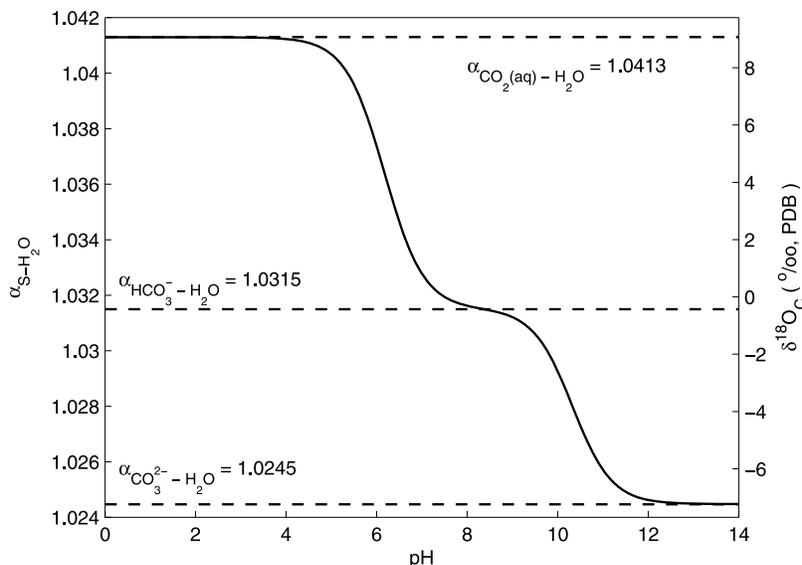


Figure 1. Overall oxygen isotope fractionation between the sum of the dissolved inorganic carbon (DIC) species and water (α_{S-H_2O} , left axis) and oxygen isotope composition of the sum of the DIC species ($\delta^{18}O_S$, right axis) as a function of pH. The α_{S-H_2O} values are calculated based on the mathematical routine by Zeebe [2007]. The $\delta^{18}O_S$ values are calculated for $\delta^{18}O$ of “ice-free” seawater (-1‰ on the SMOW scale [Shackleton and Kennett, 1975]) and reported on the PDB scale.

due to the pH effect on foraminiferal $\delta^{18}O$ and $\delta^{13}C$ values in response to modeled ΔpH during the PETM.

[14] It is important to note that, regardless of the difference in physiology (i.e., symbiont-bearing versus symbiont-barren species) and/or culturing protocols such as temperature and light levels, all of the foraminiferal species cultured so far produced calcite shells that are enriched in ^{18}O and ^{13}C at lower pH levels. The pH effect has not been definitively demonstrated for benthic foraminifera at this point. Yet the findings from core top studies [Bemis *et al.*, 1998; Schmiedl *et al.*, 2004; Mackensen, 2008; Rathmann and Kuhnert, 2008] and culture experiments [Wilson-Finelli *et al.*, 1998; McCorkle *et al.*, 2008] seem to imply that the pH effect in response to large downcore pH gradient (and hence $[CO_3^{2-}]$ gradient) of sediment pore waters may, at least to some extent, explain the offset in stable isotopes of epifaunal and infaunal taxa. Furthermore, a core top study by Rathmann and Kuhnert [2008] provides $\Delta\delta^{18}O/\Delta pH$ and $\Delta\delta^{13}C/\Delta pH$ relationship of $-0.65\text{‰}/pH$ ($r^2 = 0.69$, $n = 6$) and $-1.3\text{‰}/pH$ ($r^2 = 0.39$, $n = 6$) for infaunal species *Oridorsalis umbonatus* (although these empirical relationships are somewhat inconclusive as no direct measurements were made for the pore water $\delta^{18}O$ and $\delta^{13}C_{DIC}$). These lines of evidence suggest that the pH effect may be a universal phenomenon, and thus may apply to ancient planktonic and benthic foraminifera as well.

4. Results

4.1. Results of Model Simulations

[15] Introduction of a few thousand Pg of carbon into the ocean-atmosphere system results in a prolonged period of ocean acidification (Figures 3a–3c). Consequently foraminiferal stable isotopes during the PETM were potentially biased

toward heavier values due to the pH effect (Figures 3d and 3e). Simulated surface seawater pH values (0–100 m) were generally uniform in every major ocean basin (Atlantic, Pacific, Indian and Tethys) due to the equilibration with atmospheric CO_2 . In contrast, the pH decline in the intermediate (100–900 m) and deep ocean boxes (below 900 m) was much greater in the Atlantic than in the Pacific (Figures 3b and 3c).

[16] Observed regional differences in the extent of the subsurface ocean acidification are consistent with stratigraphic records [see Zeebe *et al.*, 2009] as well as modeling evidence [Zeebe and Zachos, 2007]. We conducted independent simulations in which the extent of the partial carbon injection into the deep Atlantic Ocean was varied from 0% to 50% (Figure 4). The results from this experiment demonstrate that the pH decline in the intermediate and deep Atlantic Ocean depends on the fraction of the carbon input that is directly introduced into the deep Atlantic Ocean, as also noted by Dickens [2000]. But it is also apparent that the pH decline in the intermediate and deep Atlantic Ocean is more severe than in the Pacific even without any partial injection. This is caused by ocean circulation changes due to additional formation of North Pacific Deep Water during the PETM in the model simulations [see Bice and Marotzke, 2002; Zeebe and Zachos, 2007]. The results also demonstrate that only the pH in the deep Atlantic Ocean was significantly affected by the assumed fraction of the partial carbon injection. Simulated seawater pH for the intermediate Atlantic Ocean shows a similar but much smaller response to the partial injection. On the contrary, seawater pH for the surface ocean and the subsurface Pacific Ocean were generally insensitive to this parameter. Thus the possible bias in our estimates of the pH effect on foraminiferal

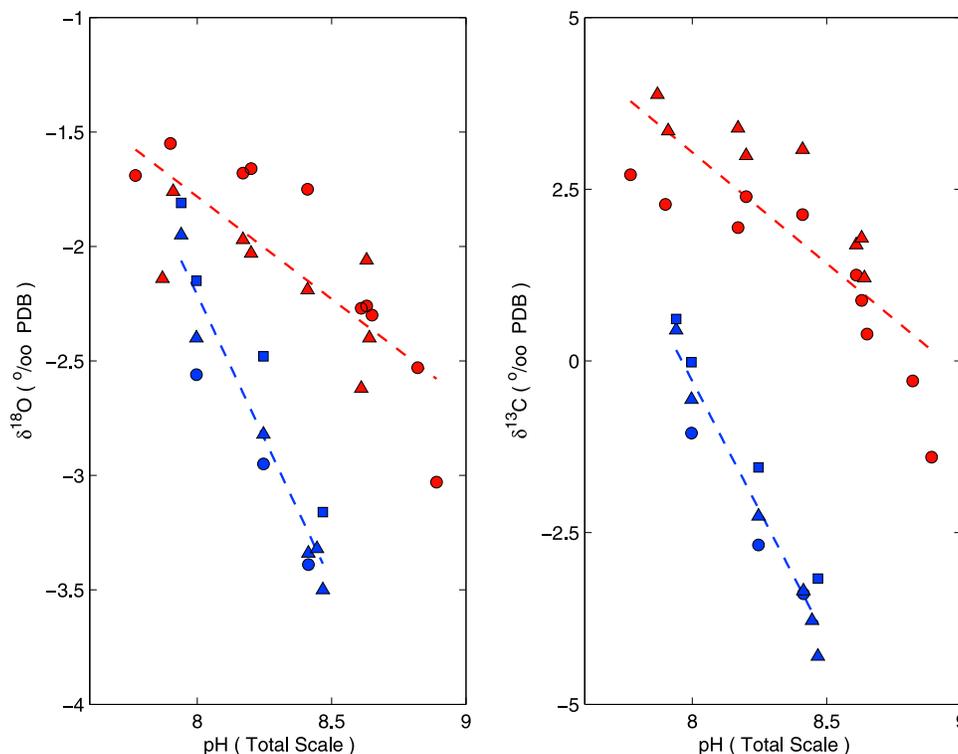


Figure 2. Effect of seawater pH on planktonic foraminiferal (left) $\delta^{18}\text{O}$ and (right) $\delta^{13}\text{C}$ from the culture experiments by Spero *et al.* [1997]. The experimental results from *Orbulina universa* are plotted as solid red symbols (triangles, low light experiments; circles, high light experiments). Solid blue symbols represent the results from *Globigerina bulloides* (squares, thirteenth chamber; triangles, twelfth chamber; circles, eleventh chamber). The results shown here are from the experiments in which the pH and alkalinity of the culturing medium were varied under constant total CO_2 . Dashed lines indicate linear regressions for the data sets. The slopes ($\Delta\delta^{18}\text{O}/\Delta\text{pH}$ and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$) and r^2 values of the linear regressions are summarized in Table 1.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ due to the assumed partial carbon injection should be limited to the intermediate and deep Atlantic Ocean.

[17] Figure 5a shows the maximum ΔpH of the average surface ocean as a function of the carbon input and release time. For every carbon input scenario tested in this study, the maximum ΔpH always occurred as a direct consequence of the initial carbon injection and not of the subsequent additional carbon source (see Figures 3a–3c). The maximum ΔpH of the averaged surface ocean ranged from -0.1 to -0.3 . In the Pacific Ocean, the maximum ΔpH in the intermediate and deep ocean boxes generally ranged from -0.1 to -0.2 units (Figures S1 and S2).¹ For the intermediate and deep Atlantic Ocean, the maximum ΔpH ranged from -0.2 to -0.5 and from -0.3 to -0.8 units, respectively (Figures S3 and S4).

[18] We note that the LOSCAR model best simulates the global CaCO_3 dissolution pattern during the PETM when the model is forced with 3000 Pg of the initial carbon injection released over 5 kyr with applied boundary conditions and assumed initial steady state described above

¹Auxiliary materials are available in the HTML. doi:10.1029/2009PA001864.

[Zeebe *et al.*, 2009]. In other words, a greater carbon input would cause more intense CaCO_3 dissolution than the stratigraphic records imply. Therefore we consider the magnitudes of the pH effect computed from the simulated ΔpH values under this specific carbon input scenario as our best estimates. The results of model simulations with this specific carbon input scenario are indicated by white pentagrams in Figure 5. Corresponding maximum ΔpH values of the average surface ocean as well as subsurface ΔpH values in the Atlantic and Pacific oceans are summarized in Table 2.

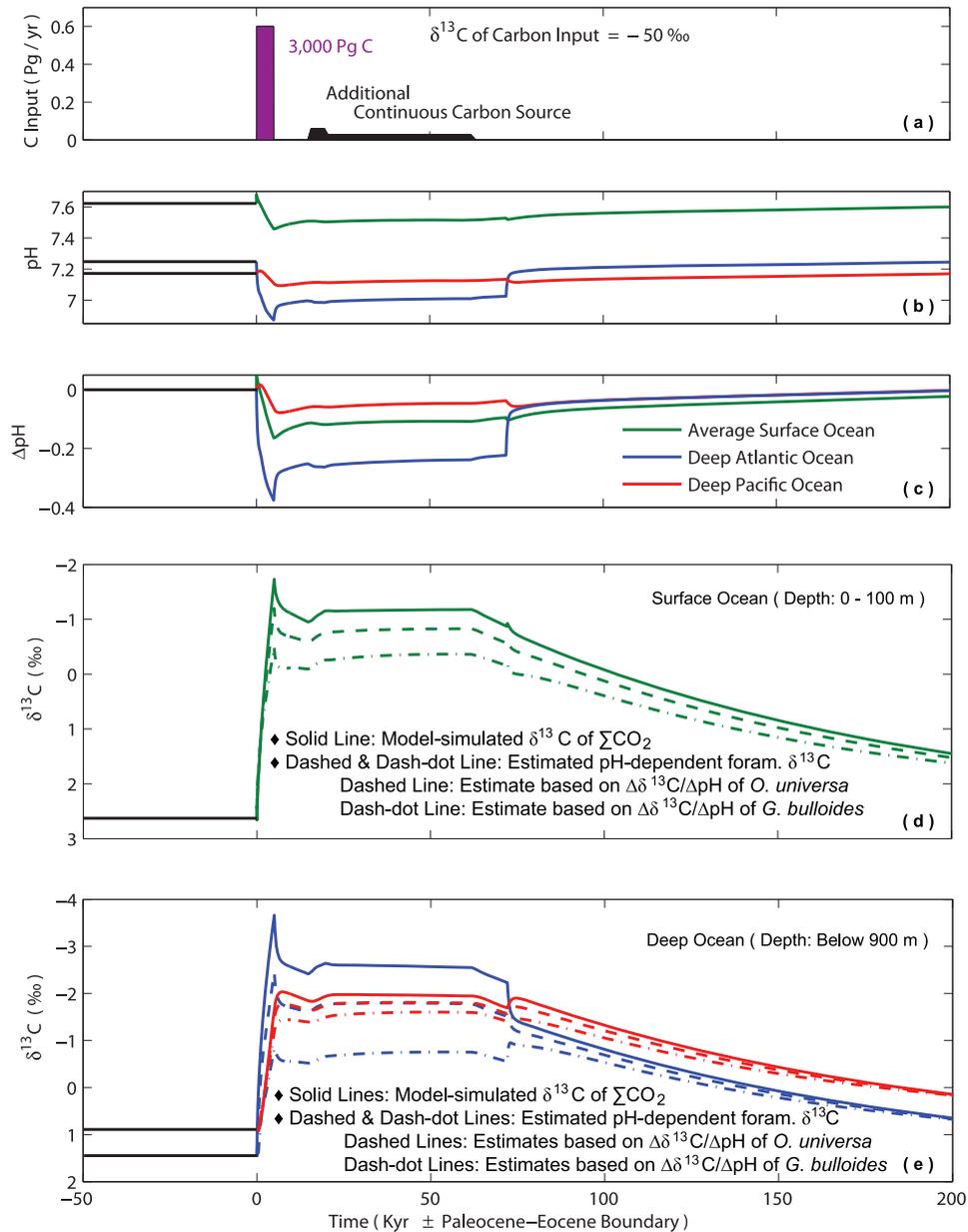
4.2. The pH Correction for Foraminiferal Stable Isotopes

[19] The empirical relationships obtained from cultured *G. bulloides* provide more extreme estimates for the magnitude of the pH effect because of comparatively larger $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ and $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ values for the species (Figure 2 and Table 1). On the contrary the estimates based on *O. universa* are more conservative.

[20] Based on the simulated ΔpH values of the average surface ocean as well as the $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ of *G. bulloides*, our estimates suggest that $\delta^{13}\text{C}$ of planktonic foraminifera

Table 1. The $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ and $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ Relationships of *O. universa* and *G. bulloides* Determined From the Experimental Results by Spero *et al.* [1997]

Species	Algal Symbionts	Major Distribution	$\Delta\delta^{18}\text{O}/\Delta\text{pH}$ (‰/pH unit)	$\Delta\delta^{18}\text{O}/\Delta\text{pH}$ r^2	$\Delta\delta^{13}\text{C}/\Delta\text{pH}$ (‰/pH unit)	$\Delta\delta^{13}\text{C}/\Delta\text{pH}$ r^2
<i>O. universa</i>	Present	Subtropical	-0.89	0.63	-3.24	0.68
<i>G. bulloides</i>	Absent	Subpolar	-2.51	0.88	-7.54	0.93

**Figure 3.** Results of the LOSCAR model simulation under 3000 Pg of carbon input released over 5 kyr. (a) Carbon input scenario. The $\delta^{13}\text{C}$ signature of the carbon input is -50‰ . (b) Simulated changes in seawater pH. (c) ΔpH , the relative pH decline from the pre-PETM initial steady state pH values. (d and e) Simulated $\delta^{13}\text{C}$ of the total dissolved CO_2 (solid lines) and calculated pH-dependent $\delta^{13}\text{C}$ that should be recorded by foraminifera (dashed and dash-dotted lines) for the average surface ocean (Figure 3d) and for the deep Atlantic and Pacific oceans (Figure 3e). Foraminiferal $\delta^{13}\text{C}$ are estimated based on the simulated $\delta^{13}\text{C}$ of the total dissolved CO_2 and the $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ values derived from cultured *O. universa* (dashed lines) and *G. bulloides* (dash-dotted lines). Time equals 0 shown here corresponds to the onset of the PETM.

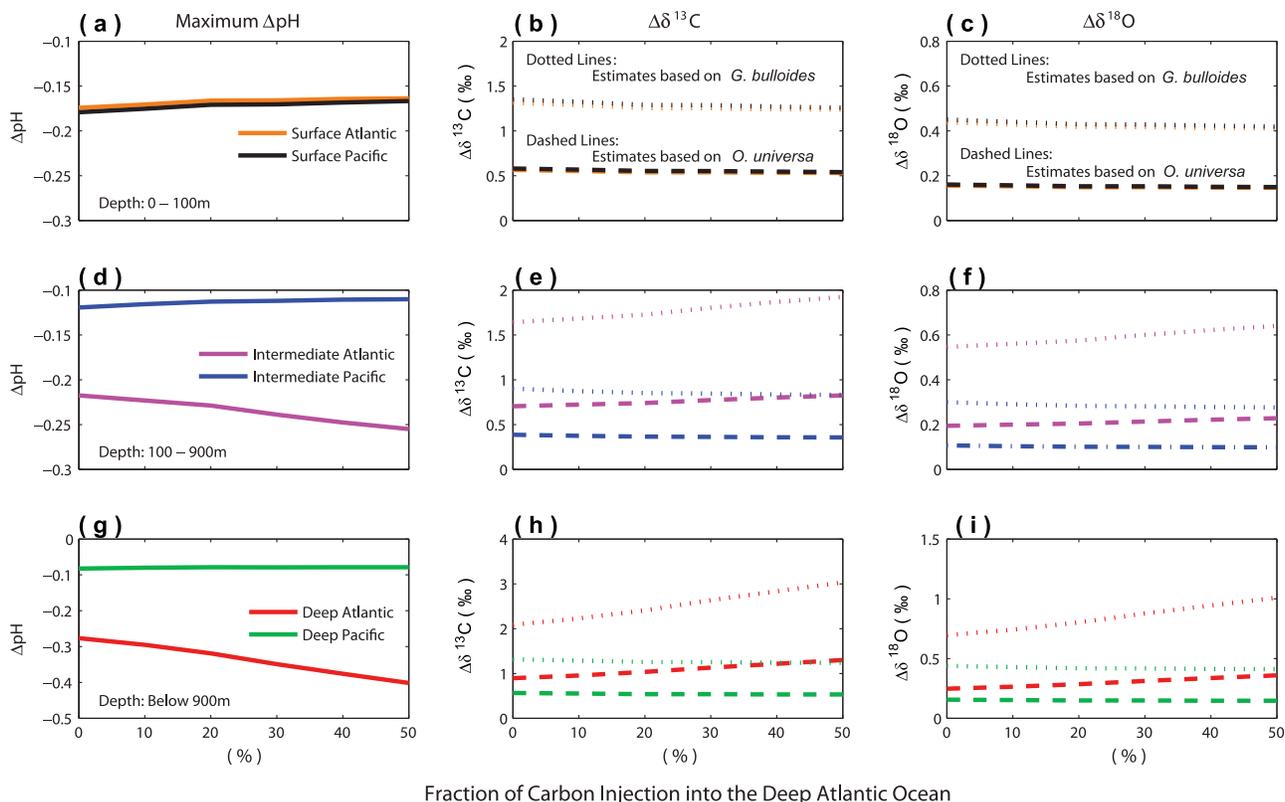


Figure 4. (a–i) Model response to the partial carbon injection into the deep Atlantic Ocean. For these simulations, total carbon input is 3000 Pg with release time of 5 kyr ($\delta^{13}\text{C} = -50\text{‰}$). The estimates for the potential magnitude of the pH effect on foraminiferal $\delta^{13}\text{C}$ (Figures 4b, 4e, and 4h) and $\delta^{18}\text{O}$ (Figures 4c, 4f, and 4i) are based on simulated maximum ΔpH (Figures 4a, 4d, and 4g) and the data from culture experiments (Table 1).

might have been increased by up to 2.1‰ due to the pH effect during the PETM (Figure 5c).

[21] Even with more conservative $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ of *O. universa*, the potential pH bias on foraminiferal $\delta^{13}\text{C}$ is still on the order of 0.9‰ at maximum (Figure 5b). Similarly, based on the $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ of *G. bulloides*, it is estimated that $\delta^{18}\text{O}$ of planktonic foraminifera during the PETM might have been increased by up to 0.7‰ (Figure 5e). If such pH bias is not corrected for, this leads to an underestimation in sea surface temperature (SST) reconstructions by as much as 3.4°C (Figure 5g). More conservative *O. universa*-based estimates suggest potential increase in $\delta^{18}\text{O}$ by up to 0.3‰. Accordingly, SST reconstructions will be 1.2°C too low (Figures 5d and 5e).

[22] The model results with the input of 3000 Pg C released over 5 kyr seems to provide the most probable estimates for the magnitude of the pH effect (see above). These estimates are summarized in Table 2. For the average surface ocean, the most probable estimates for the pH effect on $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ range from 0.5‰ to 1.2‰ and from 0.2‰ to 0.4‰, respectively. As a result, SST reconstruction would be erroneously too low by up to 2°C. For subsurface foraminiferal species, our model results suggest notable regional differences in the extent of the pH effect

between the Atlantic and Pacific oceans due to apparent ΔpH gradient. At intermediate depths, estimated magnitudes of the pH effect on $\delta^{13}\text{C}$ range from 0.4‰ to 0.8‰ in the Pacific and from 0.8‰ to 1.9‰ in the Atlantic Ocean. The probable ranges of the pH effect on $\delta^{18}\text{O}$ are 0.1‰ to 0.2‰ in the Pacific and 0.2‰ up to 0.6‰ in the Atlantic Ocean at intermediate depths. Such regional differences are even greater for the deep Atlantic and Pacific oceans. The estimated extent of the pH effect on $\delta^{13}\text{C}$ is as large as 1.2‰ to 2.8‰ in the deep Atlantic but less than 0.6‰ in the deep Pacific Ocean. The magnitude of the pH effect on $\delta^{18}\text{O}$ is expected to range from 0.3‰ to 0.9‰ in the deep Atlantic. On the contrary, the estimated pH bias in the deep Pacific Ocean is less than 0.2‰.

5. Discussion

5.1. Evidence for the pH Effect in Existing Foraminiferal Records?

5.1.1. Magnitude of the CIE

[23] We have demonstrated that foraminiferal $\delta^{13}\text{C}$ may have been increased due to the pH effect during the PETM. But is there evidence of the pH bias in the actual forami-

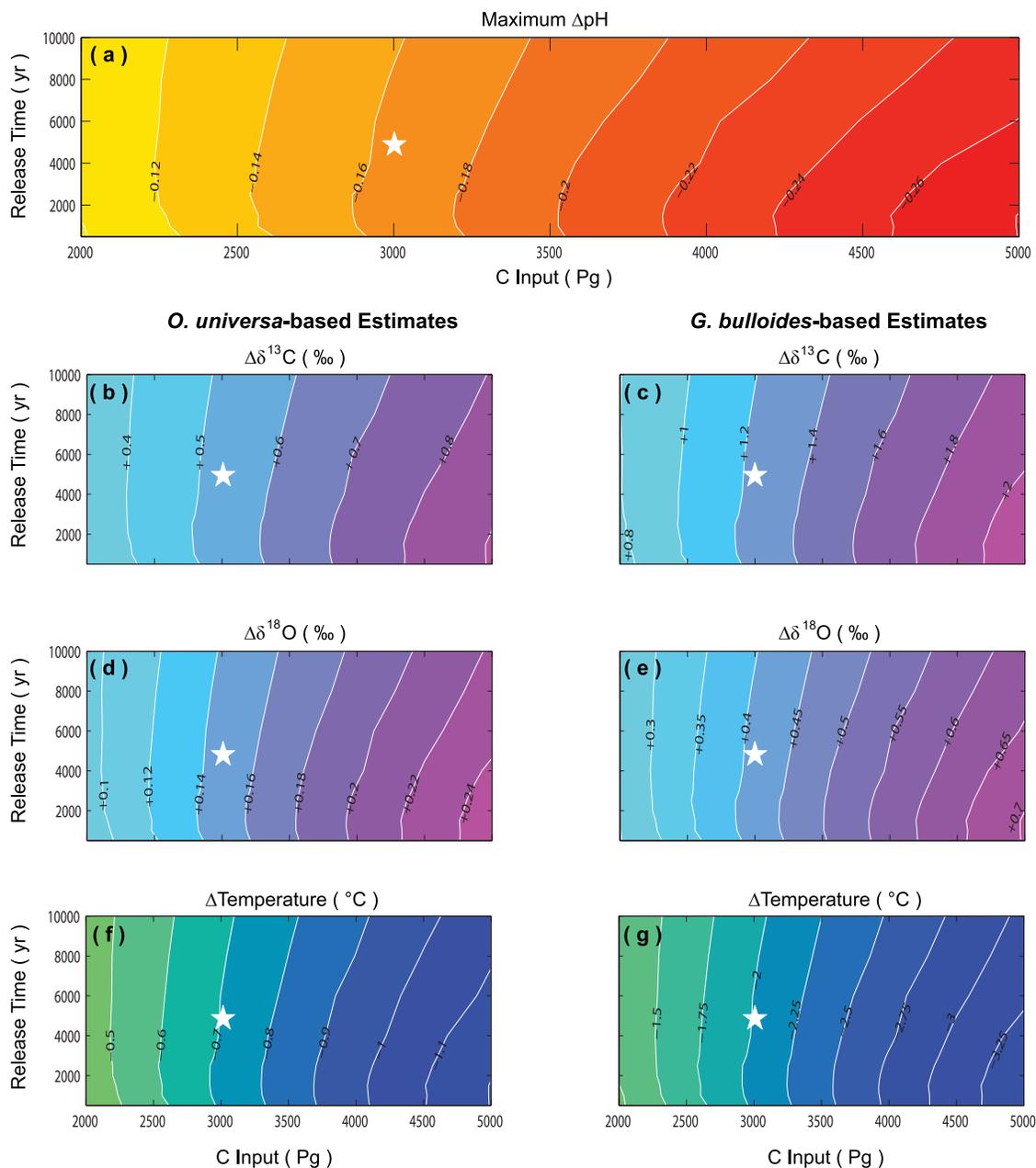


Figure 5. (a) Simulated maximum ΔpH and estimated magnitude of the pH biases on foraminiferal stable isotopes ((b and c) $\delta^{13}\text{C}$ and (d and e) $\delta^{18}\text{O}$) and (f and g) on reconstructed seawater temperatures as a function of the carbon input and release time for the average surface ocean. See Bemis *et al.* [1998] for the paleotemperature calibrations for *O. universa* and *G. bulloides*. White pentagrams indicate the most probable estimates (see text).

niferal $\delta^{13}\text{C}$ records? Here, we compare our estimates for the pH effect with the $\delta^{13}\text{C}$ data from ODP Site 690 on Maud Rise in the Southern Ocean. Site 690 is favorable because this site provides high-resolution planktonic records and benthic records with well-resolved age model [Thomas *et al.*, 2002; Nunes and Norris, 2006; Röhl *et al.*, 2000, 2007]. Because the LOSCAR model does not resolve Southern Ocean features, we use the pH effect estimates for

the Atlantic Ocean. The following comparison should therefore be taken with caution because the Southern Ocean and Atlantic Ocean show different CaCO_3 dissolution characteristics during the PETM [see Zeebe *et al.*, 2009]. As shown in Figure 6, both thermocline-dwelling genus *Subbotina* and benthic *N. truempyi* recorded contracted CIE in comparison to symbiotic surface-dwelling genus *Acarinina*. This appears to be in agreement with our model simula-

Table 2. Most Probable Estimates for the Magnitude of the pH Effect on Foraminiferal Stable Isotopes and Paleotemperature Reconstructions^a

	Maximum Δ pH (pH units)	$\Delta\delta^{13}\text{C}_{O.univ.}$ ^b (‰)	$\Delta\delta^{18}\text{O}_{O.univ.}$ ^b (‰)	$\Delta T_{O.univ.}$ ^c (°C)	$\Delta\delta^{13}\text{C}_{G.bull.}$ ^d (‰)	$\Delta\delta^{18}\text{O}_{G.bull.}$ ^d (‰)	$\Delta T_{G.bull.}$ ^e (°C)
Average surface ocean	-0.16	0.53	0.15	-0.71	1.24	0.41	-2.02
Intermediate Pacific	-0.11	0.36	0.10	-0.48	0.84	0.28	-1.36
Intermediate Atlantic	-0.25	0.80	0.22	-1.06	1.87	0.62	-3.04
Deep Pacific	-0.08	0.25	0.07	-0.34	0.59	0.20	-0.97
Deep Atlantic	-0.38	1.22	0.34	-1.61	2.84	0.94	-4.62

^aThese estimates are based on simulated Δ pH values in response to 3000 Pg of carbon input released over 5 kyr (see text and Zeebe *et al.* [2009] for details).

^bCalculations are based on the $\Delta\delta^{13}\text{C}/\Delta$ pH and $\Delta\delta^{18}\text{O}/\Delta$ pH of *O. universa*.

^cCalculations are based on the $\Delta\delta^{13}\text{C}/\Delta$ pH and $\Delta\delta^{18}\text{O}/\Delta$ pH of *O. universa*. The $\delta^{18}\text{O}$ paleotemperature equations for *O. universa* are from Bemis *et al.* [1998].

^dCalculations are based on the $\Delta\delta^{13}\text{C}/\Delta$ pH and $\Delta\delta^{18}\text{O}/\Delta$ pH of *G. bulloides*.

^eCalculations are based on the $\Delta\delta^{13}\text{C}/\Delta$ pH and $\Delta\delta^{18}\text{O}/\Delta$ pH of *G. bulloides*. The $\delta^{18}\text{O}$ paleotemperature equations for *G. bulloides* are from Bemis *et al.* [1998].

tions, which demonstrate that the severity of the acidification (and hence the magnitude of the positive shift in foraminiferal $\delta^{13}\text{C}$ due to the pH effect) increases with depth in the Atlantic Ocean (Table 2). Indeed genus *Subbotina* and *N. truempyi* data generally align with the trajectories of the most probable estimates for foraminiferal $\delta^{13}\text{C}$ computed from simulated Δ pH in response to an input of 3000 Pg C and from the $\Delta\delta^{13}\text{C}/\Delta$ pH of symbiont-bearing *G. bulloides* (Figures 6c and 6d).

[24] Large negative $\delta^{13}\text{C}$ excursions across the PETM are evident in sedimentary organic carbon components. Do isotopes records from these noncarbonate records also suggest a pH effect on foraminiferal $\delta^{13}\text{C}$? For example, Bowen *et al.* [2004] and Pagani *et al.* [2006b] argued that the disparity between the magnitude of the CIE derived from foraminiferal and terrestrial records can be attributed to the pH effect. Pagani *et al.* [2006b] observed a CIE of -4.5% to -6% based on long-chain *n* alkanes derived from plant leaf waxes in the central Arctic Ocean. This is comparatively larger than the typical magnitude of the CIE derived from foraminifera (i.e., 3 to 4‰ or so for surface planktonic foraminifera). Pagani *et al.* [2006b] argued that the CIE derived from these biomarkers reflect the true $\delta^{13}\text{C}$ of the atmospheric CO_2 in equilibrium with the ocean and thus foraminifera did not record the full extent of the CIE because of the pH effect to some extent. Our detailed examinations show that the pH effect on $\delta^{13}\text{C}$ of planktonic foraminifera can potentially account for up to 1.2‰ (or up to little over 2‰ if the carbon input was as large as 5000 Pg; see Figure 5c) of the disparity between the terrestrial and foraminiferal CIE (see Table 2). But new findings from the same site by Schouten *et al.* [2007] argue against a major pH bias on existing foraminiferal $\delta^{13}\text{C}$ records for the PETM. They suggested that the isotopic fractionation associated with photosynthetic CO_2 fixation by angiosperms increased during the PETM due to some environmental factors while conifers maintained constant fractionation. And intriguingly, their angiosperm biomarker yielded a CIE of up to -6% , whereas the conifer biomarker produced CIE of roughly -3% , which is well comparable to the magnitude of the foraminiferal CIE. Based on these lines of

evidence, Schouten *et al.* [2007] argued that the leaf wax CIE of -4.5% up to -6% by Pagani *et al.* [2006b] may reflect amplification due to the mixed *n* alkane signal from conifers and angiosperms.

[25] In addition, in the New Jersey shelf region, relatively similar magnitudes of the CIE were observed for dinoflagellate cyst (-4% to -4.5% [Suijs *et al.*, 2007]; also see Schouten *et al.* [2007, Table 1]) and planktonic foraminifera (as large as -4.3% [Zachos *et al.*, 2006; John *et al.*, 2008]). Albeit limited to only one data point, planktonic foraminifera from shallow sediments, which now outcropped along the Tanzanian coastline, also recorded the CIE as large as -4.5% [Handley *et al.*, 2008]. However, it is very likely that these foraminiferal records from shallow sites are influenced by coastal processes such as enhanced weathering and input of ^{13}C -depleted terrestrial organic matter, particularly if the hydrological cycle was indeed intensified during the PETM [Bowen *et al.*, 2004; Pagani *et al.*, 2006b]. Therefore it is difficult to confirm or reject the major pH bias in existing foraminiferal $\delta^{13}\text{C}$ records at this point.

5.1.2. The $\delta^{18}\text{O}$ Paleothermometry

[26] Our estimates suggest that, assuming a carbon input of 3000 Pg at the onset of the PETM, $\delta^{18}\text{O}$ of surface dwelling planktonic foraminifera might have been increased by 0.2‰ to 0.4‰. This would lead to SST estimates that are too low by 0.4°C up to 2°C (Table 2). If the carbon input was as large as 5000 Pg, our calculations suggest over 3°C of underestimation in SST reconstruction (Figure 5g).

[27] Zachos *et al.* [2003] analyzed $\delta^{18}\text{O}$ and Mg/Ca ratios of planktonic genus *Morozovella* and *Acarinina* from ODP Site 1209 on Shatsky Rise in the Pacific Ocean to reconstruct SST across the Paleocene-Eocene boundary. Their records demonstrate that the peak SST warming relative to the pre-PETM baseline level based on Mg/Ca data was consistently larger by approximately 2.5°C than the $\delta^{18}\text{O}$ -based reconstructions. This discrepancy may indeed be explained by the increase in $\delta^{18}\text{O}$ due to the pH effect and consequentially underestimated SST. This possibility was also addressed by Zachos *et al.* [2003]. But they rather attributed this feature to the influence of local salinity changes on $\delta^{18}\text{O}$. Lastly, the disagreement between these paleo-SST

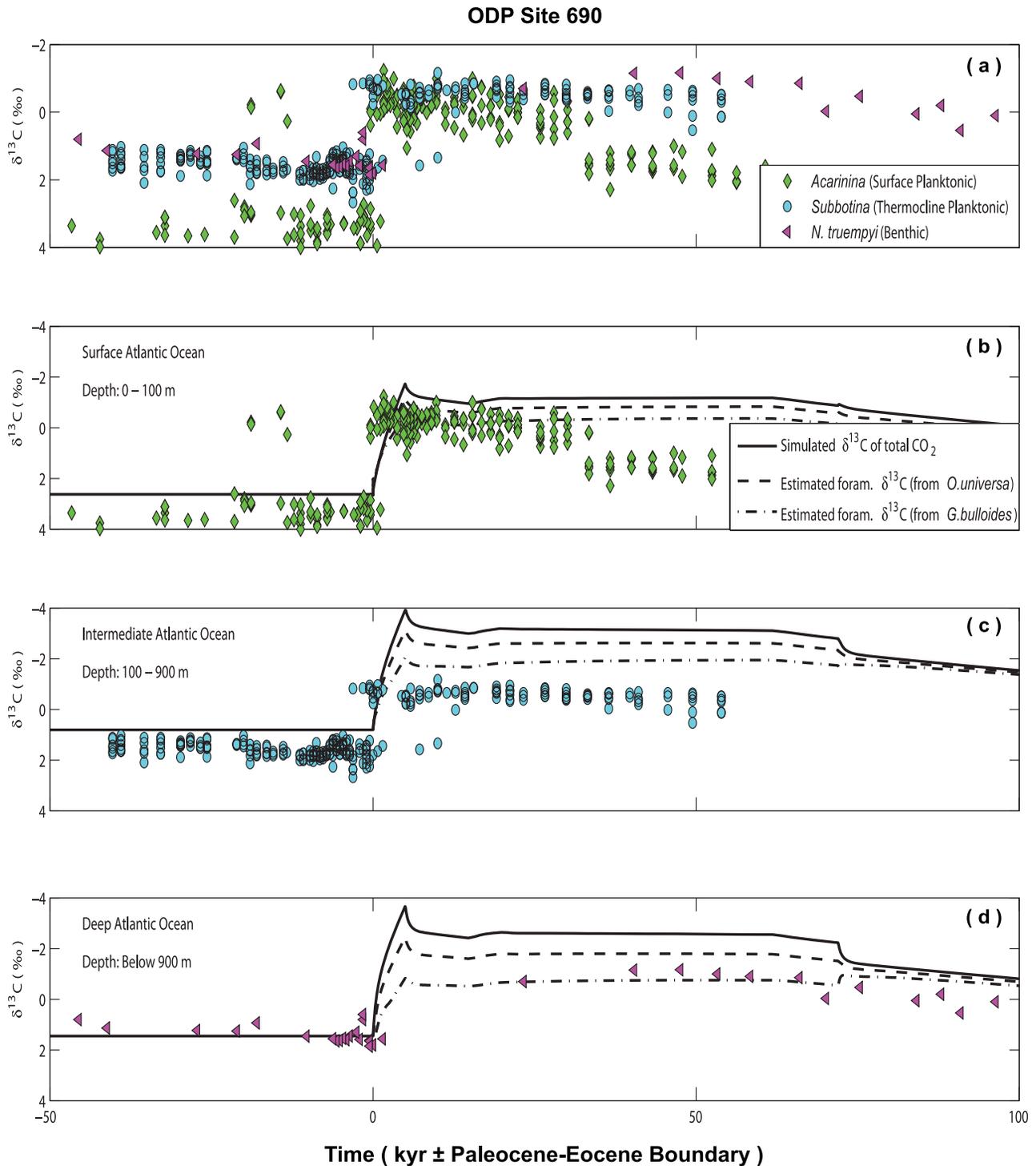


Figure 6. (a) Compilation of the foraminiferal $\delta^{13}\text{C}$ records from ODP Site 690 in the Southern Ocean and (b–d) comparison of the records with our model-based estimates for the expected foraminiferal $\delta^{13}\text{C}$ in three depth ranges. Genus *Acarinina* and *Subbotina* records are from Thomas *et al.* [2002], and *N. truempyi* record is from the compilation by Nunes and Norris [2006]. These data are plotted against the age scale based on the orbitally tuned chronology for Site 690 by Röhl *et al.* [2007]. In the original data, *Acarinina* “leads” *Subbotina* for the onset of the CIE (detailed discussion on this issue is in the work by Thomas *et al.* [2002] and is beyond the scope of this paper). Because the purpose of these plots is to simply compare the magnitude of the CIE, the *Acarinina* record was shifted so that the onset of the CIE aligns with the Paleocene-Eocene boundary (time equals 0) for a better visualization.

estimates may reflect the pH effect on Mg/Ca, instead of $\delta^{18}\text{O}$. Russell *et al.* [2004] found that, below pH of 8.2, Mg/Ca of cultured *O. universa* and *G. bulloides* increases by 7% and 16% per 0.1 unit decrease in pH. Given our simulated ΔpH of -0.16 for the average surface seawater (in response to 3000 Pg of carbon input; Table 2) and the “Mg/Ca temperature anomaly (ΔT) function” by Zachos *et al.* [2003], these experimental results suggest Mg/Ca-based temperature should be higher by 1.2°C (based on *O. universa*) to 2.5°C (based on *G. bulloides*) than $\delta^{18}\text{O}$ -based SST estimates.

[28] The data set of Zachos *et al.* [2006] from Wilson Lake (New Jersey shelf) allows comparison of high-resolution paleo-SST records derived from foraminiferal $\delta^{18}\text{O}$ and TEX_{86} . The peak PETM warming of 33°C inferred from TEX_{86} appears to be reasonably close to the $\delta^{18}\text{O}$ -derived SST estimates from genus *Morozovella* and *Acarinina*. These data may argue against major pH bias on foraminiferal $\delta^{18}\text{O}$. But it should be noted that the TEX_{86} -derived SST is subject to some biases due to the uncertainties in the calibrations. The modern core top calibrations have not been validated for temperatures above 29°C [Schouten *et al.*, 2002; Kim *et al.*, 2008]. Thus the reliability of the inferred warming of 33°C is still an open question. Furthermore, each calibration uses a distinctive approach in terms of the filtering (i.e., cold versus warm-water biased [e.g., Schouten *et al.*, 2002, 2003]) and fitting (i.e., linear versus reciprocal fitting [e.g., Kim *et al.*, 2008; Liu *et al.*, 2009]) of the core top data. As a result, the peak TEX_{86} value during the PETM reported by Zachos *et al.* [2006] can lead to more than 10°C difference in the inferred temperatures depending on the calibrations [Schouten *et al.*, 2002, 2003; Kim *et al.*, 2008; Liu *et al.*, 2009]. In fairness, Zachos *et al.* [2006] carefully evaluated this issue and used the warm-water ($20^\circ\text{C}\sim 29^\circ\text{C}$) calibration by Schouten *et al.* [2003], which provides more conservative estimates for temperatures above 25°C . The reciprocal calibration recently proposed by Liu *et al.* [2009] similarly yields conservative estimates for temperatures greater than 25°C . Nonetheless, with the peak TEX_{86} value of the Wilson Lake record, the error in the reconstructed paleotemperature caused by these two calibrations is still as large as 2°C . Therefore, it appears that comparing $\delta^{18}\text{O}$ and TEX_{86} -derived SST would not be a reliable approach to evaluate the possibility of the pH effect on foraminiferal $\delta^{18}\text{O}$ during the PETM.

[29] In summary, (1) foraminiferal $\delta^{18}\text{O}$ is a function of precipitation temperature as well as salinity changes, (2) the pH effect may simultaneously affect $\delta^{18}\text{O}$ and Mg/Ca of foraminifera, and (3) the application of TEX_{86} for the PETM is potentially biased due to calibration issues. For these reasons, it is difficult to unequivocally provide evidence for the pH effect in existing foraminiferal $\delta^{18}\text{O}$ records.

5.2. Implications

[30] At this stage, arguments can be presented against and in favor of a pH effect in existing foraminiferal stable isotope records during the PETM. But if in fact the latter was the case, our model-based estimates of the pH effect may be of significant interest.

[31] One of the most intriguing findings from this study is that there might be regional differences in the extent of the pH effect on benthic foraminifera. This may have important implications for our current understanding of the carbon dynamics during the PETM. Because the deep ocean represents the largest carbon reservoir of the ocean-atmosphere system, the magnitude of the CIE derived from benthic foraminifera served as a foundation to formulate the hypotheses for the mechanism(s) and the mass of the carbon release for the PETM [e.g., Dickens *et al.*, 1995]. But recent studies further suggest that the magnitude of the CIE recorded by the benthic species (that successfully survived the mass extinction event at the end of the Paleocene [Kennett and Stott, 1991]) may be underestimated because of the truncation due to severe dissolution [Zeebe and Zachos, 2007; McCarren *et al.*, 2008]. Besides the issue of truncation, we further argue that regional differences in the extent of the pH effect may add another layer of complexity to the existing benthic $\delta^{13}\text{C}$ records.

[32] As described above, foraminiferal $\delta^{18}\text{O}$ is a function of precipitation temperature and salinity. Hence, paired analyses of foraminiferal Mg/Ca and $\delta^{18}\text{O}$ are commonly applied to reconcile changes in paleosalinity [Zachos *et al.*, 2003; Tripathi and Elderfield, 2004]. But if foraminiferal $\delta^{18}\text{O}$ records are uncorrected for the pH effect, it would imply that reconstructed salinity changes during the PETM can also be overestimated. This can pose a major challenge to resolve the changes in the hydrological cycles as well as ocean circulation during the PETM [Tripathi and Elderfield, 2004, 2005; Nunes and Norris, 2006].

6. Concluding Remarks

[33] Over the past decade, a suite of new proxies has emerged and is being applied to reconstruct paleoclimatic and paleoenvironmental changes during the PETM [e.g., Stoll and Bains, 2003; Tripathi and Elderfield, 2004, 2005; Shuijs *et al.*, 2006, 2007; Pagani *et al.*, 2006b; Zachos *et al.*, 2006]. Still, a large number of the existing records are based on foraminiferal stable isotopes and they continue to provide invaluable paleoceanographic information during the PETM. These records, however, may require corrections in order to account for side effects that can potentially mask the primary paleoceanographic signals. In this paper, we examined the possible ranges of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ corrections required to account for the pH effect during the PETM based on a carbon cycle model and the results from culture experiments.

[34] We reiterate that our approach relies on two critical assumptions. The first is that the pH effect on stable isotopes observed in modern planktonic foraminifera is a universal phenomenon and is thus similarly applicable to ancient planktonic and benthic foraminifera. Second, we assumed that the empirical $\Delta\delta^{13}\text{C}/\Delta\text{pH}$ and $\Delta\delta^{18}\text{O}/\Delta\text{pH}$ relationships obtained from the pH range tested in the culture experiments (see Figure 2) [Spero *et al.*, 1997; Bijma *et al.*, 1998, 1999] can be applied to presumably lower pH levels of the Paleocene-Eocene ocean. This assumption may be

inappropriate particularly for $\delta^{18}\text{O}$ corrections. As shown in Figure 2, the thermodynamic theory predicts that the change in the $\delta^{18}\text{O}$ of DIC per unit pH is much greater between pH 6 and 8 (comparable to the simulated ΔpH values during the PETM) than between pH 8 and 9 (comparable to the pH levels tested in the culture experiments). If the same trend of $\delta^{18}\text{O}$ versus pH applies to the $\delta^{18}\text{O}$ of foraminiferal CaCO_3 shells [Zeebe, 1999], then $\Delta\delta^{18}\text{O}$ would be even larger (leading to more severely underestimated temperatures). Validating these assumptions obviously calls for future input from culture experiments with planktonic foraminifer under Paleocene-Eocene seawater carbonate chemistry (i.e., much lower pH yet CaCO_3 saturation similar to modern) as well as experiments with benthic foraminiferal species.

[35] Lastly, we note that our estimates are highly generalized over a broad areal coverage and depth range. Inter-

pretations of foraminiferal records are expected to be more complicated due to local changes in carbonate chemistry at each core site (i.e., due to upwelling and productivity) as well as diagenetic alterations of the primary isotopic signals. In the LOSCAR model, ocean boxes are separated into three depth horizons. Enhancing the depth resolution would certainly be useful in more closely examining the pH effect for benthic foraminiferal records from different paleodepths and planktonic foraminifera with unique depth habitats.

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at Mānoa, 1000 Pope Rd., Honolulu, HI 96822, USA. (uchikawa@hawaii.edu; zeebe@soest.hawaii.edu)

J. Uchikawa and R. E. Zeebe, Department of Oceanography, SOEST, University of Hawai'i