

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

Tali L. Babila et al.

1 **Supplementary Information**

2 **Methods**

3 Trace element analysis

4 Individual foraminifer specimens were picked from disaggregated sediments from 250-
5 355 μm size fraction to obtain $\sim 200\text{--}400\ \mu\text{g}$ CaCO_3 material. Foraminifer tests were gently
6 crushed between two glass plates in order to open the chambers and facilitate the chemical
7 cleaning procedure. Visible siliciclastic grains were removed when possible. Crushed
8 foraminifera samples were transferred into acid-leached 0.5 mL centrifuge vials and rinsed with
9 Milli-Q water (x3) and separated into trace element (100-400 μg) and stable isotope (50-100 μg)
10 aliquots.

11 Crushed foraminifera samples were chemically cleaned following the Cd-cleaning
12 protocol (Boyle and Keigwin, 1985/1986) later modified by Rosenthal et al. (1997). All reagents
13 and acids are prepared using Milli-Q water passed through a boron Q-gard purification filter to
14 obtain low boron water. Samples were rinsed with Milli-Q water and glass distilled methanol to
15 remove adhered surficial clays on the tests. Reductive and oxidative cleaning steps were
16 conducted to remove potential contaminate metal oxides and organics from foraminiferal tests. A

final dilute acid (0.001N HNO₃) leach was done before completely dissolving samples using 100 µL 0.065N HNO₃. Samples were diluted with ~100-200 µL (depending on the sample size) with 0.5N HNO₃ to a final volume of ~300-400 µL for a target calcium concentration of 4 mmol/L. Samples were monitored for potential contamination from clay and metal oxides by measuring Mn/Ca, Al/Ca and Fe/Ca to monitor for diagenetic coatings. Typical Mn/Ca values ~200-800 µmol/mol and Al/Ca values of ~200-600 µmol/mol. No significant correlation between B/Ca and Mn/Ca, Al/Ca or Fe/Ca was observed. Mg/Ca samples with high Fe/Ca and Mn/Ca were not included in the reconstructions.

Trace element analyses (B/Ca, Mg/Ca, Mn/Ca, Al/Ca and Fe/Ca) were measured at the Institute of Marine and Coastal Sciences at Rutgers University on a Thermo Finnigan Element XR Sector Field Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS) operated in low resolution ($m/\Delta m = 300$) and medium resolution ($m/\Delta m = 4300$) settings outline in the protocol of Rosenthal et al. (1999). Elemental B analysis requires several modifications to the Rosenthal et al. (1999) method to address potentially high [B] blanks and instrumental memory effect (outlined in Babila et al., 2014). Typical B blank levels are ~0.15 ppb (<3 % of [B] of foraminifera samples) and remain stable (± 1 %) throughout an analytical run.

Elemental ratios were monitored and corrected for matrix effects for each analytical run by analyzing a suite of standards using an internal spiked gravimetric standard (SGS) with the same elemental ratios but varying [Ca] (1.5 mmol/L to 8 mmol/L) (Rosenthal et al., 1999). [Ca] concentrations in sample solutions were typically maintained in the range of 1.5 to 4 mmol/L to minimize matrix effects on Mg/Ca and B/Ca. Analytical reproducibility for B/Ca $115.43 \mu\text{mol/mol} \pm 0.74 \%$ (RSD) and for Mg/Ca $3.32 \text{ mmol/mol} \pm 0.33 \%$ (RSD) based on repeated analysis of laboratory consistency standards throughout the length of the study.

40 Stable isotopes analysis

41 Stable carbon and oxygen isotopes were measured at the Department of Earth and
42 Planetary Sciences using an Optima mass spectrometer. Measurements are reported in PDB with
43 precision values of $\pm 0.05 \text{ ‰ } \delta^{13}\text{C}$ and $\pm 0.08 \text{ ‰ } \delta^{18}\text{O}$ for NBS 19 standard throughout the
44 analysis of this study.

45 **Assessing preservation**

46 To evaluate the preservation of foraminifer specimens a high-resolution scanning electron
47 microscope (SEM) was used to image *Subbotina* spp. and compared from below the CIE, within
48 the CIE, and in the recovery intervals (Fig. DR2). Foraminifers from the Vincetown Formation
49 (below the CIE) are not as well preserved as those from the overlying Marlboro Formation (CIE
50 interval) (Fig. DR1). B/Ca records from Bass River (Fig. DR1) documented relatively constant
51 values throughout the CIE despite the observation that variable degrees of test preservation were
52 present throughout the section.

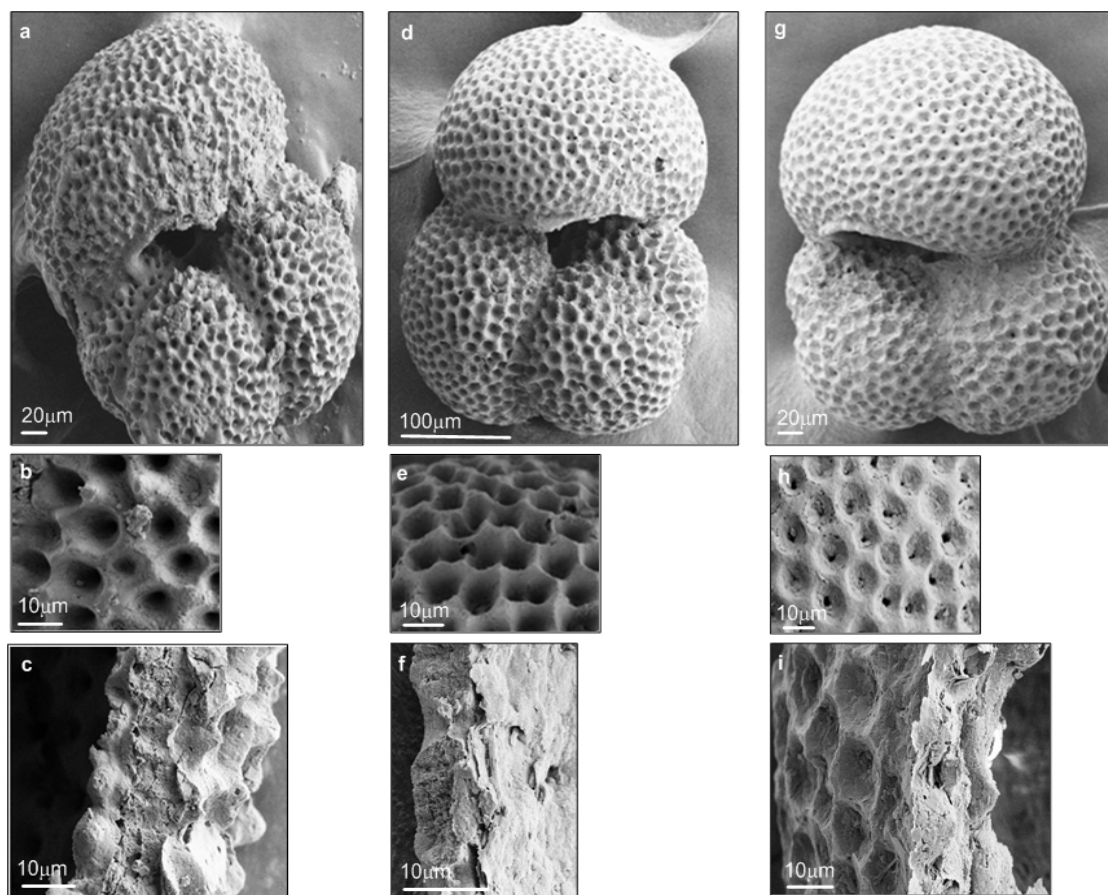
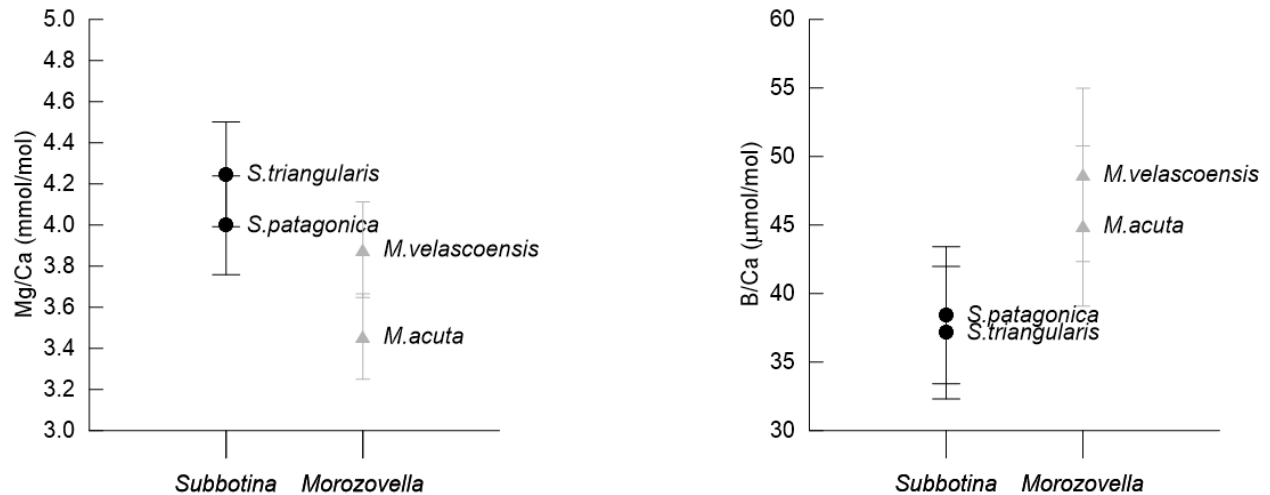


Figure DR1. SEM images of planktonic foraminifer *S. triangularis/roesnaesensis* at the following core depths a-c: 1176.3 ft, d-f: 1171.1 ft and g-i: 1169.4 ft shell texture (b, e, h) and cross section of shell walls (c, f, i).

Paleodepth estimates based on benthic foraminifera assemblages suggest that at Bass River lies well above the paleo-CCD. Observations from recent core top material demonstrate that B/Ca may be influenced by dissolution (Coadic et al., 2013). Down-core records of B/Ca with size normalized shell weight are used as an indication of dissolution (Wara et al., 2003). Foraminiferal shell weight exhibit no significant relationship with B/Ca at Bass River suggesting a negligible dissolution. Kozdon et al. (2013) demonstrated that Sr/Ca ratios in planktonic foraminifera can be used to assess preservation state during the PETM. Sr/Ca values at Bass

River are generally higher than the value (1.0 mmol/mol) typical of diagenetic calcite, indicating that diagenesis did not compromise the geochemical records, with the exception of two sample depths not included in the reconstructions.

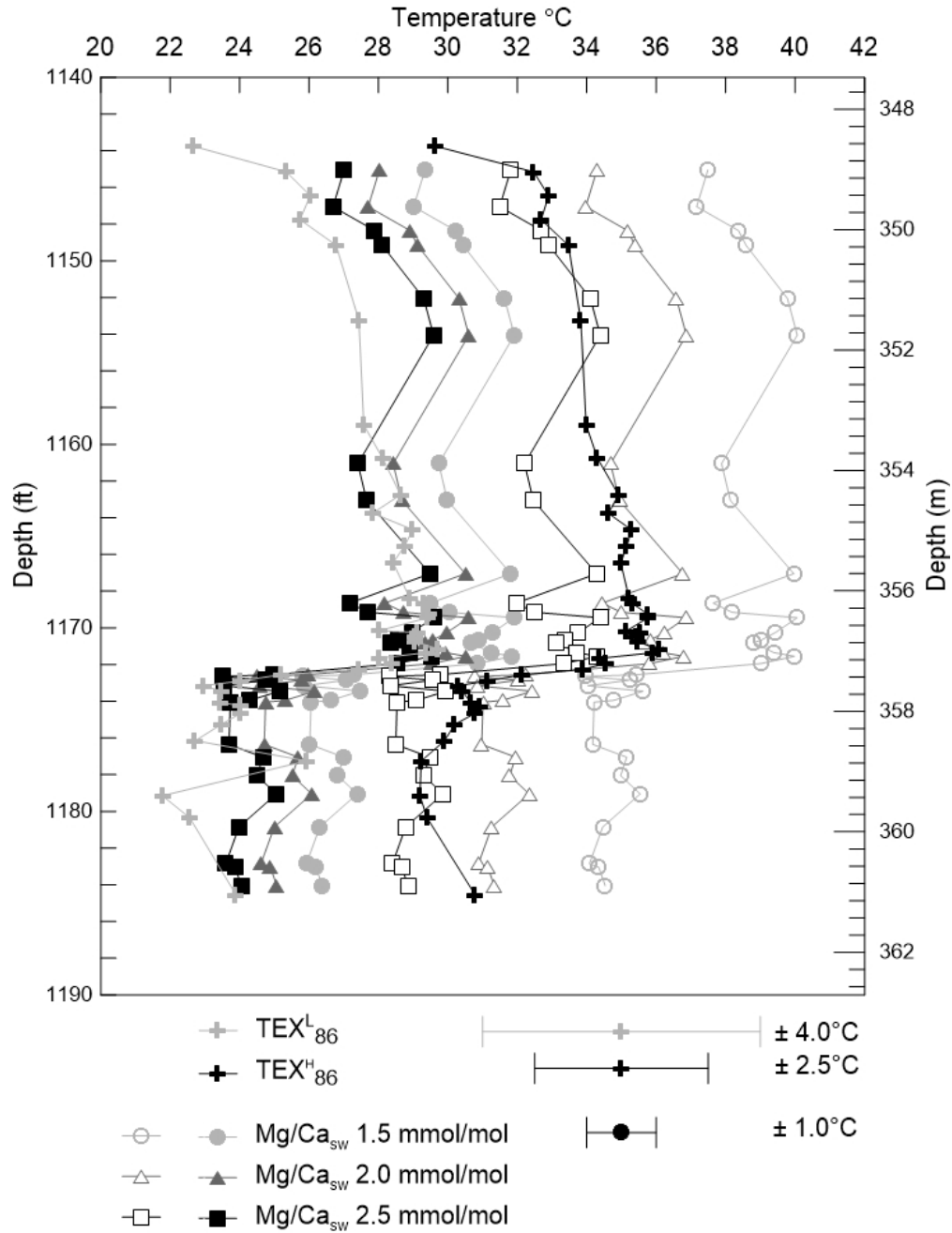


FigureDR. Comparison of Mg/Ca and B/Ca data for *S. patagonica*/*S. triangularis* (1171.5-1171.6 ft) (circle) and *M. acuta*/*M. velascoensis* (1167-1167.1 ft) (triangle) species.

Sea surface temperature

The use of Mg/Ca thermometry in deep-time paleoceanographic studies is complicated by the secular variation in the Mg/Ca composition of seawater (Mg/Ca_{sw}) over the Cenozoic (65 million years). Proxy based reconstructions for Mg/Ca_{sw} are limited during the Paleogene and only model based reconstructions span the PETM. Model based Mg/Ca_{sw} reconstructions during the PETM yield values ranging from 1.5-2.0 mmol/mol (see Evans and Müller, 2012 for recent compilation) with the exception of the Wilkinson and Algeo (1989) record. Proxy data for the late Cenozoic agree with the model estimates of a lower Mg/Ca_{sw} during the PETM. Evans and Müller (2012) suggest that a nonlinear correction is necessary to account for the change in the distribution coefficient (D_{Mg}) with Mg/Ca_{sw} . We consider a range of values for the Mg/Ca_{sw} (1.5-

2.5 mmol/mol) and a linear versus nonlinear correction to the *Subbotina* spp. Mg/Ca record at Bass River (Fig. DR3). The Mg/Ca temperature calibration used is the planktonic foraminifera multi-species equation from Anand et al. (2003). Currently, the only study that examined the relationship between D_{Mg} and Mg/Ca_{sw} in planktonic foraminifera is based on the symbiont bearing *Globigerinoides sacculifer* species (Delaney et al., 1985) which we consider most comparable to *Subbotina* spp. based on paleoecology. Comparing the different Mg/Ca temperature reconstructions with TEX₈₆ based SST lead to the following conclusions that are pertinent to this study: 1) applying a nonlinear rather than a linear correction minimizes the error in temperature estimates due to the uncertainty in the Mg/Ca_{sw} and 2) the magnitude of ocean temperature warming across the P/E boundary does not depend on the choice of Mg/Ca_{sw} or the type of correction applied to the foraminiferal data and is consistent with the magnitude suggested by TEX₈₆ records (Fig. DR3). We note that the reconstructions based on a nonlinear correction yield temperatures consistent with the TEX₈₆^L calibration (Kim et al., 2010) and substantially colder than temperature reconstructions derived from the TEX₈₆^H calibration (Kim et al., 2010), which is currently recommended for shallow Paleogene sections (Taylor et al., 2013). A further discussion on the comparison among the different temperature proxies and implication to climate are presented elsewhere (Makarova, 2014).



98

99 **Figure DR3** Ocean temperature reconstructions across the P/E boundary based on the Mg/Ca of
 100 *Subbotina* spp. with a nonlinear (solid symbols) and linear (open symbols) correction applied at
 101 variable Mg/Ca_{sw} values and TEX₈₆ derived (cross) (Sluijs et al., 2007).

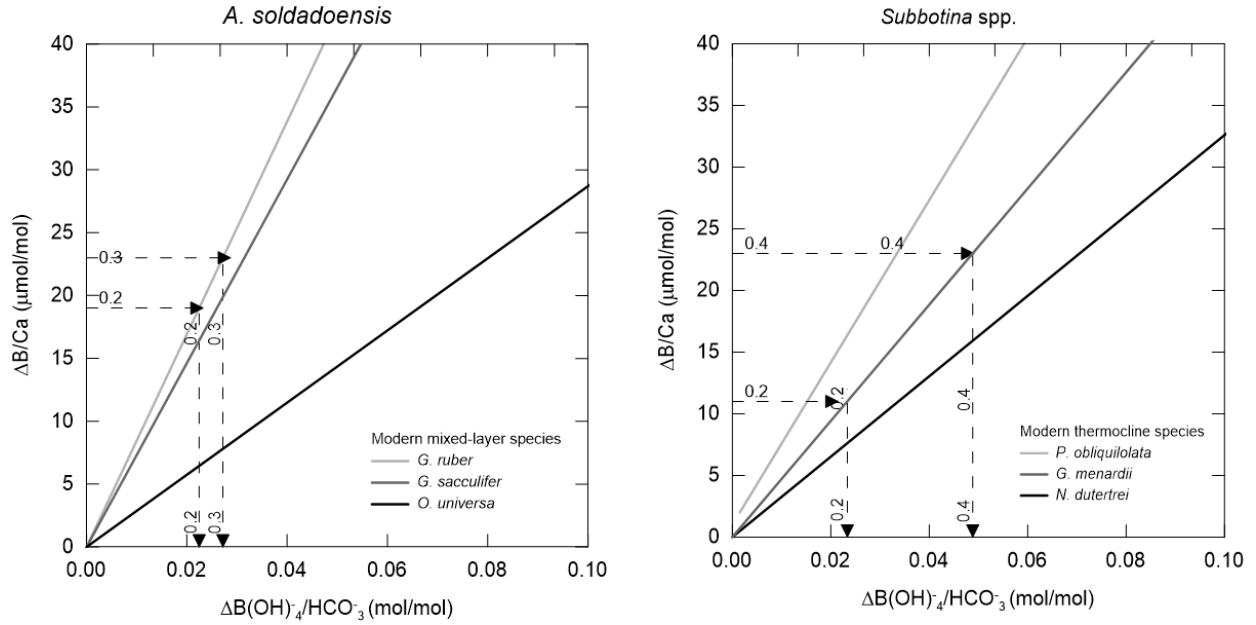
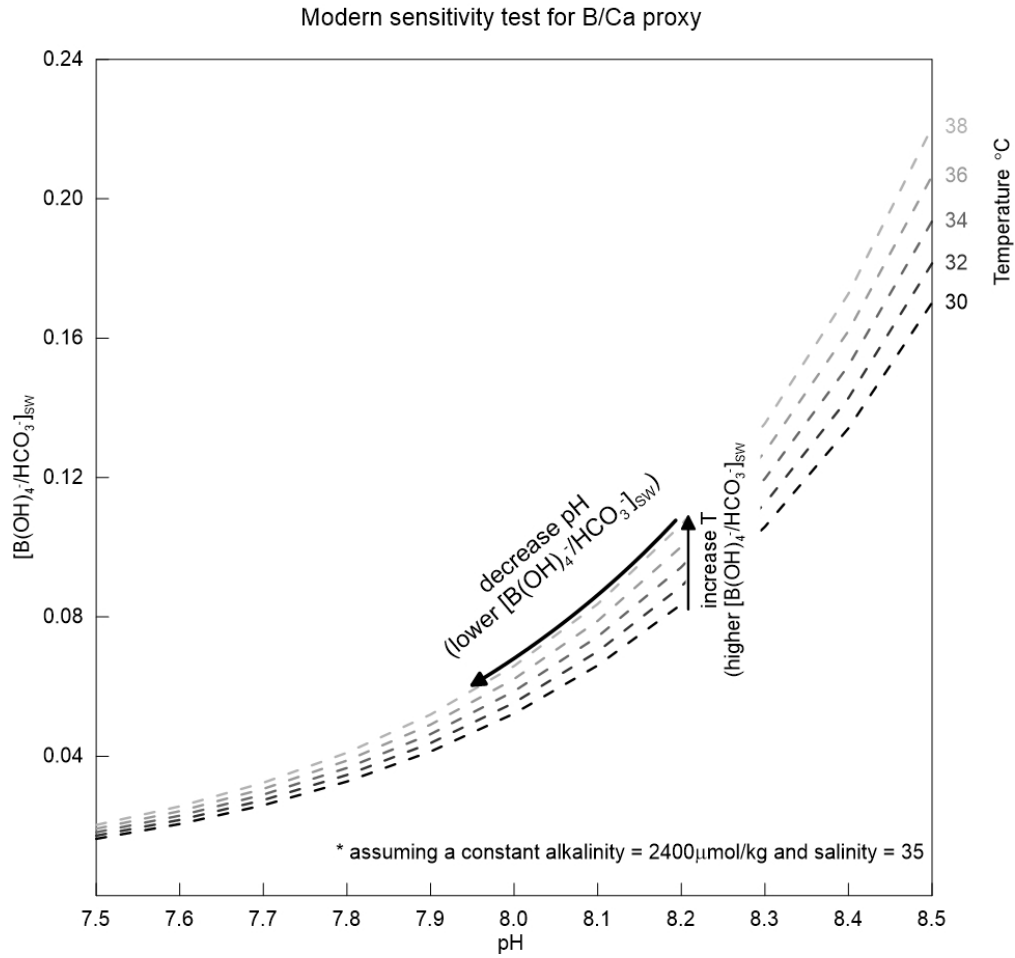


Figure DR4 Estimate of the magnitude of ocean carbonate chemistry change [$B(OH_4^-)/HCO_3^-$] and pH for *A. soldadoensis* and *Subbotina* spp. computed from a range of modern sensitivities for symbiont bearing surface dwellers (Allen et al., 2012) and thermocline dwellers (Babila, 2014).



110

111 **Figure DR5.** B/Ca proxy sensitivity test to seawater temperature and $[\text{B}(\text{OH})_4^-]/[\text{HCO}_3^-]_{\text{sw}}$ for a
 112 range of pH (7.5-8.5) was computed by assuming constant a alkalinity and salinity (boron
 113 concentration).

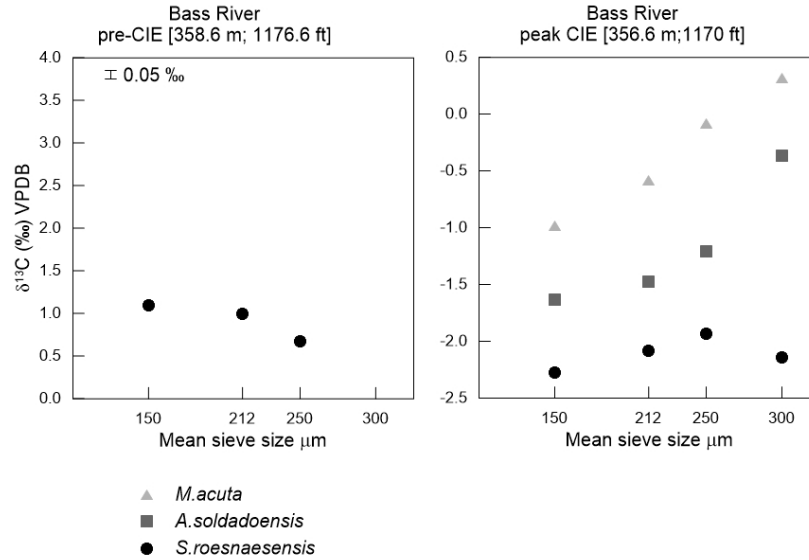


Figure DR6. Trends in $\delta^{13}\text{C}$ versus foraminifer mean test size.

References

- Allen, K. A., Hönisch, B., Eggins, S. M., and Rosenthal, Y., 2012, Environmental controls on B/Ca in calcite tests of the tropical planktic foraminifer species *Globigerinoides ruber* and *Globigerinoides sacculifer*: *Earth and Planetary Science Letters*, v. 351–352, no. 0, p. 270–280.
- Anand, P., Elderfield, H., and Conte, M. H., 2003, Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series: *Paleoceanography*, v. 18, no. 2, p. 1050.
- Babila, T. L., 2014, Boron/Calcium in planktonic foraminifera: Proxy development and application to the Paleocene-Eocene boundary: Ph.D dissertation, Rutgers, State University of New Jersey, 159p.
- Babila, T. L., Rosenthal, Y., and Conte, M. H., 2014, Evaluation of the biogeochemical controls on B/Ca of *Globigerinoides ruber* white from the Oceanic Flux Program, Bermuda: *Earth and Planetary Science Letters*, v. 404, no. 0, p. 67–76.
- Coadic, R., Bassinot, F., Dissard, D., Douville, E., Greaves, M., and Michel, E., 2013, A core-top study of dissolution effect on B/Ca in *Globigerinoides sacculifer* from the tropical Atlantic: Potential bias for paleo-reconstruction of seawater carbonate chemistry: *Geochemistry, Geophysics, Geosystems*, v. 14, no. 4, p. 1053–1068.
- Delaney, M. L., Bé, A. W. H., and Boyle, E. A., 1985, Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps, sediment cores: *Geochim. Cosmochim. Acta*, v. 49, no. 6, p. 1327–1341.
- Evans, D., and Müller, W., 2012, Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca: *Paleoceanography*, v. 27, no. 4, p. PA4205.
- Kim, J.-H., van de Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koc, N., Hopmans, E. C., and Damsté, J. S. S., 2010, New indices and calibrations derived from the distribution of crenarchaeal isoprenoid tetraether lipids: Implications for past sea surface temperature reconstructions: *Geochimica et Cosmochimica Acta*, v. 74, p. 4639–4654.

- Kozdon, R., Kelly, D. C., Kitajima, K., Strickland, A., Fournelle, J. H., and Valley, J. W., 2013, In situ $\delta^{18}\text{O}$ and Mg/Ca analyses of diagenetic and planktic foraminiferal calcite preserved in a deep-sea record of the Paleocene-Eocene thermal maximum: *Paleoceanography*, v. 28, no. 3, p. 517-528.
- Makarova, M., 2014, Paleoenvironmental changes associated with the Paleocene-Eocene Thermal Maximum, Millville (ODP 174AX), New Jersey Coastal Plain: Master of Science, Rutgers, State University of New Jersey, 98p.
- Rosenthal, Y., Boyle, E. A., and Slowey, N., 1997, Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography: *Geochimica et Cosmochimica Acta*, v. 61, no. 17, p. 3633-3643.
- Rosenthal, Y., Field, M. P., and Sherrell, R. M., 1999, Precise determination of element/calcium ratios in calcareous samples using Sector Field Inductively Couple Plasma Mass Spectrometry: *Analytical Chemistry* v. 71, p. 3248-3253.
- Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S. M., John, C. M., Zachos, J. C., Reichert, G.-J., Sinninghe Damste, J. S., Crouch, E. M., and Dickens, G. R., 2007, Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary: *Nature*, v. 450, no. 7173, p. 1218-1221.
- Taylor, K. W. R., Huber, M., Hollis, C. J., Hernandez-Sanchez, M. T., and Pancost, R. D., 2013, Re-evaluating modern and Palaeogene GDGT distributions: Implications for SST reconstructions: *Global and Planetary Change*, v. 108, no. 0, p. 158-174.
- Wara, M. W., Delaney, M. L., Bullen, T. D., and Ravelo, A. C., 2003, Possible roles of pH, temperature, and partial dissolution in determining boron concentration and isotopic composition in planktonic foraminifera: *Paleoceanography*, v. 18, no. 4, p. 1100.
- Wilkinson, B. H., and Algeo, T. J., 1989, Sedimentary carbonate record of calcium-magnesium cycling: *American Journal of Science*, v. 289, no. 10, p. 1158-1194.