

# A continental shelf perspective of ocean acidification and temperature evolution during the Paleocene-Eocene Thermal Maximum

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## ABSTRACT

A rapid and large injection of isotopically light carbon into the ocean-atmosphere reservoirs is signaled by a negative carbon isotope excursion (CIE) at the Paleocene-Eocene boundary ~56 m.y. ago. To better understand the extent of ocean warming and acidification associated with the carbon injection we generated elemental and isotopic records of surface and thermocline planktonic foraminifera across the Paleocene-Eocene boundary from an expanded section along the Mid-Atlantic coastal plain, New Jersey (USA). Ocean temperatures (derived from magnesium/calcium paleothermometer) document a lag in thermocline warming relative to surface waters, implying a progressive deepening of the mixed layer in addition to global warming. A similar magnitude of acidification (as recorded by boron/calcium, B/Ca) on the shelf compared with open ocean sites confirms widespread acidification of the surface ocean. An increase in seawater alkalinity after the CIE, as recorded by B/Ca in planktonic foraminifera, likely played an important role in neutralizing the added carbon, possibly minimizing benthic extinction along the shelf.

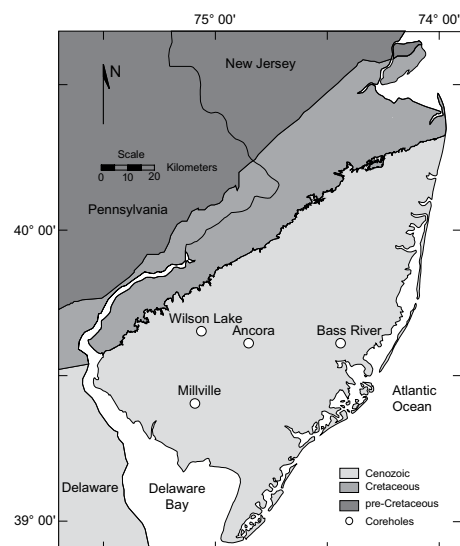
## INTRODUCTION

Associated with the Paleocene-Eocene Thermal Maximum (PETM) is a global warming of ~5 °C (Dunkley Jones et al., 2013) and negative carbon isotopic excursion (CIE) of 3‰–5‰ requiring a substantial addition of  $\delta^{13}\text{C}$ -depleted carbon into the atmosphere and ocean reservoirs (McInerney and Wing, 2011). Several sources proposed to explain the carbon perturbation include methane hydrates, comet impact, terrestrial organic matter, volcanic outgassing, and permafrost soils (McInerney and Wing, 2011). Regardless of the uncertainty in the carbon source, the predicted consequence of the massive addition of carbon would be substantial ocean acidification. Lithologic and geochemical boron-based reconstructions from open ocean sites provide evidence of acidification (Colosimo et al., 2006; Penman et al., 2014; Zachos et al., 2005). In the continental shelf environment a greater complexity of pH regulation is expected compared to the open ocean due to terrestrial inputs of carbon and nutrients as well as physical processes, including upwelling and mixing with coastal waters. Global environmental changes associated with the PETM, such as warming and an enhanced hydrologic cycle, could either counter or enhance the effect of ocean acidification on the continental paleoshelf.

Continental margin sites with high sediment accumulation rates yield expanded sections of the CIE onset and a subsequent interval of low  $\delta^{13}\text{C}$  values (as much as 15 m along the Mid-Atlantic coastal plain) with well-preserved fossil specimens that allow for detailed reconstructions. To evaluate the magnitude and spatial extent of environmental changes during the PETM, we generated geochemical-based reconstructions of ocean temperature (magnesium/calcium, Mg/Ca) and carbonate chemistry (boron/calcium, B/Ca) in planktonic foraminifera from Ocean Drilling Program (ODP) Leg 174AX (Bass River, New Jersey, USA) located along the eastern coast of North America (Fig. 1).

## GEOLOGIC SETTING AND METHODS

On the New Jersey coastal plain, upper Paleocene and lower Eocene sediments comprise the micaceous silts of the Vincentown Formation and kaolinitic clayey silts of the Marlboro Formation, respectively. Lithofacies and biofacies suggest paleodepths of 80–150 m at Bass River for the deposition of these units, interpreted as a middle shelf environment (Harris et al., 2010; Stassen et al., 2012). The Marlboro Formation at Bass River records the CIE in a clay-rich matrix that yields well-preserved foraminifera tests with glassy textures (Pearson et al., 2001; Sexton et al., 2006)



**Figure 1. Location map of coreholes drilled on the New Jersey Coastal Plain (eastern United States) discussed in this study.**

(Fig. DR1 in the GSA Data Repository<sup>1</sup>). At Bass River, the onset of the CIE occurs at 357.4–357.2 m as recorded in bulk sediment and foraminifera  $\delta^{13}\text{C}$  records (Cramer et al., 1999; John et al., 2008). The PETM interval at Bass River is composed of a condensed CIE onset and a partial preservation of the recovery; the upper section is bound by a regional unconformity, truncating the record (John et al., 2008; Stassen et al., 2012). Stable isotope and trace element analyses were carried out on multiple-specimen mixed-layer symbiotic planktonic foraminiferal genera *Morozovella*, *Acarinina*, and the asymbiotic

<sup>1</sup>GSA Data Repository item 2016083, further details on methods, foraminifera preservation, proxy reconstructions, and Bass River geochemical data, is available online at [www.geosociety.org/pubs/ft2016.htm](http://www.geosociety.org/pubs/ft2016.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

deeper dwelling genus *Subbotina* (D'Hondt et al., 1994). (For trace element and stable isotope methodologies, see the Data Repository). Species measurements at each sample depth were compiled to yield monogeneric records (i.e., *Subbotina* spp. and *Morozovella* spp.) because monospecific foraminifera were not in sufficient abundance throughout the section, with the exception of *Acarinina soldadoensis*. No discernible differences in Mg/Ca and B/Ca between the individual *Morozovella* and *Subbotina* species used to generate the genera records were observed (Fig. DR2).

## RESULTS

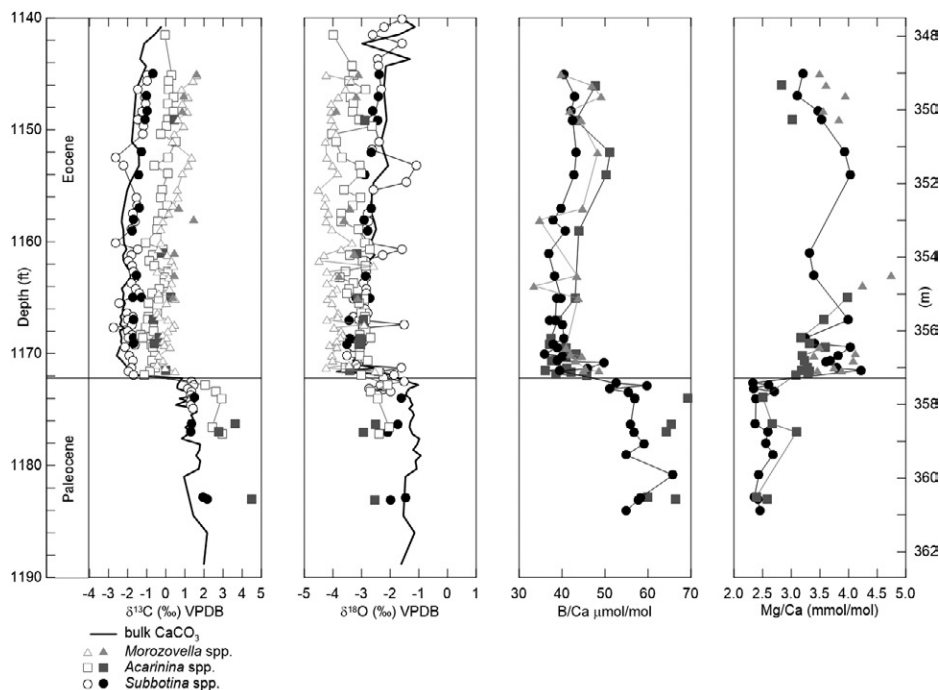
Below the onset of the CIE at 357.3 m, Mg/Ca values of the mixed-layer dweller *A. soldadoensis* and thermocline species *Subbotina* spp. are relatively constant at 2.49 and 2.48 mmol/mol, respectively (Fig. 2). Above the CIE at ~356.6 m, maximum Mg/Ca values of 3.32 for *A. soldadoensis* and 4.21 mmol/mol for *Subbotina* spp. are reached (Fig. 2). B/Ca ratios of symbiotic mixed-layer *A. soldadoensis* and deep-dwelling *Subbotina* spp. are ~60  $\mu\text{mol/mol}$  and ~55  $\mu\text{mol/mol}$ , respectively, below the CIE onset (Fig. 2). Above the onset of the CIE, B/Ca ratios in both *A. soldadoensis*, *Subbotina* spp., and *Morozovella* spp. decrease to ~40  $\mu\text{mol/mol}$  (Fig. 2).

## DISCUSSION

### Ocean Warming

Ocean temperatures are estimated using a multispecies calibration because interspecies variability in Mg/Ca temperature sensitivity is quite small in modern subtropical planktonic foraminifera (Anand et al., 2003). Although the absolute temperature depends on the choice of Mg/Ca seawater composition and species-specific coefficients, the magnitude of warming remains consistent even though the partition coefficient and temperature sensitivity changes as the Mg/Ca of seawater varies (for further discussion, see the Data Repository; Fig. DR3) (Evans and Müller, 2012). Mg/Ca measurements suggest a peak warming of 3 °C (*A. soldadoensis*) and 5 °C (*Subbotina* spp.) of subsurface waters (Fig. 2).  $\delta^{18}\text{O}$  anomalies of 0.93‰ and 1.31‰ recorded by *A. soldadoensis* and *Subbotina* spp., respectively, are consistent with Mg/Ca estimates (John et al., 2008) (Fig. 2). If we assume that *A. soldadoensis* calcifies in the mixed layer and *Subbotina* spp. calcifies below the seasonal thermocline, Mg/Ca and  $\delta^{18}\text{O}$  records suggest that in addition to a general warming, the mixed layer deepened on the continental shelf, permeating heat to deeper waters.

Paleotemperature reconstructions derived from  $\text{TEX}_{86}$  at Bass River and nearby Wilson Lake suggest 5–8 °C surface warming (Fig. 3) (Sluijs et al., 2007; Zachos et al., 2006). Although the magnitude of ocean warming

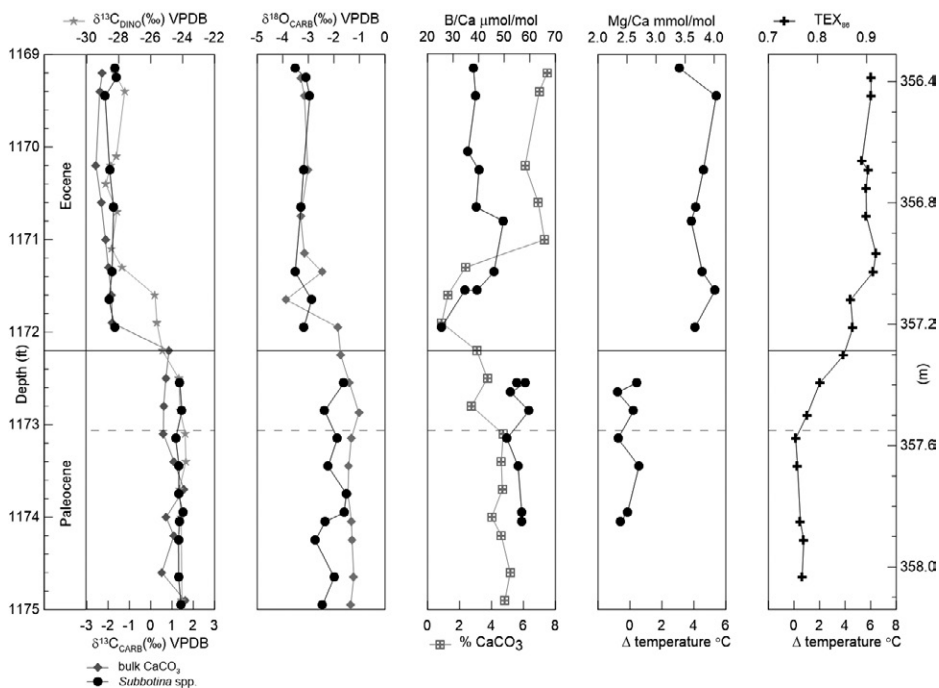


**Figure 2.** Solid horizontal line at ~357.3 m represents the onset of the carbon isotope excursion. Stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) from bulk carbonate and planktonic foraminifera (solid symbols, this study; open symbols, John et al., 2008). B/Ca and Mg/Ca ratios of planktonic foraminifera are shown. VPDB—Vienna Pee Dee belemnite.

documented by both Mg/Ca and  $\text{TEX}_{86}$  records is similar within the uncertainty of the calibrations, the trends below the CIE are different. For the depth interval spanning both temperature records (357.6–357.4 m) an ~2 °C surface warming is indicated in the  $\text{TEX}_{86}$  temperature record, whereas the *Subbotina* spp. Mg/Ca record remains unchanged (Fig. 3). Each proxy is embedded in a planktonic signal carrier with varying sediment diagenesis histories and a distinct ecology that represents different oceanic conditions related to their preferred depth habitats and seasonal production. We suggest that the apparent delay of thermocline warming (Mg/Ca *Subbotina* spp.) relative to the surface ( $\text{TEX}_{86}$ ) (Fig. 3) reflects a depth-related differential in the progression of warming in the upper water column, possibly a response to a change in seasonality (Eldrett et al., 2014) attributed to orbital-driven changes in insolation (DeConto et al., 2012). Interpreted as reflecting sea-surface temperature, the  $\text{TEX}_{86}$  record suggests that the warming below the CIE was restricted to the surface layer and had minimal effect below the seasonal thermocline represented by the Mg/Ca *Subbotina* spp. record. A similar pattern of gradual warming of the thermocline relative to the surface inferred from comparing *Acarinina* and *Subbotina* records is observed at several open ocean sites (Thomas et al., 2002; Tripathi and Elderfield, 2004), implying a broad hydrographic adjustment of the upper water column allowing for the accommodation of excess heat.

### Ocean Acidification

Planktonic foraminifera B/Ca records at Bass River exhibit significant anomalies during the PETM documenting surface ocean acidification along the continental shelf. With an emerging understanding underpinning the B/Ca proxy, we adopt a semiqualitative interpretation of acidification and consider carbonate chemistry as well as non-pH related effects. Sediment and culture studies indicate that B/Ca ratios in planktonic foraminifera, based on the model of borate ion  $[\text{B}(\text{OH})_4^-]$  incorporation into calcite, are governed by carbonate chemistry variables (Allen et al., 2012). Boron and calcium oceanic residence times are considerably longer than the duration of the PETM and are assumed to be constant through that interval (Komar and Zeebe, 2011). We apply the basic mechanism controlling boron partitioning in modern foraminifera to the extinct PETM taxa. Bass River B/Ca planktonic foraminifer values (30–60  $\mu\text{mol/mol}$ ) are significantly lower than measured values in modern analogous species (100–150  $\mu\text{mol/mol}$ ) extending beyond the calibration range. An absolute calibration approach yields negative and inconsistent values to model outputs (Penman et al., 2014); as a result, we estimate relative carbonate chemistry anomalies rather than absolute values. To constrain the magnitude of ocean carbonate chemistry change during the PETM, a range of empirical calibration sensitivities relating B/Ca to seawater  $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]_{\text{sw}}$ , largely a function of



**Figure 3.** Solid horizontal line at ~357.3 m represents the onset of the carbon isotope excursion and dashed line represent the onset of surface warming based on  $TEX_{86}$  (Sluijs et al., 2007). Stable isotope ( $\delta^{13}C$  and  $\delta^{18}O$ ) from bulk carbonate (diamond) and planktonic foraminifer *Subbotina* spp. (John et al., 2008; circle) and dinocyst (Sluijs et al., 2007; star) are shown. Squares are percent  $CaCO_3$  data (John et al., 2008). B/Ca and Mg/Ca (circle) data are from *Subbotina* spp. VPDB—Vienna Peedee belemnite.

pH, were considered (Allen et al., 2012). Based on the B/Ca anomalies (*A. soldadoensis* 25–30  $\mu\text{mol/mol}$ ; *Subbotina* spp. 15–20  $\mu\text{mol/mol}$ ) during the PETM,  $[B(OH)_4^-/HCO_3^-]_{SW}$  was estimated to change by  $0.04 \pm 0.02$  and  $0.095 \pm 0.05$  mol/mol, respectively, equivalent to a pH change of  $0.4 \pm 0.2$  units in the surface ocean and  $0.35 \pm 0.15$  units in the thermocline waters (see the Data Repository; Fig. DR4).

In addition to ocean carbonate chemistry, several other factors, such as salinity, temperature, phosphate  $[PO_4^{3-}]$ , and symbiont loss could influence the B/Ca record. Culture experiments reveal a secondary influence of salinity on boron incorporation (and hence B/Ca ratios) in planktonic foraminifera (Allen et al., 2012). To explain the entire magnitude of B/Ca in *A. soldadoensis* requires a large salinity decrease ( $>4$  psu) that is not supported by the diverse planktonic foraminifera assemblage (Stassen et al., 2012) and the derived  $\delta^{18}O$  records (John et al., 2008; Zachos et al., 2006). Although seawater  $[B(OH)_4^-/HCO_3^-]_{SW}$  is controlled by pH and temperature, a warming of  $5^\circ\text{C}$  (based on Mg/Ca *Subbotina* spp.) translates to a relatively small effect compared to the magnitude of the change predicted from the decrease in B/Ca (Fig. DR5; see the Data Repository). Evidence of nutrient loading (elevated  $[PO_4^{3-}]$ ) through freshwater runoff would increase B/Ca values (Henehan et al., 2015), which is in contrast to the downward trend observed (Fig. 3). The

loss of photosymbionts cannot account for the entire B/Ca excursion, as symbiont-bearing *A. soldadoensis* and symbiont-barren *Subbotina* spp. record a similar anomaly, suggesting that symbionts likely did not significantly bias the records (Fig. 2). Symbiont-bearing species exhibit a positive relationship between test size and  $\delta^{13}C$  attributed to the preference of using light carbon ( $^{12}C$ ) during photosynthesis and the increase of symbiont abundance in larger individuals (D'Hondt et al., 1994; Edgar et al., 2012). The  $\delta^{13}C$ -test size gradients in symbiont species (*A. soldadoensis* and *Morozovella* spp.) are preserved within the CIE, suggesting that at temperate latitudes bleaching did not occur (Fig. DR6). Given the relatively large magnitude of B/Ca change, any secondary factors are minor, and we interpret the record as evidence of surface ocean acidification.

The Bass River B/Ca record is similar to boron-based (B/Ca and  $\delta^{11}B$ ) records from a Pacific site (ODP Site 1209) in absolute values, trend, and magnitude of change (Penman et al., 2014), suggesting that both records are primarily responding to surface ocean acidification that ensued from the absorption of thousands of petagrams of carbon. ODP Site 1209 and Bass River core sites are located in different oceanographic (shelf versus pelagic) and postdepositional settings, precluding a significant preservation bias in the geochemical records. Similarity between the two B/Ca records (ODP Site 1209 and Bass

River) suggests that the degree of surface ocean acidification during the PETM was similar and confirms the global extent, as previously shown based on  $\delta^{11}B$  records (Penman et al., 2014). Estimates of acidification based on B/Ca reconstructions are consistent with model simulations within the upper range of carbon inputs (Penman et al., 2014).

Additional evidence for a large carbon perturbation comes from the predicted buffering response of the oceans needed to neutralize the carbon release and concurrent acidification. The primary response of chemical erosion is evident from the observed decline of calcium carbonate ( $CaCO_3$ ) in marine sediments, interpreted as a rapid shoaling of the calcite compensation depth (Colosimo et al., 2006; Dickens et al., 1997; Zachos et al., 2005). The secondary response involves the delivery of alkalinity (mainly as  $HCO_3^-$ ) through continental weathering. Warming and an increase in greenhouse gases likely acted as positive feedback to enhance the hydrologic cycle during the PETM, providing the necessary catalyst for intense weathering. The sedimentary response to this alkalinity pulse is an interval of high  $CaCO_3$  content, relative to pre-event values. Above the CIE at Bass River,  $CaCO_3$  content increases, an increase also recorded at the Millville and Wilson Lake sites (Fig. 1) (Wright and Schaller, 2013; Zachos et al., 2006), occurs coincidentally with  $\sim 15$   $\mu\text{mol/mol}$  increase in B/Ca followed by a return to CIE values (Fig. 3). Interpreting the  $CaCO_3$  content strictly as changes in carbonate saturation state is complicated by potential shifts in biological production and accumulation of noncalcareous sediments. The B/Ca record provides independent evidence of a local recovery in ocean carbonate chemistry, lending confidence to the interpretation of a riverine flux of alkalinity occurring directly after the CIE. The suggested buffering of the coastal ocean could explain the less severe extinction of benthic foraminifera in the shelf environment (Stassen et al., 2012).

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