Warm, not super-hot, temperatures in the early Eocene subtropics

Caitlin R. Keating-Bitonti[1]*, Linda C. Ivany[1], Hagit P. Affek[2], Peter Douglas[2], and Scott D. Samson[1]
[1]Department of Earth Sciences, Syracuse University, Syracuse, New York 13244, USA
[2]Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520-8109, USA

ABSTRACT

The early Eocene (ca. 55–48 Ma) encompasses one of the warmest intervals of the past 65 m.y. and is characterized by an unusually low equator-to-pole thermal gradient. Recent proxy studies suggest temperatures well in excess of 30 °C even at high latitudes, but conflicting interpretations derived from different types of data leave considerable uncertainty about actual early Eocene temperatures. A robust comparison among new paleotemperature proxies may provide insight into possible biases in their temperature estimates, and additional detail on the spatial distribution of temperatures will further resolve the early Eocene meridional temperature gradient. We use a suite of paleotemperature proxies based on the chemistry of bivalve shell carbonate and associated sedimentary organic matter from the United States Gulf Coastal Plain to constrain climate at a subtropical site during this key interval of Earth history. Oxygen isotope and clumped isotope analyses of shell carbonate and two tetraether lipid analyses of sedimentary organic carbon all yield temperatures of ~27 °C. High-resolution, intraannual oxygen isotope data reveal a consistent, large range of seasonal variation, but clumped isotope data suggest that seasonality is due primarily to precipitation, not to temperature. These paleotemperature estimates are 2–3 °C warmer than the northern Gulf of Mexico today, and generally consistent with early Eocene temperature estimates from other low and mid-latitude locations, but are significantly cooler than contemporaneous estimates from high southern latitudes.

INTRODUCTION

Paleotemperature estimates from a variety of geochemical and paleontological proxies indicate that the early Eocene encompasses the warmest climatic conditions of the Cenozoic (the past 65 m.y.). Intervals of extreme warmth are of great interest, as they provide analogs for a future greenhouse world. Recent estimates suggest temperatures approaching or in excess of 30 °C not only in low latitudes (Pearson et al., 2007), but also middle (Zachos et al., 2006) and high latitudes (Bijl et al., 2009; Creech et al., 2010; Hollis et al., 2009), implying very low meridional gradients. Concerns over potential biases related to preservation of carbonate microfossils (Pearson et al., 2001; Schrag, 1999) and temperature significance of the newer organic proxies (e.g., see discussion in Liu et al., 2009), however, leave some uncertainty about the actual magnitude and distribution of paleotemperatures in the early Eocene (Huber, 2008). Expanding the spatial coverage of paleotemperature estimates and corroborating inferred values with multiple proxies will enable an assessment of potential biases in any one proxy, refine interpretations of mean annual temperature (MAT) at the surface, and ultimately allow for a better understanding of processes responsible for maintaining Eocene warmth and equability.

We use multiple geochemical proxies applied to the shells of bivalve mollusks and their associated sediment to assess paleotemperatures on a subtropical continental margin. Samples come from shallow-marine sediments of the early Eocene upper Hatchetigbee Member of the Hatchetigbee Formation (ca. 54–52 Ma; see the GSA Data Repository[1] for strontium isotope age constraints) in the Gulf Coastal Plain of the southeastern United States (for details, see the Data Repository), at a paleolatitude of ~30°N (Müller et al., 2011). Sediments are unconsolidated and fossils are in excellent condition, retaining their original aragonite (see the Data Repository). Earlier oxygen isotope work revealed unexpectedly low seasonal $\delta^{18}O$ minima within individual shells, suggesting summer temperatures of ~37 °C and leading the authors to propose a scenario of seasonal freshwater mixing to locally decrease water $\delta^{18}O$ values and bias calculated temperatures (Ivany et al., 2004). These depleted $\delta^{18}O$ values, however, could also be consistent with a mean tropical sea-surface temperature of ~31 °C proposed by Pearson et al. (2007) for that same time interval. We combine stable oxygen isotope, clumped isotopes, and strontium isotope analyses of shell carbonate with tetraether lipid proxies (TEX$_{86}$, BIT [branched and isoprenoid tetraether], MBT/CBT [methylation of branched tetraethers/cyclization of branched tetraethers]) from organic matter in sediment enclosed by articulated shells to deconvolve the competing effects of temperature and salinity on the $\delta^{18}O$ record and produce reliable estimates of winter, summer, and MATs during this interval of exceptional warmth.

METHODS

The shells of two individuals of the bivalve *Venericardia hatcheplata* from each of seven stratigraphic horizons within the Hatchetigbee Formation were cut along the maximum growth axis from umbo to ventral margin, and polished. Because these bivalves grow more or less continuously throughout the year, high-resolution sequential microsampling of accretionary shell carbonate can recover seasonal variation (Ivany et al., 2004). Multiple, sequential, growth-band–parallel samples were milled from each couplet of light and dark growth bands in the inner shell layer using a Merchantek (New Wave) MicroMill. Within each bivalve, at least three full years of growth were sampled wherever possible. Aragonite powders were analyzed for stable carbon and oxygen isotope values at the University of Michigan's Stable Isotope Laboratory using MAT 251 and MAT 253 mass spectrometers. Resulting oxygen isotope values were converted to paleotemperatures using the corrected biogenic aragonite temperature equation of Grossman and Ku (1986; Kobashi and Grossman, 2003) and assuming seawater $\delta^{18}O$ is the latitude-corrected ice-free marine value ($-0.36‰$ at 30°N; Zachos et al., 1994).

Aliquots from light and dark growth band increments of four venericards, as well as two bulk-shell samples that ranged across multiple years of growth, were analyzed for clumped isotopes (Δ_{47}). Carbonate samples were measured for Δ_{47} values using methodology described elsewhere (Affek and Eiler, 2006; Ghosh et al., 2006; Huntington et al., 2009). Temperature estimates were calculated from Δ_{47} values using the calibration of Ghosh et al. (2006).

Sediments enclosed within six pairs of articulated valves of *Venericardia*, two from each of three horizons, were analyzed for tetraether lipid distributions. TEX$_{86}$ values were calculated following Schouten et al. (2002), and converted to sea-surface temperatures (SSTs) using the nonlinear calibration of Liu et al. (2009). The BIT index, a measure for terrestrial organic matter input to sediments, was calculated following Hopmans et al. (2004). Terrestrial mean annual temperature (MAT) estimates were calculated from MBT and CBT values following Weijers et al. (2007).

---

*Current address: Department of Geoscience, University of Wisconsin–Madison, Madison, Wisconsin 53706, USA; E-mail: keatingbiton@wisc.edu.

RESULTS

$\delta^{18}O$ values vary approximately sinusoidally between −5.7‰ and −1.4‰ along all 14 shell transects, reflecting seasonal cycles (Fig. 1). Dark (translucent) bands correspond to more negative $\delta^{18}O$ values, suggesting, in the absence of other evidence, formation during warm seasons. Assuming normal marine salinity, calculated winter minimum temperatures are consistent within and among shells of all horizons, with an overall mean of 26.6 ± 1.1 °C (±1 standard deviation) (Fig. 2; Table DR1 in the Data Repository). Inferred summer maximum temperatures, however, are very warm and significantly more variable, ranging between 31 and 43 °C (Fig. 2; Ivany et al., 2004).

Clumped isotopes analyses suggest a MAT of 26.5 ± 1.0 °C (±1 standard error, n = 10) (Fig. 2; Table DR2). Mean summer and winter samples produce paleotemperatures of 25.5 ± 2.1 °C and 27.1 ± 1.7 °C, respectively (see the Data Repository). Paired clumped isotope analyses of light and dark growth bands within shells reveal summer and winter temperatures that are within error (based on the analytical error for individual samples; Fig. 1; Table DR2). The variability among shells is larger (22.4 ± 1.9 °C to 31.1 ± 0.7 °C) and likely reflects a combination of analytical uncertainty and real temperature variability on time scales longer than the lifetime of an individual bivalve. These results argue that negative $\delta^{18}O$ values from shell carbonate do not reflect seasonally warm temperatures, but rather a substantial seasonal contribution of ^{18}O-depleted freshwater. Seasonal clumped isotope temperatures likely reflect integrated seasonal means, as the relatively large sample size required does not allow for the capture of seasonal temperature extremes. The $\delta^{18}O$ values of the samples used for clumped isotopes analysis illustrate that, while micromilled carbonate from light and dark growth bands generally differ by ~2.5‰, corresponding samples measured for clumped isotopes differ by 1.5‰–2‰.

Temperatures derived from tetraether lipid analyses are within error or slightly higher than those from clumped isotopes. TEX_{86} indicates temperatures between 27 and 29 °C (Fig. 2; see the Data Repository). BIT values are between 0.3 and 0.4 (see the Data Repository), indicating a coastal setting with significant terrestrial organic matter input (Hopmans et al., 2004), consistent with the inference of seasonal precipitation and runoff drawn from seasonally depleted shell isotope values and corroborated by the abundance of terrestrial vascular plant organic debris in the sediments. These relatively high BIT values indicate a possible source of uncertainty in TEX_{86} derived temperatures because isoprenoid tetraether lipids derived from soils can influence TEX_{86} values in settings with large terrestrial organic matter inputs (Weijers et al., 2006). Nevertheless, the TEX_{86} derived temperatures basically agree with those from isotopic analyses of shell carbonates, and since the latter are not affected by organic inputs, the agreement suggests that TEX_{86} reliably reflects the temperature of coastal waters in this setting. The MBT/CBT paleotemperature proxy, however, specifically targets terrestrially derived organic matter, and suggests soil paleotemperatures between 25 and 28 °C (Fig. 2; see the Data Repository). Although a large uncertainty exists concerning the source regions for soil-derived branched tetraether lipids in marine sediments, consistency in inferred temperatures suggests that nearby continental MATs were similar to coastal sea-surface temperatures.

DISCUSSION

Good agreement among paleotemperatures derived from winter $\delta^{18}O$, clumped isotopes, TEX_{86}, and MBT/CBT indicates that the MAT on the U.S. Gulf Coast during the early Eocene was ~27 °C. Latest Paleocene TEX_{86} derived temperatures from a core in nearby southeastern Mississippi (van Roij, 2009) are in line with those presented here. Winter and summer temperatures are statistically indistinguishable using clumped isotopes, implying that the range of seasonal temperature variation is significantly lower than suggested by $\delta^{18}O$ data. The very negative "summer" $\delta^{18}O$ values instead indicate that the primary manifestation of the
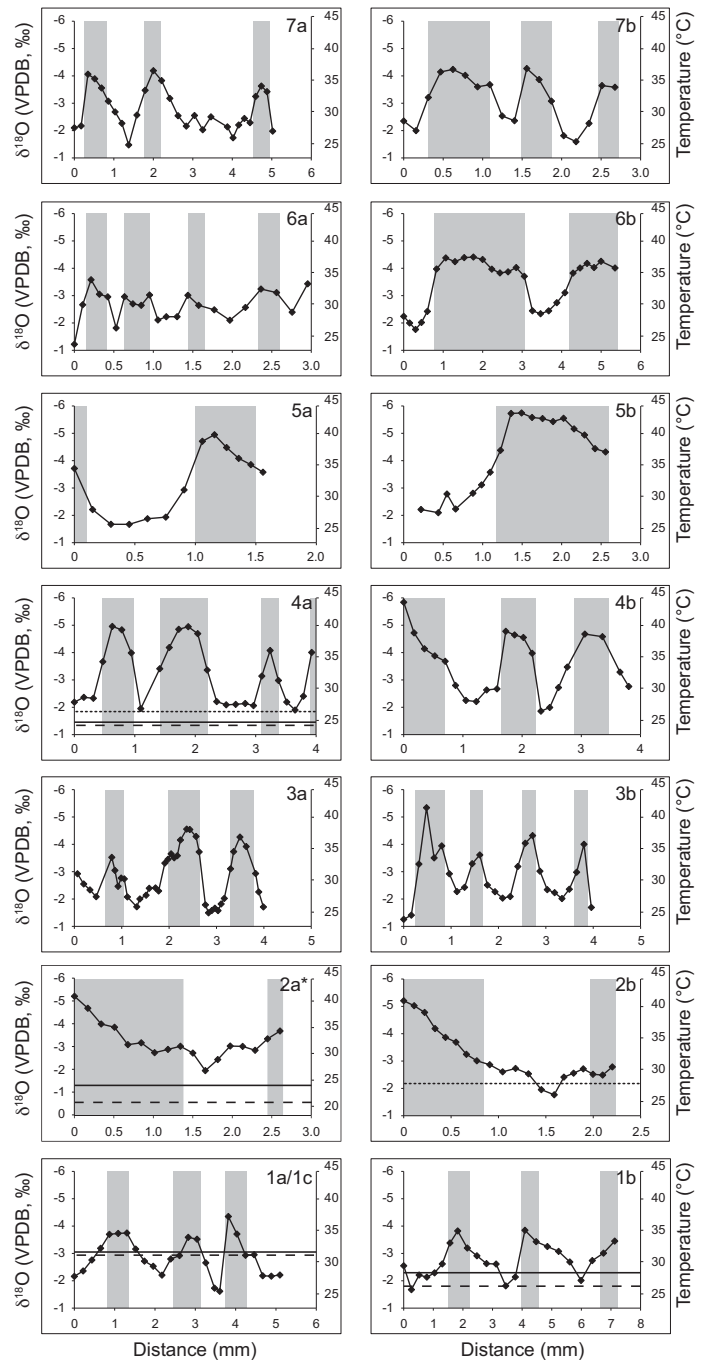

Figure 1. Variation in $\delta^{18}O$ of *Venericardia* carbonate sequentially sampled in direction of shell growth. Shells are arranged in stratigraphic order. Inferred temperatures are reported assuming constant $\delta^{18}O_w$ value of −0.36‰. Shaded gray bars indicate dark (translucent) growth bands. Horizontal solid, dashed, and dotted lines denote mean clumped isotope-derived "winter," "summer," and bulk temperatures, respectively. Analytical error for clumped isotope data is ~±2 °C. Plot 1a/1c represents $\delta^{18}O_c$ values of venericard 1a and clumped isotope values of venericard 1c. Note different scale of y axis for plot 2a*. (See the Data Repository [see footnote 1] for all clumped isotope data and details.) VPDB—Vienna Peedee belemnite.

seasonal cycle was related to precipitation, making it the wet season. Seasonally resolved $\delta^{18}O$ values from more typical marine facies elsewhere in the upper Hatchetigbee Member and underlying Bashi Marl Member of the Hatchetigbee Formation yield low seasonal ranges and similar "winter"/dry season values, reinforcing this interpretation (Ivany et al., 2003;
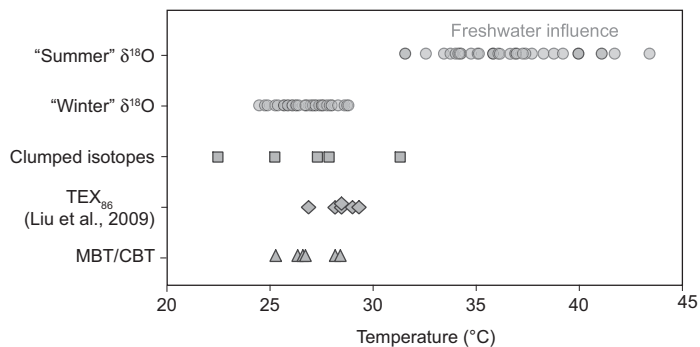
Figure 2. Summary of all early Eocene paleotemperature estimates from different proxies, showing good agreement among "winter" (marine) $\delta^{18}O$, clumped isotopes, TEX_{86}, and MBT/CBT (methylation of branched tetraethers/cyclization of branched tetraethers). Clumped isotope data are shown as mean of all measurements per shell. Analytical error for clumped isotope data is ~2 °C. Calibration error for TEX_{86} is ~4 °C (Liu et al., 2009), and for MBT is ~5 °C (Weijers et al., 2007). Very warm temperatures implied by "summer" $\delta^{18}O$ values reflect variable contribution of ^{18}O-depleted fresh water.
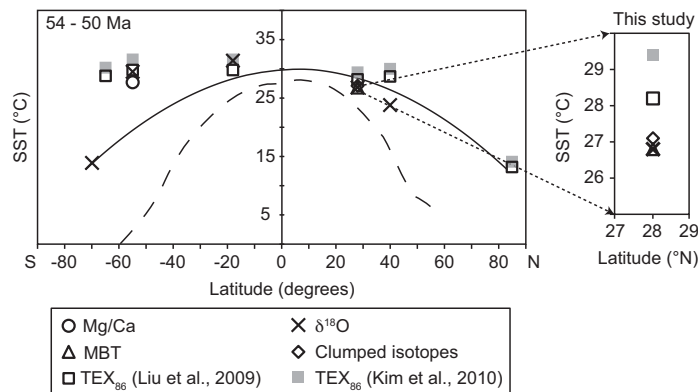

Figure 3. Latitudinal gradient for the early Eocene (54–50 Ma) based on paleotemperature reconstructions in the literature (Bijl et al., 2009; Creech et al., 2010; Hollis et al., 2009; Pearson et al., 2007; Sluijs et al., 2006; Zachos et al., 2006) and this study. All $\delta^{18}O$-derived paleotemperatures were recalculated using paleolatitude-corrected δ_w appropriate for each site (following Zachos et al., 1994). Tex_{86} temperatures were recalculated using equations of both Liu et al. (2009) and Kim et al. (2010). Solid and dashed lines represent early Eocene latitudinal temperature gradient based on compiled data and present-day latitudinal temperature gradient (from Bijl et al., 2009), respectively. TEX_{86}—tetraether index of tetraethers with 86 carbon atoms; MBT—methylation of branched tetraethers/cyclization of branched tetraethers; SST—sea-surface temperature.

Kobashi et al., 2001). A MAT of ~27 °C, minimal temperature seasonality, and significant seasonal precipitation is in good accord with paleobotanical data supporting tropical to paratropical conditions in the early Eocene Gulf Coast (Fricke and Wing, 2004; Harrington, 2003; Wolfe, 1978; Wolfe and Dilcher, 2000).

The multiple paleotemperature proxies used in this study enable a comparison among them. This is the first time that the clumped isotopes technique has been tested on ancient or modern biogenic carbonates where other independent proxies have been simultaneously applied. That clumped isotope temperatures generally agree with conventional oxygen isotope–derived temperatures determined a priori with an independent estimate of seawater composition, as well as with two organic geochemical proxies, demonstrates conclusively that the technique can be effective on carbonates as old as 50 m.y., despite concerns about the effects of diagenesis (Came et al., 2007; Dennis and Schrag, 2010). The Gulf Coast, however, is perhaps a best-case scenario, with sediments that have never been deeply buried or tectonically deformed. The narrower range of temperatures derived from the organic molecular proxies is likely due to attenuation of short-term variability by time averaging associated with sedimentation. The accretionary, in situ growth of shell carbonate instead records intraannual and interannual variation in conditions.

Paleotemperature estimates derived from TEX_{86} are often somewhat warmer than corresponding $\delta^{18}O$ or Mg/Ca-derived temperatures, raising concerns about temperature calibration, especially in high-latitude settings during greenhouse intervals (Huber, 2008). Several calibrations have been developed for deriving SST from TEX_{86} (Kim et al., 2010, 2008; Liu et al., 2009; Schouten et al., 2002) and it is not yet clear which is the most relevant relationship. The processes controlling the temperature dependence of archaeal lipid distributions are poorly understood, thereby preventing a process-based choice between calibrations. Early linear calibrations are likely problematic, as reflected by their inability to fit values at high-SST locations (Kim et al., 2010; Liu et al., 2009; Schouten et al., 2003), because physiological responses to temperature change are typically nonlinear. We therefore prefer the nonlinear, reciprocal relationship reported by Liu et al. (2009) that provides the simplest relationship covering the entire temperature range of modern core top data. This calibration results in lower temperatures than those derived through the logarithmic calibration of Kim et al. (2010) (Fig. 3). Our TEX_{86} derived temperatures using the Liu et al. (2009) calibration are consistent with those from clumped isotopes, lending support for that calibration (Fig. 3, inset). Although the MBT/CBT index proxy for continental temperatures is new and requires

further testing and calibration (Weijers et al., 2006), its agreement with the SST proxies in this case provides support for its application in low-lying coastal sediments rich in terrestrial soil organic matter.

A mean early Eocene paleotemperature of ~27 °C on the U.S. Gulf Coast is only 2–3 °C warmer than modern sea-surface MAT in the northern Gulf of Mexico (Levitus and Boyer, 1994) and is consistent with non–Paleocene-Eocene Thermal Maximum temperatures observed at a mid-latitude site to the north (New Jersey; Sluijs et al., 2007; Zachos et al., 2006). These temperatures are, however, as much as 4 °C cooler than recently reported early Eocene values at both lower and higher latitudes (Fig. 3). Tropical temperatures of ~31 °C (Tanzania; Pearson et al., 2007) are not necessarily in conflict with temperatures of 27 °C in the subtropics, but temperatures warmer than this at higher latitudes (New Zealand and the Tasman Rise; Bijl et al., 2009; Creech et al., 2010; Hollis et al., 2009) are more difficult to reconcile without considering potential unrecognized biases among proxies. Multiproxy temperature estimates from the U.S. Gulf Coast suggest warm, but not super-hot, paleotemperatures with low seasonal variation in the U.S. subtropics, provide further evidence for a reduced meridional temperature gradient during the early Eocene, and highlight the anomalous warmth implied by temperature reconstructions from the southwest Pacific Ocean.

REFERENCES CITED

Affek, H., and Eiler, J.M., 2006, Abundance of mass 47 CO_2 in urban air, car exhaust, and human breath: Geochimica et Cosmochimica Acta, v. 70, p. 1–12, doi:10.1016/j.gca.2005.08.021.

Bijl, P.K., Schouten, S., Sluijs, A., Reichart, G.-J., Zachos, J.C., and Brinkhuis, H., 2009, Early Palaeogene temperature evolution of the southwest Pacific Ocean: Nature, v. 461, p. 776–779, doi:10.1038/nature08399.

Came, R.E., Eiler, J.M., Veizer, J., Azmy, K., Brand, U., and Weidman, C.R., 2007, Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic Era: Nature, v. 449, p. 198–201, doi:10.1038/nature06085.

Creech, J.B., Baker, J.A., Hollis, C.J., Morgans, H.E.G., and Smith, E.G.C., 2010, Eocene sea temperatures for the mid-latitude southwest Pacific from Mg/Ca ratios in planktonic and benthic foraminifera: Earth and Planetary Science Letters, v. 299, p. 483–495, doi: 10.1016/j.epsl.2010.09.039.

Dennis, K.J., and Schrag, D.P., 2010, Clumped isotope thermometry of carbonatites as an indicator of diagenetic alteration: Geochimica et Cosmochimica Acta, v. 74, p. 4110–4122, doi:10.1016/j.gca.2010.04.005.

Fricke, H.C., and Wing, S.L., 2004, Oxygen isotope and paleobotanical estimates of temperature and $\delta^{18}O$-latitude gradients over North America during the early Eocene: American Journal of Science, v. 304, p. 612–635, doi:10.2475/ajs.304.7.612.

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., and Eiler, J.M., 2006, ^{13}C-^{18}O bonds in carbonate minerals: A new kind of paleothermometer: Geochimica et Cosmochimica Acta, v. 70, p. 1439–1456, doi:10.1016/j.gca.2005.11.014.

Grossman, E.L., and Ku, T.-L., 1986, Oxygen and carbon isotope fractionation in biogenic aragonite: Temperature effects: Chemical Geology, v. 59, p. 59–74, doi:10.1016/0168-9622(86)90057-6.

Harrington, G.J., 2003, Wasatchian (early Eocene) pollen floras from the Red Hot Truck Stop, Mississippi, USA: Palaeontology, v. 46, p. 725–738, doi:10.1111/1475-4983.00318.

Hollis, C.J., Handley, L., Crouch, E.M., Morgans, H.E.G., Baker, J.A., Creech, J., Collins, K.S., Gibbs, S.J., Huber, M., Schouten, S., Zachos, J.C., and Pancost, R.D., 2009, Tropical sea temperatures in the high-latitude South Pacific during the Eocene: Geology, v. 37, p. 99–102, doi:10.1130/G25200A.1.

Hopmans, E.C., Weijers, J.W.H., Schefuss, E., Herfort, L., Sinninghe Damste, J.S., and Schouten, S., 2004, A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoidal tetraether lipids: Earth and Planetary Science Letters, v. 224, p. 107–116, doi:10.1016/j.epsl.2004.05.012.

Huber, M., 2008, A hotter greenhouse?: Science, v. 321, p. 353–354, doi:10.1126/science.1161170.

Huntington, K.W., Eiler, J.M., Affek, H.P., Guo, W., Bonifacie, M., Yeung, L.Y., Thiagarajan, N., Passey, B., Tripati, A., Daëron, M., and Came, R., 2009, Methods and limitations of 'clumped' CO_2 isotope (Δ_{47}) analysis by gas-source isotope ratio mass spectrometry: Journal of Mass Spectrometry, v. 44, p. 1318–1329, doi:10.1002/jms.1614.

Ivany, L.C., Lohmann, K.C., and Patterson, W.P., 2003, Paleogene temperature history of the US Gulf Coastal Plain inferred from $\delta^{18}O$ of fossil otoliths, in Prothero, D.R., et al., eds., From greenhouse to icehouse: The marine Eocene-Oligocene transition: New York, Columbia University Press, p. 232–251.

Ivany, L.C., Wilkinson, B.H., Lohmann, K.C., Johnson, E.R., McElroy, B.J., and Cohen, G.J., 2004, Intra-annual isotopic variation in Venericardia bivalves: Implications for early Eocene temperature, seasonality, and salinity on the US Gulf Coast: Journal of Sedimentary Research, v. 74, p. 7–19, doi:10.1306/052803740007.

Kim, J.-H., Schouten, S., Hopmans, E.C., Donner, B., and Sinninghe Damste, J.S., 2008, Global sediment core-top calibration of the TEX_{86} paleothermometer in the ocean: Geochimica et Cosmochimica Acta, v. 72, p. 1154–1173, doi:10.1016/j.gca.2007.12.010.

Kim, J.-H., van der Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koç, N., Hopmans, E.C., and Damsté, 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, doi:10.1016/j.gca.2010.05.027.

Kobashi, T., and Grossman, E.L., 2003, The oxygen isotopic record of seasonality in Conus shells and its application to understanding late middle Eocene (38 Ma) climate: Paleontological Research, v. 7, p. 343–355, doi:10.2517/prpsj.7.343.

Kobashi, T., Grossman, E.L., Yancey, T.E., and Dockery, D.T., 2001, Reevaluation of conflicting Eocene tropical temperature estimates: Molluskan oxygen isotope evidence for warm low latitudes: Geology, v. 29, p. 983–986, doi:10.1130/0091-7613(2001)029<0983:ROCETT>2.0.CO;2.

Levitus, S., and Boyer, T., 1994, World Ocean Atlas Volume 4: Temperature: NOAA Atlas NESDIS 4: Washington, D.C., U.S. Government Printing Office, 117 p.

Liu, Z., Pagani, M., Zinniker, D., DeConto, R., Huber, M., Brinkhuis, H., Shah, S.R., Leckie, R.M., and Pearson, A., 2009, Global cooling during the Eocene-Oligocene climate transition: Science, v. 323, p. 1187–1190, doi:10.1126/science.1166368.

Müller, D., Gurnis, M., and Torsvik, T., 2011, GPlates version 1.0.1: http://www.gplates.org/.

Pearson, P.N., Ditchfield, P.W., Singano, J., Harcourt-Brown, K.G., Nicholas, C.J., Olsson, R.K., Shackleton, N.J., and Hall, M.A., 2001, Warm tropical sea surface temperatures in the Late Cretaceous and Eocene Epochs: Nature, v. 413, p. 481–487, doi:10.1038/35097000.

Pearson, P.N., van Dongen, B.E., Nicholas, C.J., Pancost, R.D., Schouten, S., Singano, J.M., and Wade, B.S., 2007, Stable warm tropical climate through the Eocene Epoch: Geology, v. 34, p. 211–214, doi:10.1130/G23175A.1.

Schouten, S., Hopmans, E.C., Schefuss, E., and Sinninghe Damste, J.S., 2002, Distributional variations in marine crenarchaeotal membrane lipids: A new tool for reconstructing ancient sea water temperatures?: Earth and Planetary Science Letters, v. 204, p. 265–274, doi:10.1016/S0012-821X(02)00979-2.

Schouten, S., Hopmans, E.C., Forester, A., van Breugel, Y., Kuypers, M.M.M., and Sinninghe Damste, J.S., 2003, Extremely high sea-surface temperatures at low latitudes during the middle Cretaceous as revealed by archaeal membrane lipids: Geology, v. 31, p. 1069–1072, doi:10.1130/G19876.1.

Schrag, D.P., 1999, Effects of diagenesis on the isotopic record of late Paleogene tropical sea surface temperatures: Chemical Geology, v. 161, p. 215–224, doi:10.1016/S0009-2541(99)00088-1.

Sluijs, A., and 15 others, 2006, Subtropical Arctic Ocean temperatures during the Paleocene/Eocene thermal maximum: Nature, v. 441, p. 610–613, doi:10.1038/nature04668.

Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S.M., John, C.M., Zachos, J.C., Reichart, 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, p. 1218–1221, doi:10.1038/nature06400.

van Roij, L., 2009, The Paleocene-Eocene Thermal Maximum in the Gulf of Mexico [M.S. thesis]: Utrecht, Netherlands, Utrecht University, 26 p.

Weijers, J.W.H., Schouten, S., Spaargaren, O.C., and Sinninghe Damste, J.S., 2006, Occurrence and distribution of tetraether membrane lipids in soils: Implications for the use of the BIT index and the TEX_{86} SST proxy: Organic Geochemistry, v. 37, p. 1680–1693, doi:10.1016/j.orggeochem.2006.07.018.

Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., and Sinninghe Damste, J.S., 2007, Environmental controls on bacterial tetraether membrane lipid distributions in soils: Geochimica et Cosmochimica Acta, v. 71, p. 703–713, doi:10.1016/j.gca.2006.10.003.

Wolfe, J.A., 1978, A paleobotanical interpretation of Tertiary climates in the Northern Hemisphere: American Scientist, v. 66, p. 694–703.

Wolfe, J.A., and Dilcher, D.L., 2000, Late Paleocene through middle Eocene climates in lowland North America: GFF, v. 122, p. 184–185, doi:10.1080/11035890001221184.

Zachos, J.C., Stott, L.D., and Lohmann, K.C., 1994, Evolution of early Cenozoic marine temperatures: Paleoceanography, v. 9, p. 353–387, doi:10.1029/93PA03266.

Zachos, J.C., Schouten, S., Bohaty, S.M., Quattlebaum, T., Sluijs, A., Brinkhuis, H., Gibbs, S.J., and Bralower, T.J., 2006, Extreme warming of mid-latitude coastal ocean during the Paleocene-Eocene Thermal Maximum: Inferences from TEX_{86} and isotope data: Geology, v. 34, p. 737–740, doi:10.1130/G22522.1.

WARM, NOT SUPER-HOT, TEMPERATURES IN THE

EARLY EOCENE SUBTROPICS

CAITLIN R. KEATING-BITONTI[1,3], LINDA C. IVANY[1], HAGIT P. AFFEK[2], PETER DOUGLAS[2], & SCOTT D. SAMSON[1]

SUPPLEMENTAL INFORMATION (SI)

Geological Background

The US Gulf Coastal Plain preserves a record of marine shelf deposition through the Paleogene characterized by excellent preservation of primary shell aragonite and minimal diagenesis. Sediments are generally unlithified even after 55 million years, and include fossils that offer great potential for isotope-derived climate information (2003; Ivany et al., 2004; Kobashi et al., 2001). Sampled bivalves come from the upper Hatchetigbee Member of the Hatchetigbee Formation, a highstand deposit consisting of fossiliferous, glauconitic, muddy sands grading up into thin, alternating beds of sand and clay suggesting estuarine conditions (Dockery, 1980; Gibson, 1982; Ivany et al., 2004; Mancini, 1984; Seisser, 1984; Toulmin, 1977). Bivalves were collected at Hatchetigbee Bluff on the Tombigbee River in Washington County, AL (Fig. S1). An early Eocene age is constrained biostratigraphically (Gibson, 1982; Mancini, 1984) and using Sr isotopes (see below). X-Ray diffraction demonstrates the retention of primary aragonite mineralogy, and scanning electron microscopy shows shell microtextures comparable to those of modern relatives (the genus *Cyclocardia*). Regular seasonal variation in shell

δ^{18}O with ontogeny argues strongly for preservation of original shell material and its isotopic signals in fossil mollusks (Ivany and Runnegar, 2010).

Strontium Isotope Ratios

The ^{87}Sr/^{86}Sr ratios of shell material were analyzed, anticipating that dark growth bands would be more radiogenic than light bands if the latter were formed under conditions of significant freshwater mixing. However, ratios from light and dark growth bands in multiple shells are statistically indistinguishable (Fig. S3) and fall within the expected range for normal marine seawater in the early Eocene (Hodell et al., 2007), suggesting that either the ^{87}Sr/^{86}Sr ratio of local runoff was close to the early Eocene marine value and/or that the Sr concentration in runoff was too low to have an impact on the ratio of the water mixture.

The age of the Hatchetigbee Formation can be further constrained by the ^{87}Sr/^{86}Sr ratios of the venericard bivalves relative to the global marine Sr isotope seawater curves of McArthur et al. (2001) and Hodell et al. (2007). The ^{87}Sr/^{86}Sr ratios of the Hatchetigbee Formation yield ages of ~52.5 to 54.5 Ma relative to the Hodell et al. (2007) curve, which has better coverage for the early Paleogene. These strontium isotope age estimates generally agree with the biostratigraphy of the US Gulf Coast.

Additional Insights from Inter-Proxy Comparisons: δ^{18}O and Clumped Isotopes

A significant limitation of the δ^{18}O-based temperature proxy has always been the need to make an assumption about the δ^{18}O value of the water from which the carbonate precipitated. Clumped isotopes analysis offers an independent paleotemperature estimate

that can then be used together with the measured mean winter shell $\delta^{18}O$ (-1.94‰) and the corrected biogenic aragonite-temperature equation of Grossman and Ku (1986; Kobashi and Grossman, 2003) to determine the oxygen isotope composition of seawater on the early Eocene Gulf Coast. The calculated seawater ('winter', or dry season) composition is -0.33‰, very close to the completely independent, latitude-corrected ice free value of -0.36‰ (based on Zachos et al., 1994), and thus providing support for the correction to global seawater composition at this latitude.

The degree to which temperature rather than salinity influences the 'summer' $\delta^{18}O$ values can be evaluated by comparing summer carbonate $\delta^{18}O$ with other independent temperature proxies. The mean clumped isotope paleotemperature of 27˚C in combination with 'summer' shell $\delta^{18}O$ values yield an average 'summer' water composition of -2.57‰. If fully marine waters of -0.36‰ mixed with freshwater runoff with a composition of about -4.7‰, based on comparisons with both modern precipitation and river water in the Gulf today, corrected for the ice free early Eocene (Ivany et al., 2004) to produce the measured 'summer' water values, the resulting mixture should have a salinity of, on average, ~17 ppt during the wet season. These seasonally brackish conditions are consistent with the low-diversity fauna and abundance of terrestrially-derived organic matter found in these sediments.

DETAILED METHODS

Stable Oxygen Isotopes

Two individuals of *Venericardia hatcheplata* from each of seven stratigraphic horizons were cut along the maximum growth axis from umbo to ventral margin and

polished. On average, 8 growth-band-parallel samples were milled from each couplet of light and dark growth bands in the inner shell layer using a Merchantek (New Wave) Micromill; earlier work showed that such couplets in Hatchetigbee Bluff venericards are annual in nature (Ivany et al., 2004). Within each bivalve, at least three full years of growth were sampled wherever possible. Resulting aragonite powders were analyzed for stable carbon and oxygen isotope values at the University of Michigan's Stable Isotope Laboratory on MAT 251 and 253 mass spectrometers. Analytical error was less than 0.2 per mil.

Oxygen isotope values are converted to paleotemperature using the biogenic aragonite-temperature equation of Grossman and Ku (1986), adjusted to correct for the difference between "average marine water" and standard mean ocean water (SMOW) $[T(\degree C) = 19.7 - 4.34 \times (\delta^{18}O_{CaCO3} - \delta_W)]$ (Kobashi and Grossman, 2003). A global mean $\delta^{18}O$ value for seawater (δ_W) of -1.0‰ is assumed, representing the ice free world of the early Eocene (Huber et al., 2003; Zachos et al., 1994); this value is then adjusted for latitudinal variation in salinity of the global ocean (Zachos et al., 1994) for 30$\degree$N (+0.68‰) yielding δ_W = -0.36‰).

Carbonate $\delta^{18}O$ local maxima and minima within each shell transect identify what are provisionally recognized as winters and summers, and the means of these provide estimates of mean winter temperature (MWT) and mean summer temperature (MST) within shells, horizons, and the entire section. Mean annual temperature (MAT) is the midpoint between MST and MWT, and mean annual range of temperature (MART) is the difference between them, at the various levels of resolution. Shell isotope profiles are not markedly asymmetric or scalloped, suggesting relatively continuous growth year-round.

Clumped Isotopes

The carbonate clumped isotopes technique yields paleotemperature estimates that are independent of the composition of the water from which the shell carbonate precipitated (Eiler, 2007; Ghosh et al., 2006), thereby circumventing concerns of freshwater mixing and other sources of variation in $\delta^{18}O_W$, and providing a less ambiguous temperature proxy. Aliquots from the same light and dark growth band increments of four of the venericard shells that were analyzed for oxygen isotopes, plus one additional venericard from the Hatchetigbee Formation not sampled for $\delta^{18}O$, were analyzed for clumped isotopes (Δ_{47}). Also analyzed were large bulk-shell samples that ranged across multiple years of growth from each of two bivalves to produce time-integrated average values. Samples were analyzed in 1-4 replicates for each growth band depending on material availability. We typically consider at least 3 replicates (of 3-4 mg each) to be required for a reliable temperature determination. To compensate for the small number of replicates possible in some samples due to the limited amount of carbonate available from individual growth bands, the results from all shells were pooled to yield a seasonal mean Δ_{47} value. This resulted in an estimated SST for the entire time period, even though the range of values suggests at least some short-term variability (at the scale of the 5-10 years lifetime of an individual shell) through the interval. Samples were measured over the course of a year (October 2009 to November 2010) and were normalized using a set of standards measured together with the samples (following Huntington et al., 2009).

Carbonate samples were measured for Δ_{47} values in the Earth Systems Center for

Stable Isotopic Studies at Yale University, using the same methodology described

previously (Affek and Eiler, 2006; Ghosh et al., 2006; Huntington et al., 2009).

Carbonate samples were digested by an overnight reaction with 105% phosphoric acid at

25˚C. Resulting CO_2 was purified cryogenically on a vacuum line using ethanol-dry ice

and liquid N_2 traps, and by passing it through a GC column (QPlot column, 30m long,

530 µm ID) at -20˚C. CO_2 was then analyzed by dual inlet for the abundance of masses

44 to 49 using a MAT-253 mass spectrometer with cup configuration that is identical to

that used for the original development of the clumped isotopes method (Eiler, 2007; Eiler

and Schauble, 2004).

Each CO_2 sample was analyzed 9 times. Each analysis consisted of 10 cycles of

sample standard-comparison with 20-second integration at a signal intensity of 12-16V

for mass 44. Δ_{47} is calculated from the measured ratios of masses 45, 46, and 47 to mass

44, as given in the following equation:

$$\Delta_{47} = \left[\frac{R^{47}}{2R^{13} \bullet R^{18} + 2R^{17} \bullet R^{18} + R^{13} \bullet (R^{17})^2} - \frac{R^{46}}{2R^{18} + 2R^{13} \bullet R^{17} + (R^{17})^2} - \frac{R^{45}}{R^{13} + 2R^{17}} + 1 \right] \times 1000$$

Data were standardized using a set of CO_2 samples that were heated at 1000˚C for

~2h, resulting in a random distribution of isotopes among all CO_2 isotopologues ($\Delta_{47} =$

0‰). This served as a correction for subtle non-linearity and to isotopic scrambling in

the ion source (for details see Huntington et al., 2009). Scrambling correction requires

knowing the unscrambled Δ_{47} value of the reference working gas. We determined the

value through measurements of Δ_{47} in CO_2 equilibrated with water at 25˚C, whose

nominal value is 0.871‰. This scrambling correction was validated using a set of

carbonate samples that have been previously analyzed (Affek et al., 2008; Ghosh et al., 2006) to give nominally defined values resulting in a mean offset of 0.009‰, comparable to the mean analytical standard error of 0.007‰ of these materials. This was further verified by measurements of CO_2 equilibrated with water at 10˚C, 25˚C, and 50˚C as part of an interlaboratory calibration, through comparison with theoretically determined values (Wang et al., 2004), resulting in a mean offset of 0.002‰ (Dennis et al., submitted).

The mass spectrometer raw data has a Gaussian distribution of 90 measurements of Δ_{47} values (for a single replicate), due to noise in ion collection by the mass spectrometer detectors. This results in internal analytical precision that is close to the shot noise limit (Merritt and Hayes, 1994), which is approximately 0.010‰ for the mass 47 signal measured under the conditions given above. Further improvement of precision is then possible through replicates (Huntington et al, 2009), which also improve errors associated with sample preparation (external precision). The typical external precision of the measurements can be estimated through multiple replicates of a laboratory standard (Carara marble) of about 0.004‰ (1 SE, n=49, analyzed between November 2008 and July 2010). This long-term external precision reflects a combination of mass spectrometer noise, and errors associated with long-term variability in standardization and with sample preparation. The mean standard error in the bivalve analysis described in this work is 0.010‰, equivalent to a paleotemperature error of approximately $\pm$ 2˚C.

Temperature estimates were calculated from Δ_{47} values using the calibration of Ghosh et al. (2006):

$\Delta_{47} = 0.0592$ x $10^6/T^2 - 0.02$ (where T is in K).

This calibration was originally developed using synthetic calcite (Ghosh et al., 2006), and has subsequently been verified for biogenic carbonates, including mollusk shells (Came et al., 2007) and a variety of other marine organisms grown at known temperatures (summarized by Tripati et al., 2010). To verify the Δ_{47}-T relationship for bivalves, we measured Δ_{47} values in shells of two modern bivalves from Long Island Sound (*Mytilus edulis*, the blue mussel, and *Crassostrea virginica*, the eastern oyster) (P. Douglas and H. Affek, unpublished). The Δ_{47}-derived temperatures are 17.5 ± 1.1 and $18.3 \pm 3.1°C$, respectively. Came et al. (2007) used a six-warm-month mean temperature as an approximation for bivalve shell growing season temperatures. The growing season for the Long Island Sound *M. edulis* is April to September with a mean temperature of $17.5°C$ (Hilbish, 1986), while the growing season for *C. virginica* is May to October with a mean temperature of $18.1°C$ (Dame, 1974). These growing season temperatures are in close agreement with the observed Δ_{47} derived temperatures, suggesting that indeed the shell is recording the conditions during growth. The $\delta^{18}O$ profiles from the early Eocene US Gulf Coast show year-round growth in venericard shells, suggesting that clumped isotopes reflect mean annual temperatures.

Tetraether Lipid Analyses

TEX$_{86}$ offers another independent and relatively new approach for determining paleotemperatures in marine sediments containing organic matter. Sediments enclosed within six pairs of articulated valves of *Venericardia*, two from each of three horizons, were sampled, processed, and analyzed separately for tetraethers in the Organic

Biogeochemistry and Paleoclimatology Laboratory at Yale University using methodology described previously (Schouten et al., 2002). Freeze dried sediment samples were extracted with a soxhlet extractor using a 2:1 dichloromethane:methanol solvent mixture. The lipid extracts were then separated into apolar, ketone, and polar fractions via silica gel pipette column chromatography. Glycerol dialkyl glycerol tetraether (GDGT) lipids were further purified via alumina pipette chromatography and filtered through 0.45 μm glass fiber filters. GDGTS were analyzed by high-performance liquid chromatography-mass spectrometry (HPLC/MS) on an Agilent 1100 series LC/MSD. A Prevail Cyano column was used with 99:1 hexane:isopropanol as eluent. TEX_{86} values were calculated using the formula of Schouten et al. (2002):

$$TEX_{86} = \frac{[GDGT2 + GDGT3 + crenarchaeol regioisomer]}{[GDGT1 + GDGT2 + GDGT3 + crenarchaeol regioisomer]}$$

TEX_{86} values were converted to SSTs using the non-linear calibration of Liu et al. (2009):

$$SST = 50.475 - 16.332(1/TEX_{86})$$

To assess differences between TEX_{86}-temperature calibrations, we also calculated SSTs using the high-temperature logarithmic calibration of Kim et al. (2010):

$$SST = 68.4[\log(TEX_{86})] + 38.6$$

For comparison purposes, paleotemperatures were also calculated using several alternative linear TEX_{86} calibrations (see Table S3 and references therein). The difference in SST estimates for two samples from the same stratigraphic horizon is less than 1˚C when using the Liu et al. (2009) calibration.

The Branched and Isoprenoid Tetraether Index, a proxy for terrestrial organic matter input to sediments, was calculated following Hopmans et al. (2004) to evaluate the potential for terrestrial organic matter input that could bias the TEX_{86}–derived temperatures:

$$BIT = \frac{[I + II + III]}{[I + II + III] + [IV]}$$

where compounds I, II, and III are branched GDGTs primarily derived from soil-dwelling bacteria, and compound IV is crenarcheol, an isoprenoidal GDGT primarily derived from marine archaea. Note that crenarcheol is a distinct compound from the crenarcheol regioisomer used in the calculation of TEX_{86} values.

Another novel proxy for terrestrial paleotemperatures, the MBT/CBT index, is based on the distribution of branched tetraether lipids derived from soil-dwelling bacteria. The methylation index of tetraethers (MBT) and cyclisation ratio of tetraethers (CBT) were calculated following Weijers et al. (2007). MBT indicates the degree of methylation at the C-5 and C-5' position of branched GDGTs and is calculated as follows:

$$MBT = \left[\frac{I + Ib + Ic}{\left(I + Ib + Ic\right) + \left(II + IIb + IIc\right) + \left(III + IIIb + IIIc\right)} \right]$$

where I, Ib, Ic, II, IIb, IIc, III, IIIb, and IIIc are branched tetraether lipids with varying degrees of methylation as described in Weijers et al. (2007). High MBT values indicate a low degree of methylation and reflect a combination of soil temperature and pH. CBT

indicates the abundance of cyclopentyl moieties in branched tetraethers and is calculated as follows:

$$CBT = \frac{[Ib]+[IIb]}{[I]+[II]}$$

High CBT ratios indicate increased cyclopentyl moieties and reflect soil pH. Terrestrial MAT estimates are calculated from the combination of MBT and CBT values using the empirical relationship of Weijers et al. (2007):

$$MAT = \frac{[MBT-(0.187\times CBT)-0.122]}{0.02}$$

Temperatures derived from these values reflect mean annual temperature in the continental regions that are sources for terrestrial organic matter in Hatchetigbee Formation sediments. As the MBT/CBT index is a relatively new temperature proxy and requires further testing, these particular temperature estimates should be considered preliminary.

Strontium Isotope Analyses

We measured $^{87}Sr/^{86}Sr$ in samples of light and dark ('winter' and 'summer') growth bands from a subset of venericards. Sample preparation for strontium isotope measurement is described in Ivany et al. (2006). Procedures for strontium separation, filament loading, and mass spectrometry followed Samson et al. (1995). Samples were analyzed on the Sector 54 thermal ionization mass spectrometer at the Syracuse University Radiogenic Isotope Laboratory. Ratios are compared to marine seawater

values reported by Hodell et al. (2007) for the early Eocene standardized using the NIST-987 standard.

Supplemental Tables

Table S1. Stable oxygen isotope values, δ^{18}O-calculated temperatures*, and calculated water δ^{18}O values† for local 'winter' maxima and 'summer' minima within shells from different horizons (see Fig. S2). Error estimates are ± 1 SD.

*Temperatures calculated assuming a latitude-corrected, local marine $\delta^{18}O_W$ value of -0.36‰ (see text). †Water values calculated using the clumped-isotope-derived mean temperature of 27˚C (Table S2). Individual milled data are available upon request.

Table S2. Clumped isotopes results for seasonal and bulk samples of bivalves, including inferred temperatures, associated δ^{13}C and δ^{18}O values of samples, and calculated water compositions based on those values.

*Equal to the mean of all shell data calculated from 'winter', 'summer', and bulk values. †Error estimates are ± 1 SE for replicate analyses of individual samples. In bold, errors are ± 1 SE of 'winter', 'summer' layers, or all data together.

Table S3. TEX$_{86}$ results and BIT index. Temperatures inferred based on calibrations in Liu et al. (2009), Schouten et al. (2002), Schouten et al., (2003; high temperature calibration), Kim et al. (2008), and Kim et al. (2010). Error estimates are ± 1 SD.

Table S4. MBT/CBT results and inferred temperatures. Error estimates are ± 1 SD.

Supplemental Figures

Figure S1. Stratigraphic, geographic, and morphologic details of sampled bivalves. **A)** Late Paleocene – early Eocene lithostratigraphic units and biostratigraphic zonations of southwest Alabama based on Mancini (1984). **B)** Map of outcrop area of the Hatchetigbee Formation in southern AL. Star represents location of Hatchetigbee Bluff. **C)** The bivalve *Venericardia hactheplata.*

Figure S2. Example of the variation in $\delta^{18}O$ of *Venericardia* carbonate sequentially sampled in the direction of shell growth. Shaded gray bars mark positions of dark (translucent) growth bands exposed in cross-section. Shell and corresponding $\delta^{18}O$ come from sample 6b from horizon 6.

Figure S3. Strontium isotope ratios for venericard shells in horizons 2, 4 and 6 measured in this study and the venericard from Ivany et al. (2004). Closed symbols represent dark growth bands corresponding to more negative $\delta^{18}O$ values and open symbols represent light growth bands corresponding to more positive $\delta^{18}O$ values. Gray band brackets ± 1 SE of the mean $^{87}Sr/^{86}Sr$ value for all Hatchetigbee Bluff samples. Range of early Eocene marine ratios reported by Hodell et al. (2007) indicated at right.

REFERENCES

Affek, H., and Eiler, J. M., 2006, Abundance of mass 47 CO_2 in urban air, car exhaust, and human breath: Geochimica et Cosmochimica Acta, v. 70, p. 1-12.

Affek, H. P., Bar-Matthews, M., Ayalon, A., Matthews, A., and Eiler, J. M., 2008, Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry: Geochimica et Cosmochimica Acta, v. 72, p. 5351-5360.

Came, R. E., Eiler, J. M., Veizer, J., Azmy, K., Brand, U., and Weidman, C. R., 2007, Coupling of surface temperatures and atmospheric CO_2 concentrations during the Palaeozoic Era: Nature, v. 449, p. 198-201.

Dame, R. F., 1974, The ecological energies of growth, respiration and assimilation in the intertidal American oyster *Crassostrea virginica*: Marine Biology, v. 17, p. 243-250.

Dennis, K. J., Affek, H., Passey, B. H., Schrag, D., and Eiler, J. M., submitted, Defining an absolute reference frame for 'clumped' isotope studies of CO_2: Geochimica et Cosmochimica Acta.

Dockery, D. T., 1980, The invertebrate macropaleontology of the Clarke County, Mississippi, area: Mississippi Department of Natural Resources Bureau of Geology Bulletin, v. 122, p. 387.

Eiler, J. M., 2007, "Clumped-isotope" geochemistry - The study of naturally-occurring, multiply-substituted isotopologues: Earth and Planetary Science Letters, v. 262, p. 309-327.

Eiler, J. M., and Schauble, E. A., 2004, $^{18}O^{13}C^{16}O$ in Earth's atmosphere: Geochimica et Cosmochimica Acta, v. 68, p. 4767-4777.

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E. A., Schrag, D., and Eiler, J. M., 2006, ^{13}C-^{18}O bonds in carbonate minerals: A new kind of paleothermometer: Geochimica et Cosmochimica Acta, v. 70, p. 1439-1456.

Gibson, T. G., 1982, Revision of the Hatchetigbee and Bashi Formations (Lower Eocene) in the Eastern Gulf Coastal Plain: U.S. Geological Survey Bulletin, v. 1529-H, p. H33-H41.

Grossman, E. L., and Ku, T.-L., 1986, Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects: Chemical Geology, v. 59, p. 59-74.

Hilbish, T. J., 1986, Growth trajectories for shell and soft tissue in bivalves: seasonal variation in *Mytilus edulis* Journal of Experimental Marine Biology and Ecology, v. 96, p. 103-113.

Hodell, D. A., Kamenov, G. D., Hathorne, E. C., Zachos, J. C., Röhl, U., and Westerhold, T., 2007, Variations in the strontium isotope composition of seawater during the Paleocene and early Eocene from ODP Leg 208 (Walvis Ridge): Geochemistry Geophysics Geosystems, v. 8, no. 9, p. Q09001, doi:09010.01029/02007GC001607.

Hopmans, E. C., Weijers, J. W. H., Schefuss, E., Herfort, L., Sinninghe Damste, J. S., and Schouten, S., 2004, A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoidal tetraether lipids: Earth and Planetary Science Letters, v. 224, p. 107-116.

Huber, M., Sloan, L., and Shellito, C., 2003, Early Paleogene oceans and climate: A fully coupled modeling approach using the NCAR CCSM, *in* Wing, S. L., Gingerich, P. D., Schmitz, B., and Thomas, E., eds., Causes and Consequences of Globally Warm

Climates in the Early Paleogene, Volume Special Paper 369: Boulder, CO, Geological Society of America, p. 25-47.

Huntington, K. W., Eiler, J. M., Affek, H. P., Guo, W., Bonifacie, M., Yeung, L. Y., Thiagarajan, N., Passey, B., Tripati, A., Daëron, M., and Came, R., 2009, Methods and limitations of 'clumped' CO_2 isotope ($\Delta 47$) analysis by gas-source isotope ratio mass spectrometry: Journal of Mass Spectrometry, v. 44, p. 1318-1329.

Ivany, L. C., Lohmann, K. C., and Patterson, W. P., 2003, Paleogene temperature history of the US Gulf Coastal Plain inferred from $\delta^{18}O$ of fossil otoliths, *in* Prothero, D. R., Ivany, L. C., and Nesbitt, E., eds., From Greenhouse to Icehouse: the Marine Eocene-Oligocene Transition: New York, Columbia University Press, p. 232-251.

Ivany, L. C., and Runnegar, B., 2010, Early Permian seasonality from bivalve $\delta^{18}O$ and implications for the oxygen isotopic composition of seawater: Geology, v. 38, no. 11, p. 1027-1030.

Ivany, L. C., Van Simaeys, S., Domack, E. W., and Samson, S. D., 2006, Evidence for an earliest Oligocene ice sheet on the Antarctic Peninsula: Geology, v. 34, p. 377-380.

Ivany, L. C., Wilkinson, B. H., Lohmann, K. C., Johnson, E. R., McElroy, B. J., and Cohen, G. J., 2004, Intra-annual isotopic variation in *Venericardia* bivalves: Implications for early Eocene temperature, seasonality, and salinity on the US Gulf Coast: Journal of Sedimentary Research, v. 74, p. 7-19.

Kim, J.-H., Meer, J. v. d., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koç, N., Hopmans, E. C., and Damsté, 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.

Kobashi, T., and Grossman, E. L., 2003, The oxygen isotopic record of seasonality in *Conus* shells and its application to understanding late middle Eocene (38 Ma) climate: Paleontological Research, v. 7, no. 4, p. 343-355.

Kobashi, T., Grossman, E. L., Yancey, T. E., and Dockery, D. T., 2001, Reevaluation of conflicting Eocene tropical temperature estimates: Molluskan oxygen isotope evidence for warm low latitudes: Geology, v. 29, no. 11, p. 983-986.

Liu, Z., Pagani, M., Zinniker, D., DeConto, R., Huber, M., Brinkhuis, H., Shah, S. R., Leckie, R. M., and Pearson, A., 2009, Global cooling during the Eocene-Oligocene climate transition: Science, v. 323, p. 1187-1190.

Mancini, E. A., 1984, Biostratigraphy of Paleocene strata in southwestern Alabama: Micropaleontology, v. 30, p. 268-291.

McArthur, J. M., Howarth, R. J., and Bailey, T. R., 2001, Strontium isotope stratigraphy: LOWESS Version 3: Best fit to the marine Sr-isotope curve for 0-509 Ma and accompanying look-up table for deriving numerical age: The Journal of Geology, v. 109, p. 155-170.

Merritt, D. A., and Hayes, J. M., 1994, Factors controlling precision and accuracy in isotope-ratio-monitoring mass spectrometry: Analytical Chemistry, v. 66, p. 2336-2347.

Samson, S. D., Matthews, S. V. L., Mitchell, C. E., and Goldman, D., 1995, Tephrochronology of highly altered ash beds: The use of trace element and strontium isotope geochemistry of apatite phenocrysts to correlate K-bentonites: Geochimica et Cosmochimica Acta, v. 59, p. 2527-2536.

Schouten, S., Hopmans, E. C., Schefuss, E., and Sinninghe Damste, J. S., 2002, Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures?: Earth and Planetary Science Letters, v. 204, p. 265-274.

Seisser, W. G., 1984, Paleogene sea levels and climates: U.S.A. Eastern Gulf Coastal Plain: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 47, p. 261-275.

Toulmin, L. D., 1977, Stratigraphic Distribution of Paleocene and Eocene Fossils in the Eastern Gulf Coast Region, Volumes 1 and 2, Geological Survey of Alabama Monograph, 602 p.:

Tripati, A. K., Eagle, R. A., Thiagarajan, N., Gagnon, A. C., Bauch, H., Halloran, P. R., and Eiler, J. M., 2010, ^{13}C-^{18}O isotope signatures and 'clumped isotope' thermometry in foraminifera and coccoliths: Geochimica et Cosmochimica Acta, v. 74, p. 5697-5717.

Wang, Z., Schauble, E. A., and Eiler, J. M., 2004, Equilibrium thermodynamics of multiply-substituted isotopologues of molecular gases: Geochimica et Cosmochimica Acta, v. 68, p. 4779-4797.

Weijers, J. W. H., Schouten, S., van den Donker, J. C., Hopmans, E. C., and Sinninghe Damste, J. S., 2007, Environmental controls on bacterial tetraether membrane lipid distributions in soils: Geochimica et Cosmochimica Acta, v. 71, p. 703-713.

Zachos, J. C., Stott, L. D., and Lohmann, K. C., 1994, Evolution of early Cenozoic marine temperatures: Paleoceanography, v. 9, no. 2, p. 353-387.

WARM, NOT SUPER-HOT, TEMPERATURES IN THE

EARLY EOCENE SUBTROPICS

CAITLIN R. KEATING-BITONTI[1,3], LINDA C. IVANY[1], HAGIT P. AFFEK[2], PETER DOUGLAS[2],

& SCOTT D. SAMSON[1]

SUPPLEMENTAL INFORMATION (SI)

Supplemental Tables

Table S1.

Horizon	'winter' $\delta^{18}O_C$ (PDB)	'winter' Temp (˚C)	'winter' $\delta^{18}O_W$ (SMOW)	'summer' $\delta^{18}O_C$ (PDB)	'summer' Temp (˚C)	'summer' $\delta^{18}O_W$ (SMOW)
7	-2.1	27.3	-0.487	-4.06	35.8	-2.447
	-1.48	24.6	0.133	-4.19	36.3	-2.577
	-1.74	25.7	-0.127	-3.63	33.9	-2.017
	-2	26.8	-0.387	-4.24	36.5	-2.627
	-2.36	28.4	-0.747	-4.27	36.7	-2.657
	-1.59	25.0	0.023	-3.65	34.0	-2.037
6	-1.82	26.0	-0.207	-3.58	33.67	-1.97
	-2.11	27.3	-0.497	-3.02	31.24	-1.41
	-2.1	27.3	-0.487	-3.01	31.20	-1.40
	-2.39	28.5	-0.777	-3.24	32.20	-1.63
	-1.76	25.8	-0.147	-4.41	37.28	-2.80
	-2.34	28.3	-0.727	-4.01	35.54	-2.40
5	-1.67	25.4	-0.057	-4.95	39.6	-3.337
	-2.1	27.3	-0.487	-5.74	43.0	-4.127
4	-2.19	27.6	-0.577	-4.96	39.7	-3.347
	-1.95	26.6	-0.337	-4.95	39.6	-3.337
	-2.06	27.1	-0.447	-4.08	35.8	-2.467
	-1.9	26.4	-0.287	-4.01	35.5	-2.397
	-2.21	27.7	-0.597	-4.78	38.9	-3.167
	-1.86	26.2	-0.247	-4.68	38.4	-3.067
3	-2.08	27.2	-0.467	-3.52	33.4	-1.907
	-1.72	25.6	-0.107	-4.56	37.9	-2.947
	-1.49	24.6	0.123	-4.27	36.7	-2.657
	-1.41	24.3	0.203	-5.34	41.3	-3.727
	-2.27	28.0	-0.657	-3.61	33.8	-1.997
	-2.03	26.9	-0.417	-4.32	36.9	-2.707
	-2.02	26.9	-0.407	-4	35.5	-2.387
2	-1.94	26.6	-0.327	-5.2	40.7	-3.587
	-1.77	25.8	-0.157	-5.2	40.7	-3.587
1	-2.21	27.7	-0.597	-3.75	34.4	-2.137
	-1.62	25.2	-0.007	-3.59	33.7	-1.977
	-2.17	27.6	-0.557	-4.35	37.0	-2.737
	-1.68	25.4	-0.067	-3.82	34.7	-2.207
	-1.81	26.0	-0.197	-3.85	34.8	-2.237
	-2.01	26.9	-0.397	-3.45	33.1	-1.837
Average	**-1.94** ± 0.26	**26.6** ± 1.1	**-0.33** ± 0.26	**-4.18** ± 0.67	**36.3** ± 2.9	**-2.57** ± 0.67

Table S2.

'winter' (light growth band) samples	n	Δ_{47} †	Temperature (°C)	$\delta^{13}C_C$ (PDB)	$\delta^{18}O_C$ (PDB)	$\delta^{18}O_W$ (SMOW)
4a	3	0.647 ± 0.005	24.8	-0.04	-2.41	-1.38
2a	3	0.650 ± 0.015	24.0	-1.24	-2.49	-1.50
1b	4	0.631 ± 0.014	28.3	-0.12	-2.64	-0.66
1c	1	0.618	31.4	-0.03	-2.73	-0.03
Average	**4**	**0.637 ± .007**	**27.1 ± 1.7**	**-0.36**	**-2.57**	**-0.89**
'summer' (dark growth band) samples	n	Δ_{47}	Temperature (°C)	$\delta^{13}C_C$ (PDB)	$\delta^{18}O_C$ (PDB)	$\delta^{18}O_W$ (SMOW)
4a	3	0.650 ± 0.014	24.2	0.14	-4.04	-3.15
2a	3	0.665 ± 0.010	20.8	-1.61	-4.16	-3.92
1b	3	0.641 ± 0.008	26.1	-0.67	-3.35	-1.89
1c	2	0.620 ± 0.005	31.0	-1.17	-4.18	-1.58
Average	**4**	**0.644 ± .009**	**25.5 ± 2.1**	**-0.83**	**-3.93**	**-2.63**
Bulk Shell	n	Δ_{47}	Temperature (°C)	$\delta^{13}C_C$ (PDB)	$\delta^{18}O_C$ (PDB)	$\delta^{18}O_W$ (SMOW)
4a	4	0.638 ± 0.013	26.3	-0.06	-3.92	-2.30
2b	4	0.634 ± 0.006	27.8	-1.59	-2.94	-1.08
ALL*	**10**	**0.639 ± 0.005**	**26.5 ± 1.0**	**-0.64**	**-3.29**	**-1.75**

Table S3.

Horizon	TEX$_{86}$	Temp °C (Liu 2009)	Temp °C (Schouten 2002)	Temp °C (Schouten 2003)	Temp °C (Kim 2008)	Temp °C (Kim 2010)	BIT
4a	0.74	28.4	30.7	28.0	30.8	29.7	0.36
4b	0.73	28.2	30.2	27.7	30.4	29.4	0.30
4	**0.74 ± .007**	**28.3 ± 0.1**	**30.4 ± 0.4**	**27.9 ± 0.2**	**30.6 ± 0.3**	**29.5 ± 0.2**	**0.33 ± 0.4**
3a	0.77	29.2	32.6	29.1	32.4	30.8	0.37
3b	0.76	29.0	32.1	28.8	32.0	30.5	0.41
3	**0.77 ± .007**	**29.1 ± 0.1**	**32.3 ± 0.4**	**28.9 ± 0.2**	**32.2 ± 0.3**	**30.6 ± 0.2**	**0.39 ± 0.3**
2a	0.69	26.8	27.4	26.2	28.0	27.6	0.39
2b	0.74	28.4	30.8	28.1	30.9	29.7	0.37
2	**0.72 ± .03**	**27.6 ± 1.1**	**29.1 ± 2.4**	**27.1 ± 1.3**	**29.5 ± 2.0**	**28.7 ± 1.5**	**0.38 ± 0.01**
ALL	**0.74 ± .03**	**28.3 ± 0.8**	**30.6 ± 1.8**	**28.0 ± 1.0**	**30.8 ± 1.5**	**29.6 ± 1.1**	**0.37 ± .03**

Table S4.

Horizon	MBT	CBT	pH	Temp ˚C
4a	0.76	0.70	6.93	25.2
4b	0.76	0.59	7.21	26.6
				25.9 ± 0.7
3a	0.78	0.68	6.97	26.5
3b	0.81	0.69	6.94	28.1
				27.3 ± 0.8
2a	0.78	0.73	6.85	26.3
2b	0.82	0.73	6.84	28.3
				27.3 ± 1.0
ALL	0.79 ± 0.03	0.69 ± 0.05	6.96 ± 0.1	**26.83** ± 1.2