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Merging late Holocene molecular organic and foraminiferal-based geochemical records of sea surface temperature in the Gulf of Mexico

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[1] A molecular organic geochemical proxy (TEX_{86}) for sea surface temperature (SST) is compared with a foraminifera-based SST proxy (Mg/Ca) in a decadal-resolution marine sedimentary record spanning the last 1000 years from the Gulf of Mexico. We assess the relative strengths of the organic and inorganic paleoceanographic techniques for reconstructing high-resolution SST variability during recent climate events, including the Little Ice Age (LIA) and the Medieval Warm Period (MWP). SST estimates based on the molecular organic proxy TEX_{86} show a similar magnitude and pattern of SST variability to foraminiferal Mg/Ca-SST estimates but with some important differences. For instance, both proxies show a cooling (1°C–2°C) of Gulf of Mexico SSTs during the LIA. During the MWP, however, Mg/Ca-SSTs are similar to near-modern SSTs, while TEX_{86} indicates SSTs that were cooler than modern. Using the respective SST calibrations for each proxy results in TEX_{86}-SST estimates that are 2°C–4°C warmer than Mg/Ca-SST throughout the 1000 year record. We interpret the TEX_{86}-SST as a summer-weighted SST signal from the upper mixed layer, whereas the Mg/Ca-SST better reflects the mean annual SST. Downcore differences in the SST estimates between the two proxies ($\Delta T = TEX_{86} - Mg/Ca$) are interpreted in the context of varying seasonality and/or changing water column temperature gradients.

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1. Introduction

[2] Accurate reconstruction of the spatial and temporal patterns of sea surface temperature (SST) variability in the low latitude oceans is critical to understanding the range of natural climate variability over the past millennium. While the low latitude oceans are a major source of heat and moisture to the middle and high latitudes, global and hemispheric climate reconstructions are predominantly based on extratropical terrestrial proxy records [cf. *National Research Council*, 2006]. There are few locations in the low latitude oceans from which continuous decadal resolution SST proxy records covering the past 1000 years have been published [*Lund and Curry*, 2006; *Newton et al.*, 2006; *Richey et al.*, 2007; *Black et al.*, 2007; *Oppo et al.*, 2009]. These SST reconstructions, although widely distributed geographically, all show significant SST fluctuations (1°C–2°C) over the past 1000 years.

[3] Paleoclimate records from the Atlantic Warm Pool (AWP), which includes much of the western tropical/subtropical Atlantic Ocean, provide further evidence for significant climate fluctuations over the past 6 centuries [cf. *Richey et al.*, 2009]. The AWP is defined by the >28.5°C SST isotherm, and encompasses the northern Caribbean, Gulf of Mexico (GOM) and western tropical North Atlantic during the summer [cf. *Wang et al.*, 2008]. Multidecadal variability in the size/intensity of the AWP is correlated with rainfall anomalies in the Caribbean region, formation and intensification of North Atlantic hurricanes, and variability in moisture transport to the North American continent via interactions with atmospheric circulation [*Wang et al.*, 2008].

[4] A number of geochemical proxy records from the region encompassed by the AWP provide evidence for a large (2°C–3°C) cooling during the LIA (circa 400–150 years B.P.) [*Winter et al.*, 2000; *Watanabe et al.*, 2001; *Nyberg et al.*, 2002; *Haase-Schramm et al.*, 2003; *Richey et al.*, 2007; *Black et al.*, 2007; *Kilbourne et al.*, 2008; *Richey et al.*, 2009]. However, two additional SST proxy records from within the AWP show a subtler LIA cooling (~1°C): A Mg/Ca-SST record from a sediment core from the Great Bahamas Bank [*Lund and Curry*, 2006], and a coral growth rate-based SST record from the Bahamas [*Saenger et al.*, 2009]. Additional multiproxy studies are needed to determine whether the discrepancies observed are real regional differences in the climate response during the LIA, or whether there are site- and proxy-specific factors that are influencing the SST records.

[5] Presently, there are four viable SST proxies derived from marine sedimentary archives: $U^{K'}_{37}$, TEX_{86}, foraminiferal Mg/Ca, and foraminiferal $\delta^{18}O$. The $U^{K'}_{37}$ index, an organic geochemical SST proxy based on the ratio of long-chain diunsaturated ($C_{37:2}$) to triunsaturated ($C_{37:3}$) alkenones

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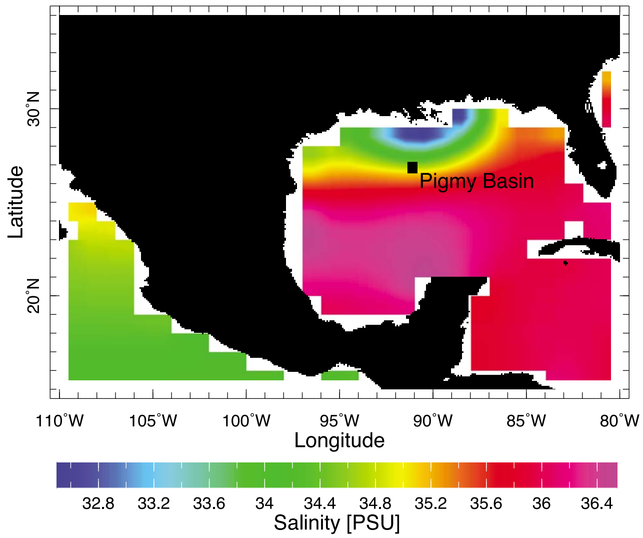

Figure 1. Map of the Gulf of Mexico, indicating the location of the Pigmy Basin (27°11.61′N, 91°24.54′W, 2259 m water depth). Mean annual surface salinity (1° × 1° grid) is plotted from the World Ocean Atlas 2005 (WOA05) data set [*Antonov et al.*, 2006]. The low-salinity anomaly in the northern Gulf of Mexico is the result of freshwater input from the Mississippi River and can cause salinity in the waters overlying the Pigmy Basin to be up to 1 psu lower that the central Gulf of Mexico.

[*Brassell et al.*, 1986], is not ideal in low latitude marine settings where SSTs exceed 28°C. The $U_{37}^{K'}$-temperature relationship is not well known at temperatures exceeding 28°C, as the ratio approaches a value of 1 [*Prahl and Wakeham*, 1987]. Determination of the $U_{37}^{K'}$ index in warm regions is also difficult due to the analytical challenges of measuring very small concentrations of $C_{37:3}$ relative to the $C_{37:2}$ [cf. *Pelejero and Calvo*, 2003]. Although *Jasper and Gagosian* [1989] generated a low-resolution 100 kyr $U_{37}^{K'}$-SST record from Pigmy Basin sediments, there are insufficient alkenone concentrations in late Holocene Pigmy Basin sediments to provide an SST record of the past 1000 years.

[6] A novel molecular organic SST proxy, TEX_{86} (the TetraEther IndeX of tetraethers with 86 carbon atoms), is based on the relative abundance of isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs) with varying numbers of cyclopentane moieties [*Schouten et al.*, 2002]. GDGTs are membrane lipids biosynthesized by marine Crenarchaeota, and the number of cyclopentane moieties in these crenarchaeotal membrane lipids has been observed to increase with increasing growth temperature [*Wuchter et al.*, 2004]. Although Crenarchaeota are ubiquitous throughout the water column [*Karner et al.*, 2001] and have been found living deep within subsurface sediments [*Lipp et al.*, 2008], TEX_{86} has been shown to correlate linearly with mean annual SST [*Schouten et al.*, 2002; *Kim et al.*, 2008] throughout the global oceans. Mesocosm studies suggest that salinity and nutrients do not significantly influence TEX_{86} measurements [*Wuchter et al.*, 2004]. It has been shown that terrestrial organic matter often contains isoprenoid GDGTs [*Weijers et al.*, 2006], and thus, TEX_{86}-SST estimates may be biased in marine settings with large terrestrial input. However, the contribution of terrestrial relative to marine GDGTs can be monitored downcore via the branched to isoprenoid tetraether (BIT) index [*Hopmans et al.*, 2004].

[7] Foraminiferal $\delta^{18}O$ and Mg/Ca have been widely accepted as SST proxies. The $\delta^{18}O$ is a function of both temperature and the oxygen isotopic composition of seawater, therefore the temperature signal can be confounded by changes in salinity or global ice volume. Factors such as diagenetic overgrowths [e.g., *Boyle*, 1983; *Barker et al.*, 2003; *Pena et al.*, 2005], salinity [e.g., *Nürnberg et al.*, 1996; *Ferguson et al.*, 2008] and dissolution [e.g., *Dekens et al.*, 2002] have been shown to influence the Mg/Ca of foraminiferal calcite. In this study we present the first direct comparison of foraminiferal Mg/Ca with a molecular organic (TEX_{86}) SST proxy, from co-occurring sediments in a decadally resolved 1000 year long sedimentary record from the Gulf of Mexico. Using a multiproxy approach we can better constrain the effects of the local ecology and other oceanographic factors on each paleothermometer. Coupling the new TEX_{86} record with the previously published Mg/Ca record from the Pigmy Basin [*Richey et al.*, 2007] expands our ability to assess SST conditions, and thus will provide a more complete picture of regional ocean climate variability (e.g., seasonality, vertical temperature gradients) during the late Holocene.

2. Study Location

[8] The location of our study is the Pigmy Basin, an intraslope basin located in the northern Gulf of Mexico (27°11.61′N, 91°24.54′W, water depth 2259 m), ~200 km south of the Mississippi River mouth (Figure 1). The Mg/Ca and TEX_{86} records discussed in this study are derived from two different subcores (PBBC-1E and PBBC-1F, respectively) isolated from a single box core recovered from the Pigmy Basin in 2003 aboard the R/V *Longhorn*. Sedimentation rates during the late Holocene are relatively high (43 cm/kyr) as a result of the large volume of terrigenous material delivered via the Mississippi River. The high sedimentation rate combined with a 0.5 cm sampling interval allow for detailed study of multidecadal to centennial-scale climate variability of the past millennium.

[9] An age model was constructed for subcore PBBC-1E based on 7 accelerator mass spectrometer radiocarbon dates on planktonic foraminifera [*Richey et al.*, 2007]. Calibrated calendar ages (calibrated using the CALIB 5.0 program with a 400 year reservoir correction [*Stuiver et al.*, 1998]) were plotted against core depth, and a least squares linear regression (r^2 = 0.995) indicates a sedimentation rate of 43 cm/kyr. The core top radiocarbon date indicates post-1950 deposition, and therefore we infer a near-modern core top. The age model for PBBC-1E was projected onto subcore PBBC-1F (i.e., the core top age was set to 0 years B.P., and a 12.3 year interval was assigned to each 0.5 cm sample). The discrepancy between the lengths of the two subcores (PBBC-1E is 59 cm long and PBBC-1F is 44 cm long) is due to their relative positions within the box core. The shovel of the box core is curved such that cores taken in the center of the

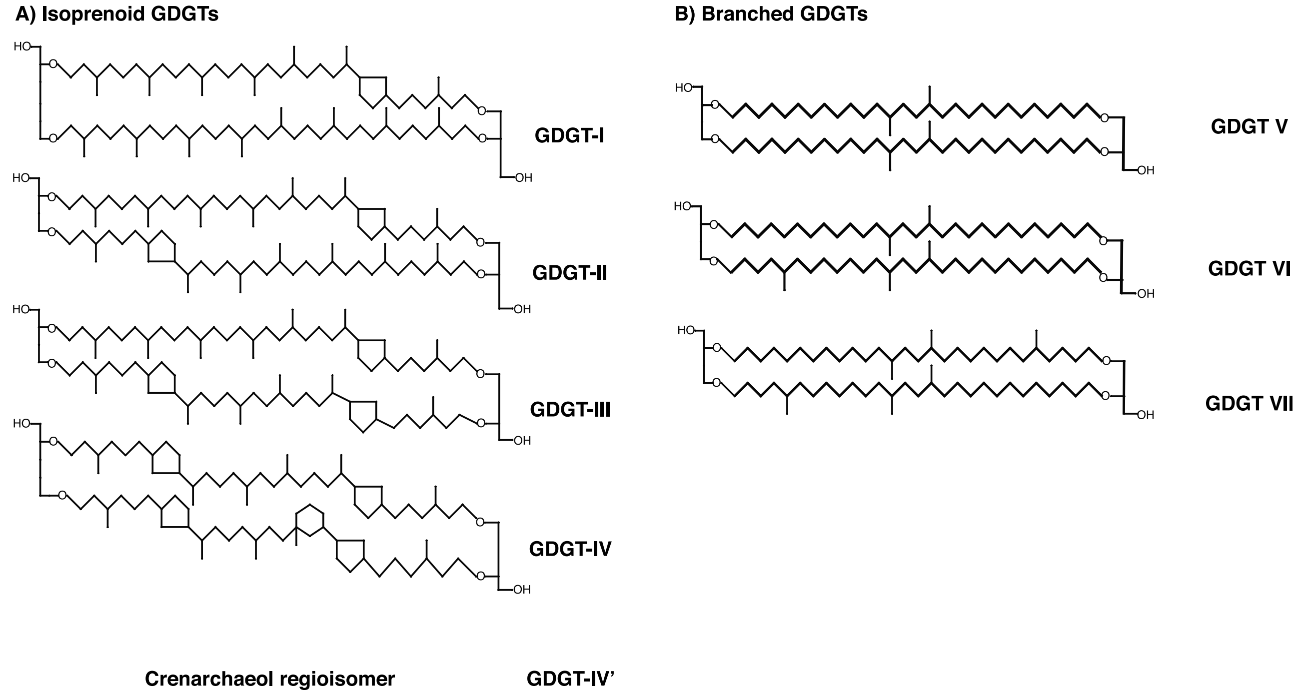

Figure 2. Molecular structures of the (a) isoprenoid and (b) branched glycerol dialkyl glycerol tetraethers (GDGTs) used in the TEX_{86} [*Schouten et al.*, 2002] and BIT [*Hopmans et al.*, 2004] indices.

box core are longer than core taken on the sides of the box core.

3. Methods

3.1. Extraction and Isolation of GDGTs

[10] Core PBBC-1F was sampled at 0.5 cm intervals and freeze-dried. Samples were solvent extracted with a DIONEX Accelerated Solvent Extractor (ASE 200) using a solvent mixture of 9:1 dichloromethane (DCM) to methanol (MeOH) at the College of Marine Science, University of South Florida. The resulting total lipid extract (TLE) then underwent a base hydrolysis (in 0.5 M KOH in MeOH), and was separated into an acid and neutral fraction via liquid-liquid extraction under neutral and acidic conditions, respectively. The neutral fraction was then separated into an apolar, ketone and polar fraction via silica pipette column chromatography using hexane, 3:2 (vol:vol) hexane/DCM, and 1:1 (vol:vol) DCM/MeOH, respectively.

3.2. TEX_{86} and BIT Analysis

[11] The polar fraction, containing the GDGTs, was dissolved in a 99:1 (vol:vol) mixture of hexane:propanol, then filtered through 0.45 μm PFTE filters. Analyses of GDGTs for TEX_{86} and BIT index determination were performed by high-pressure liquid chromatography-mass spectrometry (HPLC-MS) at the Woods Hole Oceanographic Institution. Samples were analyzed on an Agilent 1200 series LC/MSD SL operating in positive APCI mode, with an autoinjector and Chemstation software. A Prevail Cyano column (150 × 2.1 mm, 3 μm from Grace Davison Discovery Sciences) was used with 99:1 hexane:isopropanol (vol:vol) as an eluent. After the first 5 min, the eluent increased by a linear gradient up to 1.8% isopropanol (vol) over the next 45 min at a flow rate of 0.2 mL/min. Scanning was performed in single ion monitoring (SIM).

[12] The TEX_{86} and BIT indices were calculated according to the following equations [from *Schouten et al.*, 2002]:

$$TEX_{86} = \left([II] + [III] + \left[IV'\right]\right)/[I] + [II] + [III] + \left[IV'\right])$$

[from *Hopmans et al.*, 2004]

$$BIT = ([V] + [VI] + [VII])/([V] + [VI] + [VII] + [IV])$$

where the roman numerals refer to the GDGT structures shown in Figure 2. In the most recent TEX_{86}-SST calibration, *Kim et al.* [2010] suggest using separate equations for subpolar versus subtropical regions. In the case of the Pigmy Basin, it is appropriate to use the $TEX^{H}{}_{86}$ index (which is simply the logarithm of the TEX_{86} index from *Schouten et al.* [2002]) with the following SST equation [from *Kim et al.*, 2010]:

$$SST(^{\circ}C) = 68.4 * TEX^{H}_{86} + 38.6$$

Each of the 88 GDGT samples in this study was analyzed in triplicate. The average standard deviation for TEX_{86} among triplicate analyses is ±0.007, which corresponds to ±0.4°C

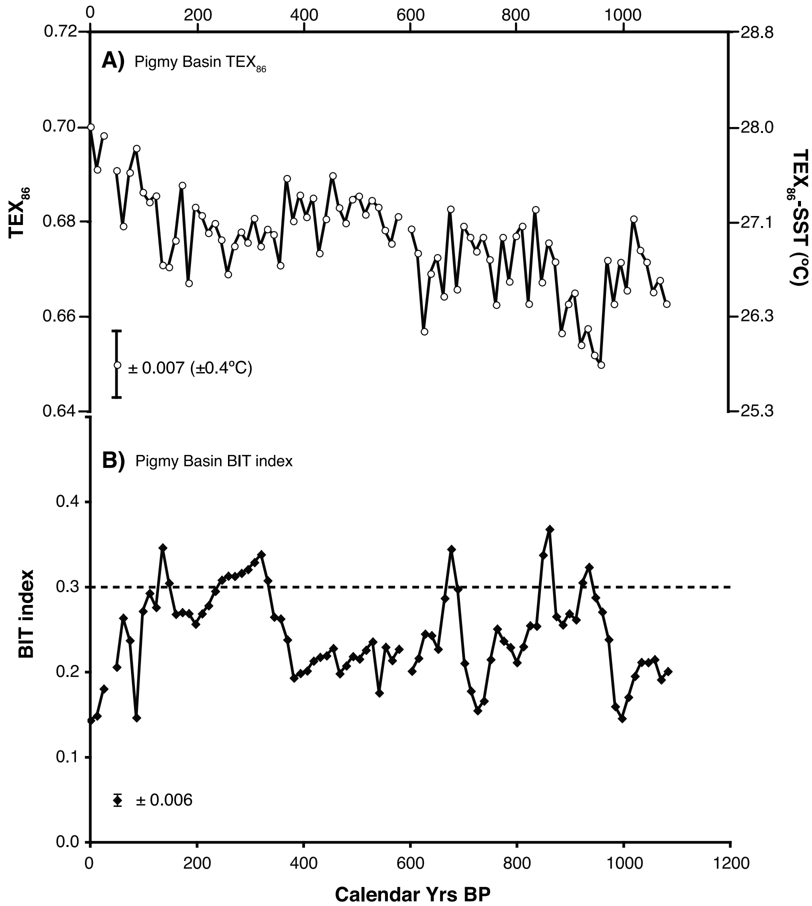

Figure 3. GDGT-based proxy records for a Pigmy Basin box core (PBBC-1F). (a) TEX_{86} record with corresponding temperature scale, calibrated using the equation SST = 68.4 * (TEX^{H}_{86}) + 38.6, from *Kim et al.* [2010]. The pooled standard deviation of triplicate TEX_{86} measurements is indicated (±0.007) which corresponds to ±0.4°C. (b) BIT index for PBBC-1F. The pooled standard deviation among triplicate analyses is ±0.006. The dashed lined indicates the threshold BIT value of 0.3, above which input of terrestrial organic matter may influence TEX_{86} [*Weijers et al.*, 2006].

using the calibration equation of *Kim et al.* [2010]. For the BIT index, the average standard deviation among triplicates is ±0.006.

4. Results and Discussion

4.1. TEX_{86}-SST Record From Pigmy Basin

[13] The TEX_{86} record from the Pigmy Basin indicates significant SST fluctuations over the past 1000 years (Figure 3a) and varies between 0.65 and 0.70 (25.8°C–28.0°C). The analytical error (pooled standard deviation among triplicate measurements) for TEX_{86} in this study is ±0.4°C, and thus, we do not emphasize variations of <1°C among individual samples but rather focus on shifts in the mean temperature of multidecadal to centennial intervals. The TEX_{86} record displays an overall warming trend from a mean SST of 26.4°C circa 1100–900 years B.P. to a core top SST of 28.0°C. The core top TEX_{86}-SST indicates that the 20th century was the warmest of the past millennium. Superimposed on the 1000 year warming trend are centennial changes such as a century-long excursion between 1000 and 900 years B.P. in which temperatures were 1°C cooler, and a rapid transition to 1°C warmer SSTs circa 600 years B.P. The LIA (400–150 years B.P.) is marked by a 0.5°C drop in mean SSTs from the preceding two centuries (600–400 years B.P.), and followed by a rapid 1°C warming into the 20th century.

[14] Thus far we have only discussed uncertainty associated with the precision of our TEX_{86} measurements. The standard error reported for temperature estimates from the TEX_{86}-SST calibration equation used in this study is 2.5°C [*Kim et al.*, 2010]. This relatively large uncertainty in the temperature calibration can be attributed to scatter in the global core top data set that results from differences in regional ecology (i.e., depth and seasonal distribution of crenarchaeotal production) and discrepancies in the time represented by core top samples from different oceanographic settings (i.e., decades to millennia). These sources of uncertainty do not necessarily apply to the variability observed in a downcore record from a single location, especially during the past 1000 years, when significant shifts in crenarchaeotal production were unlikely. Thus, it is

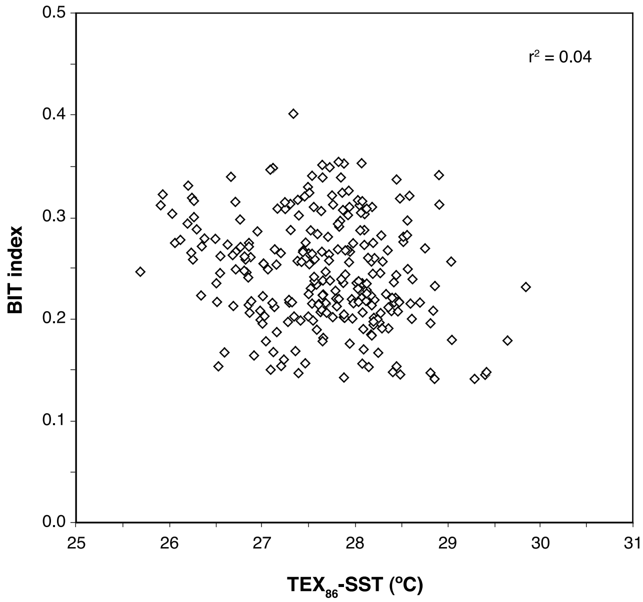

Figure 4. Cross plot between BIT index and TEX_{86}-SST for Pigmy Basin box core (PBBC-1F). There is no significant correlation between TEX_{86} and BIT indices ($r^2 = 0.04$).

important to distinguish the degree of uncertainty in the magnitude of a temperature shift from the uncertainty associated with the assigning an absolute SST value to a given TEX_{86} measurement. The uncertainty on the slope of the linear SST equation (SST = 68.4 (±1.8) * TEX_{86}^{H} + 38.6) is small, such that the uncertainty in a 1°C shift (our estimated warming from the LIA to modern) is <0.1°C.

4.2. Influence of Terrestrial Input on Pigmy Basin TEX_{86}

[15] In marine marginal settings proximal to major fluvial systems such as the Mississippi River (Figure 1), there is concern that the TEX_{86}-SST proxy may be influenced by delivery of isoprenoid GDGTs derived from terrestrial sources. The Branched and Isoprenoid Tetraether (BIT) index, based on the relative abundance of terrestrially derived branched tetraether lipids (GDGT V, VI, and VII) versus the marine-derived crenarchaeol (GDGT IV), can be used to monitor the relative contribution of soil organic matter to sediments [*Hopmans et al.*, 2004]. *Weijers et al.* [2006] found that in marine sediments with a large contribution of soil-derived organic matter, TEX_{86} values tended to be biased toward warmer temperatures. Using a two end-member mixing model (GDGT distribution in African soils versus GDGT distribution in marine sediments of the Niger deep sea fan), *Weijers et al.* [2006] predicted a +1°C temperature bias in the TEX_{86}-SST of sediments with BIT values of 0.2–0.3, and the influence of terrestrial input on TEX_{86} temperature estimates was found to increase nonlinearly at BIT values >0.3. However, this specific temperature bias depends heavily upon the composition and source of terrestrial organic matter, and therefore is not necessarily applicable to other marine basins.

[16] In the Pigmy Basin (core PBBC-1F) the BIT index varies between 0.14 and 0.40 (mean = 0.25) over the past 1000 years (Figure 3b), which lies between the values observed for coastal and open marine environments [*Hopmans et al.*, 2004]. Figure 3 shows a downcore comparison of both the BIT and TEX_{86} indices from Pigmy Basin, and although there are intervals during which they show strongly opposing trends (e.g., the most recent 150 years), there is no statistically significant covariance between the two indices. The lack of linear correlation is illustrated in a cross plot of the BIT index versus TEX_{86}-SST from the Pigmy Basin (r^2 = 0.04) (Figure 4). Unlike the *Weijers et al.* [2006] study, where an elevated BIT index imparted a positive bias on TEX_{86} values, intervals of elevated BIT index in the Pigmy Basin correspond in some cases to periods of decreased TEX_{86}-SST (e.g., 400–150 years B.P., during the LIA). In order to quantify the potential bias to the TEX_{86}-SST record introduced by the moderately elevated BIT index in Pigmy Basin sediments, the GDGT composition of soil organic matter delivered to the GOM via the Mississippi River would have to be characterized. Although we cannot directly assess to what degree, if any, terrestrially derived GDGTs are influencing the TEX_{86} measurements, we adopt the working hypothesis that downcore variability in soil organic matter input does not significantly affect downcore TEX_{86} variability.

4.3. Inferring Depth and Seasonality for TEX_{86} Signal in the Gulf of Mexico

[17] The global core top calibration of *Kim et al.* [2008, 2010] indicates that TEX_{86} best reflects mean annual SST of the upper mixed layer (0–30 m). Although Crenarchaeota are living and biosynthesizing GDGTs throughout the water column, *Wuchter et al.* [2006] showed that the TEX_{86} signal recorded in deep sediment trap samples (>500 m) still reflects surface temperatures, rather than water temperatures resulting from deep water column GDGT production. This is most likely due to the effective packaging and export of GDGT-containing crenarchaeal cells from the upper water column in fecal pellets via zooplankton grazing. Due to lack of a packaging process and mechanism of transport to sediments, deep-water crenarchaeotal production likely has an insignificant effect on TEX_{86} SST estimates [*Wuchter et al.*, 2005].

[18] The TEX_{86} value of 0.70 (±0.008) in the Pigmy Basin corresponds to an SST of 28.0°C (±0.5°C), which is >2°C warmer than the mean annual SST for the GOM (25.4°C), and equivalent to the mean summer (June–September) SST for the GOM mixed layer [*Levitus*, 2003]. Taking the core top TEX_{86}-SST estimate at face value suggests that the TEX_{86} record in the Pigmy Basin is a heavily summer-weighted signal and that crenarchaeotal production and/or export via zooplankton grazing must be significantly higher during the summer in the Gulf of Mexico. This is contrary to the observation of *Wuchter et al.* [2005] that GDGTs occurred in higher abundances during the winter and spring in a number of marine settings, including the subtropical and tropical Atlantic sites, Bermuda Atlantic Time series Study (BATS) and in the Cariaco Basin. In contrast, in Bermuda Rise, *Shah et al.* [2008] found core top sediments that TEX_{86} indicated SSTs ~2°C warmer than those estimated from co-occurring foraminiferal $\delta^{18}O$, a fact consistent with

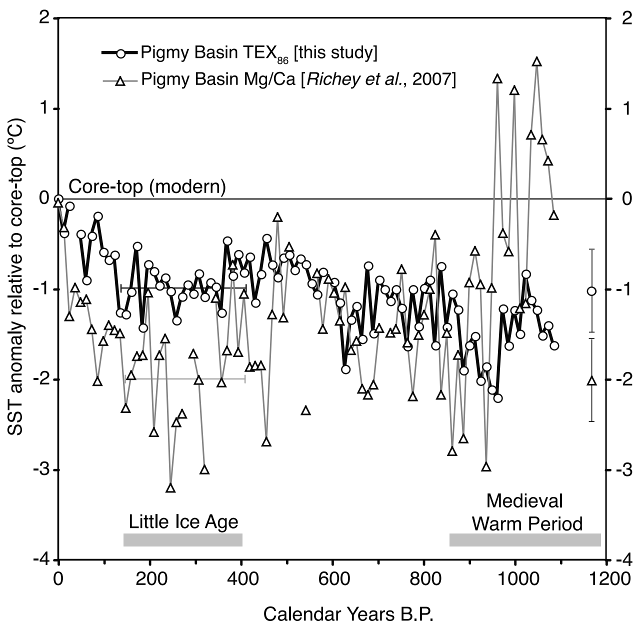

Figure 5. TEX_{86} [this study] and Mg/Ca [*Richey et al.*, 2007] records plotted as anomalies relative to their respective calibrated core top temperatures. Individual data points are shown with open circles (TEX_{86}) and open triangles (Mg/Ca). Error bars combine uncertainty in the slope (TEX_{86}) or exponential constant (Mg/Ca) of the respective paleotemperature equations and the analytical error. Uncertainty associated with absolute SST is not considered as the diagram displays SST variability relative to the core top value of each record. Both records are derived from separate subcores within the same Pigmy Basin box core. Subcore PBBC-1F (TEX_{86}) is 15 cm shorter than PBBC-1E (Mg/Ca) due to position within the box core.

our findings in the Pigmy Basin. At present, there are no data from the GOM on seasonal changes in crenarchaeotal production.

4.4. Comparison of Pigmy Basin TEX_{86}-SST to Mg/Ca-SST Record

[19] Comparison of two or more different paleotemperature proxy records from co-occurring sediments often reveals strikingly different climate histories. This can be attributed to a number of physical, biological and chemical factors, including separate transport mechanisms to the sediment, different ecologies of the signal carrying organisms, and susceptibility to separate diagenetic processes of the different sediment components. In this section we compare the SST records derived from both foraminiferal Mg/Ca and TEX_{86} in the Pigmy Basin box core (PBBC-1). There are important similarities between the two records, such as the timing and magnitude of LIA cooling, and the rate of warming over the past 150 years. There are also significant differences between the two records, which may be attributed to the different ecologies of the two biogenic proxy recorders.

[20] It has been well documented that organic compounds, which are attached to fine-grained particles, can be laterally transported long distances [e.g., *Ohkouchi et al.*, 2002; *Mollenhauer et al.*, 2005] causing age and temperature offsets between molecular organic proxies (e.g., $U^{K'}_{37}$ and TEX_{86}) and planktonic foraminifera-based proxies. Compound-specific radiocarbon dating suggests that GDGTs may be more labile than alkenones, and thus do not survive transport over long distances under oxic conditions as well as alkenones [*Mollenhauer et al.*, 2007; *Shah et al.*, 2008]. Thus GDGTs are more likely to contain a local signal that is contemporaneous with the foraminiferal signal.

[21] Each paleo-SST proxy is based on the geochemistry of a planktonic organism, each of which has a different depth and seasonal distribution. These depth and seasonal distributions for a signal carrier can vary depending on geography and local controls on productivity. For example, *Huguet et al.* [2006] find a 2.5°C difference between the estimates of LGM to present warming between $U^{K'}_{37}$-SST and TEX_{86}-SST in the Arabian Sea. They attribute these discrepancies to differences in seasonality between the crenarchaeota and haptophyte algae, which are the planktic source of the TEX_{86} and $U^{K'}_{37}$ signals, respectively. *Castañeda et al.* [2010] found that $U^{K'}_{37}$ and TEX_{86}-based SST estimates in the eastern Mediterranean were similar during the LGM, but TEX_{86}-SSTs were generally 1°C–2°C warmer than $U^{K'}_{37}$-SSTs during the Holocene. They also attribute this discrepancy to changing seasonality of crenarchaeota and haptophyte blooms during the last deglaciation.

[22] The TEX_{86}-based SST record generated from the Pigmy Basin (core PBBC-1F) shows similar patterns of variability to the Mg/Ca-based SST record (core PBBC-1E) previously published by *Richey et al.* [2007] from the same box core, but with important differences. Due to the potential implications of offsets in absolute SST calibration between the two different paleotemperature proxies (TEX_{86} and Mg/Ca), similarities in the decadal to centennial-scale patterns of variability are discussed first. Figure 5 shows the down core SST variability in both records plotted as a temperature anomaly relative to their respective core top SSTs. An important similarity between the two records is the rate of warming over the most recent 150 years. The Mg/Ca record indicates that SSTs have warmed at a rate of 1°C (±0.2°C)/100 years, and TEX_{86} indicates warming at a rate of 0.7°C (±0.1°C)/100 years. Both the TEX_{86} and Mg/Ca records indicate that SSTs during the LIA (circa 150–400 years B.P.) were significantly cooler than modern. While the Mg/Ca record shows that the mean SST was 2°C (±0.2°C) cooler than modern, the TEX_{86} record indicates a subtler LIA cooling of 1°C (±0.2°C). From 850 to 600 years B.P. both records indicate SSTs that were ~1.5°C cooler than their modern core top SSTs. The major discrepancies between the 2 records are (1) The LIA is not the coolest interval during the past millennium as recorded by TEX_{86} and (2) the period prior to 900 years B.P. was similar to the core top SST as recorded by foraminiferal Mg/Ca but significantly (~2°C) cooler in the TEX_{86} record.

4.5. Inferring Depth and Seasonality for *Globigerinoides ruber* in the Gulf of Mexico

[23] The white variety of the planktonic foraminifer, *Globigerinoides ruber*, is abundant throughout the tropical

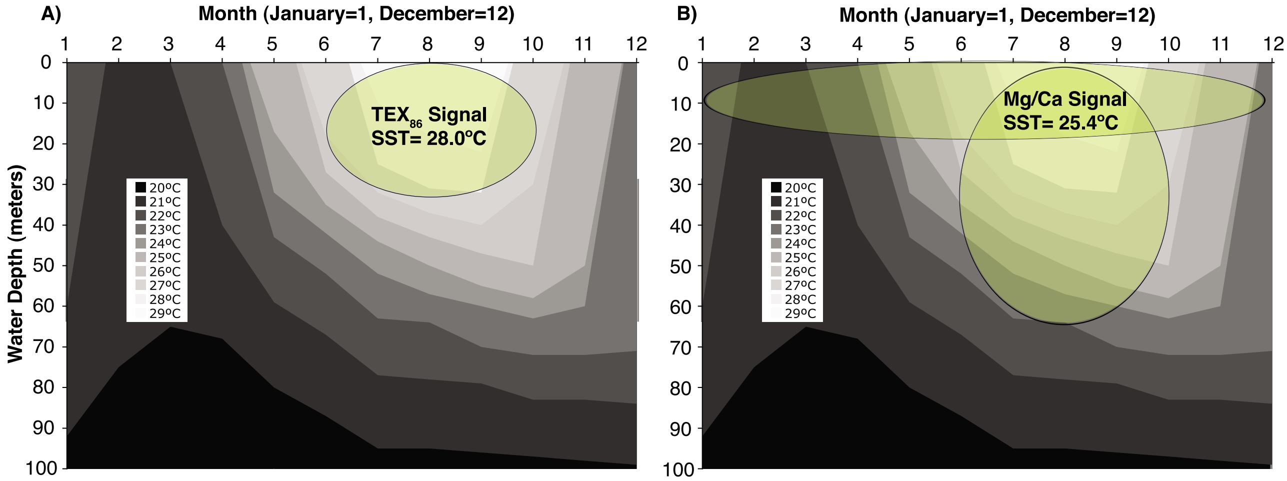

Figure 6. Annual cycle of water temperature variability in the upper 100 m of the water column. Data are monthly averages from the climatic means for the Gulf of Mexico [*Levitus*, 2003]. (a) The circled region indicates the dominant depth and seasonal range of the TEX_{86} signal, based on the core top TEX_{86}-SST of 28.0°C. (b) The circled regions indicate the two possible distributions of *G. ruber* in the Gulf of Mexico. The modern SST (25.4°C) recorded by *G. ruber* indicates that they are living in the upper mixed layer (0–30 m) throughout the year or they are limited to the summer months (June–September) but living over a greater depth range (0–75 m).

and subtropical oceans, and is constrained to the euphotic zone by its photoautotrophic dinoflagellate symbionts. The seasonal and depth distribution of *G. ruber* (white) has been reported from sediment trap [e.g., *Deuser*, 1987; *Tedesco and Thunell*, 2003; *Tedesco et al.*, 2009] and plankton tow studies [e.g., *Tolderlund and Bé*, 1971; *Fairbanks et al.*, 1980; *Bé*, 1982] in a number of different locations proximal to the Gulf of Mexico. The modern depth preference of *G. ruber* (white) has been documented in a number of Sargasso Sea plankton tows studies, but there are limited data specific to the Gulf of Mexico. *Fairbanks et al.* [1980] found that *G. ruber* (white) was common throughout the upper 100 m of the water column in a November 1975 plankton tow study, while a series of monthly plankton tows in the Sargasso Sea indicated that *G. ruber* (white) was most abundant in the uppermost 10 m of the water column [*Tolderlund and Bé*, 1971]. *Bé* [1982] confirmed the presence of *G. ruber* (white) throughout the upper 50 m of the water column in the western Gulf of Mexico.

[24] The Mg/Ca of the white variety of *G. ruber* is typically interpreted as a mean annual mixed layer signal in the Gulf of Mexico [e.g., *Flower et al.*, 2004; *LoDico et al.*, 2006; *Richey et al.*, 2007]. Flux data from a sediment trap study in the Sargasso Sea indicate that *G. ruber* are present throughout the annual cycle, with peak fluxes in early spring and late summer [*Deuser*, 1987]. A 1 year sediment trap study in the northern Gulf of Mexico indicates that *G. ruber* (white) is present throughout the year, with little apparent seasonal variability in flux (i.e., the flux varies by <1%, seasonally) [*Tedesco et al.*, 2009].

[25] The Mg/Ca record in the Pigmy Basin was generated from a well-constrained size fraction (250–300 μm) of the white variety of *G. ruber* [*Richey et al.*, 2007]. A mean Mg/Ca core top value of 4.43 mmol/mol (±0.03) for the Pigmy Basin was determined from replicate analyses of core top (0–0.5 cm) samples from 7 GOM core tops. This robust core top value corresponds to an SST of 25.4°C (Mg/Ca = 0.449 * exp(0.09 * SST) [from *Anand et al.*, 2003], which is the modern mean annual SST for the GOM [*Levitus*, 2003].

[26] Unlike the TEX_{86} signal, which must be weighted toward summer surface conditions in the Pigmy Basin core (Figure 6a), the core top Mg/Ca-SST of 25.4°C can be produced by a number of different scenarios (Figure 6b). (1) The *G. ruber* (white) depth habitat is limited to the uppermost 30 m of the water column and flux to the sediments is equally weighted throughout the year. (2) The flux of *G. ruber* (white) is summer weighted, but *G. ruber* (white) has a greater range (0–75 m) in the water column. In either case, increases (decreases) in SST, as recorded by the Mg/Ca of *G. ruber*, may be influenced by warmer (colder) winters or deeper (shallower) mixed layers.

4.6. Mg/Ca-SST to TEX_{86}-SST Gradients

[27] Using the assumptions we have made about the depth and seasonal distribution of GDGTs versus *G. ruber* (white) in the GOM, we can exploit the differences between the two SST records to make inferences about changing upper water column structure and/or seasonality over the past millennium. To do this we take the difference (ΔT) between the TEX_{86} and Mg/Ca-based SST records using their respective paleotemperature calibrations. As the uncertainties in the calibration of each of these proxies to an absolute SST are rather large (±2.5°C and ±1.5°C for TEX_{86} and Mg/Ca, respectively), interpretation of the ΔT requires the assumption that the SST estimates in this study are accurate. The results of this exercise are plotted in Figure 7, and suggest that the greatest difference between the TEX_{86} and Mg/Ca SST

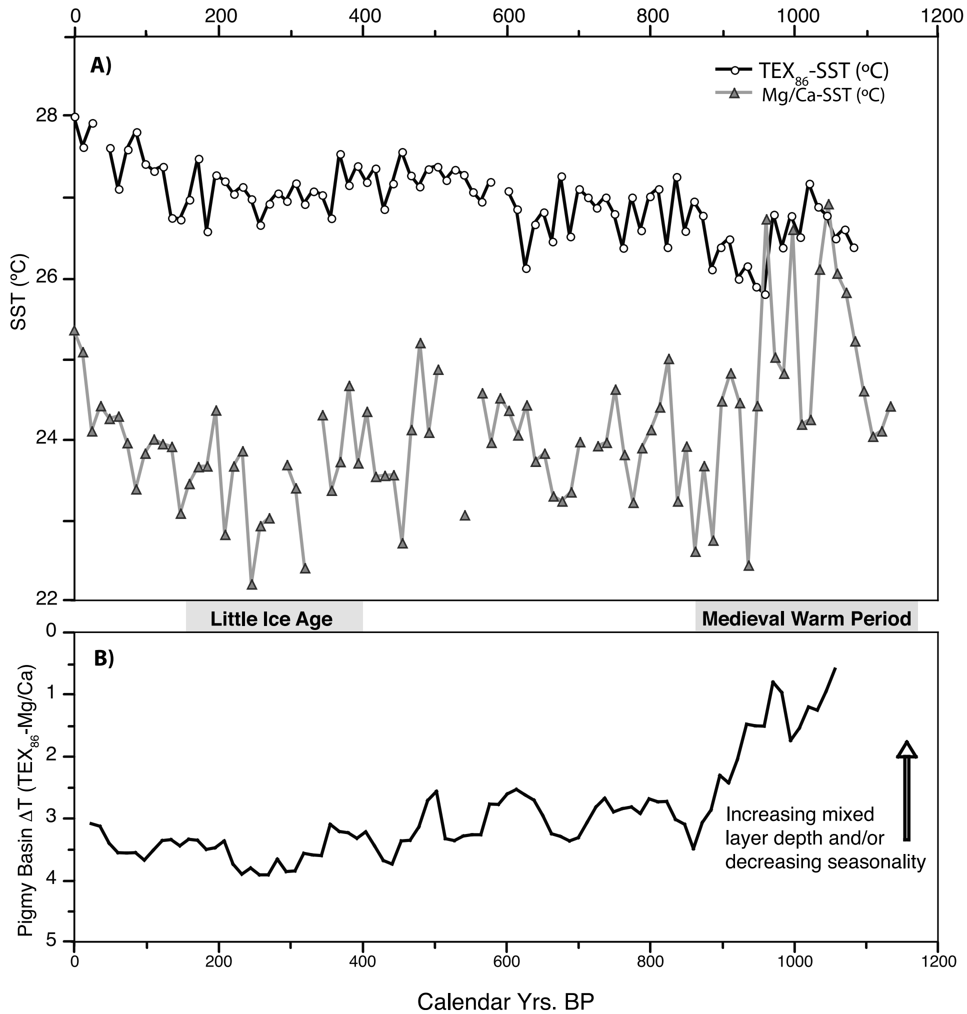

Figure 7. (a) The SST records derived from TEX_{86} (open circles) and Mg/Ca (solid circles), calibrated to SST using their independent paleotemperature equations. (b) The ΔT (TEX_{86}-Mg/Ca) for the Pigmy Basin, Gulf of Mexico. The largest ΔT (>4°C) occurs during the LIA, while minimum ΔT (<1°C) occurs during the MWP. Note that when uncertainties associated with respective calibrations to SST and analytical errors associated with both proxies are compounded, the error of the ΔT record is >2.5°C.

occurs circa 250 years B.P., during the maximum LIA cooling. The maximum is controlled by greater cooling of Mg/Ca-SST. This implies that the LIA cooling observed in the GOM may have been dominated by enhanced winter cooling relative to summer cooling, or shoaling of the thermocline (shallow mixed layer). The minimum difference between the TEX_{86} and Mg/Ca-SST records occurs 1100–900 years B.P., during the MWP. This implies that during this time there was a decrease in seasonality and/or increase in mixed layer depth.

[28] Without seasonally resolved flux data for Crenarchaeota or *G. ruber* specific to the Gulf of Mexico, we cannot evaluate whether the differences between TEX_{86} and Mg/Ca SST estimates result from differences in seasonal or depth distribution. Figure 8 depicts the different scenarios by which the ΔT between the two proxies could change over time. Figures 8a and 8c depict the theoretical LIA scenarios, in which there was an especially shallow mixed layer (causing a steep thermal gradient in the upper 100 m of the water column) or increased seasonality. In either of these scenarios we would expect the ΔT between TEX_{86} and Mg/Ca temperatures to be greater. The converse is shown in Figures 8b and 8d, where the mixed layer is deeper (causing a decreased thermal gradient in the upper water column), or decreased seasonality. In these scenarios, a smaller ΔT between TEX_{86} and Mg/Ca temperatures would be expected.

[29] The interpretation of the ΔT (TEX_{86}-Mg/Ca) as a record of changing upper water column hydrography requires the assumption that the two signal carriers maintain their relative depth/seasonal distributions through time. It must be recognized that the seasonal or depth preferences of either signal carrier may have been influenced by some other environmental factor over the past 1000 years, such as changes in nutrient availability or salinity. For instance, in the Caribbean Sea decreased *G. ruber* (white) abundance has been associated with low salinity or freshwater lenses,

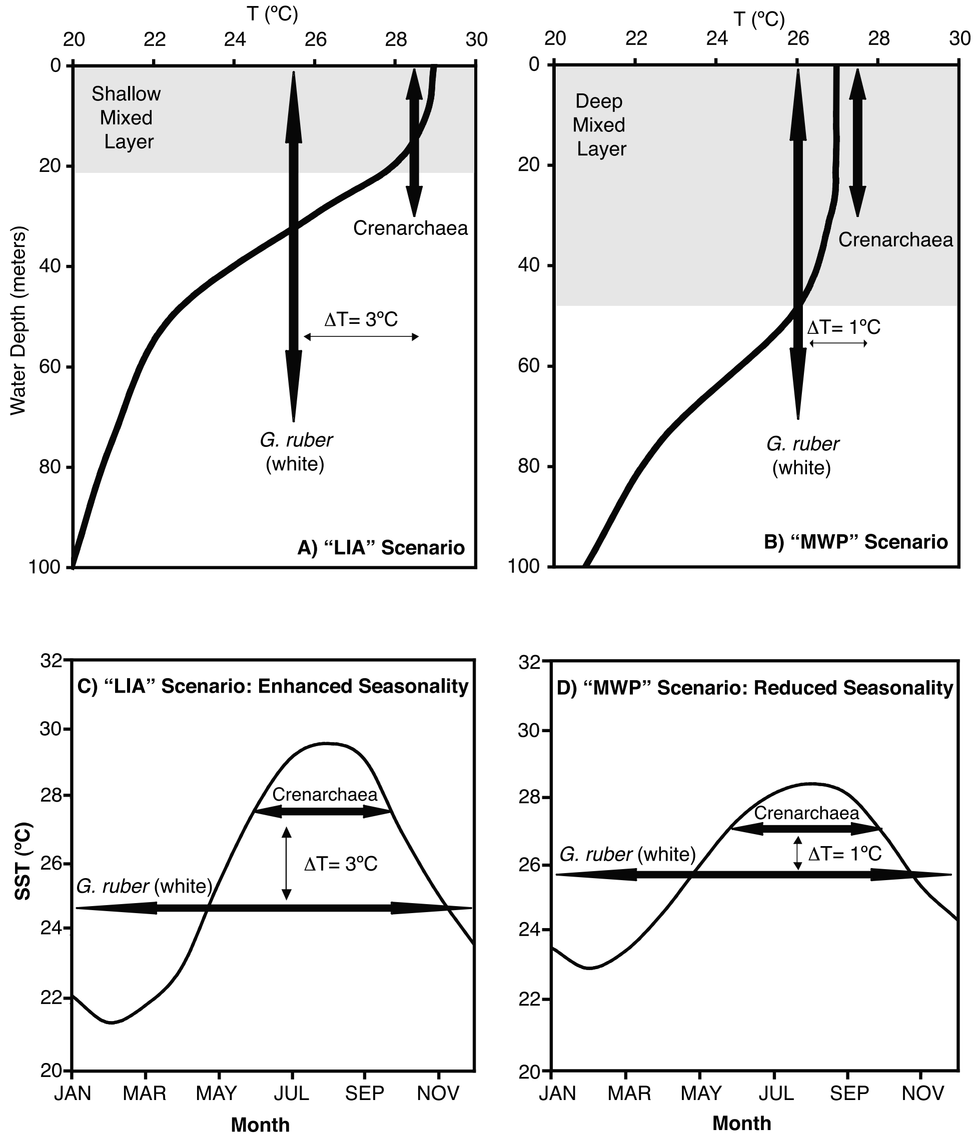

Figure 8. An illustration of the working hypotheses that (a and b) the changes in ΔT (TEX_{86}-Mg/Ca) over time may be indicative of changes in the thermal gradient in the upper water column in the Gulf of Mexico and/or (c and d) changes in ΔT over time may be indicative of changes in the seasonality in the Gulf of Mexico. The "LIA scenario," in which we observe the greatest ΔT, is illustrated by a steeper thermal gradient (or shallow mixed layer) in Figure 8a or by a greater seasonal range of SST in the Gulf of Mexico in Figure 8c. The "MWP scenario," in which we observe the smallest ΔT, is illustrated by a reduced thermal gradient (or deeper mixed layer) in Figure 8b or by a reduced seasonal range in the Gulf of Mexico in Figure 8d. Both scenarios require the assumption that the Mg/Ca and TEX_{86} signals maintain their relative depth and/or seasonal distributions throughout the past millennium.

while increased abundance has been associated with areas of high primary productivity [*Schmuker and Schiebel*, 2002]. In the Gulf of Mexico, it is conceivable that significant changes in the timing or magnitude of Mississippi River discharge would lead to changes in surface salinity or productivity, causing *G. ruber* (white) to respond by adjusting its habitat preference. In the same way, the seasonality of the TEX_{86} signal could be influenced by changes in zooplankton productivity, as the GDGTs are exported to the sediments via fecal pellets.

4.7. Potential Implications for the ΔT Record

[30] The changes in ΔT between the TEX_{86} and Mg/Ca SST records in the Pigmy Basin can be interpreted in terms of changes in the amplitude of the seasonal SST cycle and/or changes in mixed layer depth. Either scenario, (1) a deepening of the mixed layer or (2) a decreased seasonal SST variability with reduced winter cooling, would result in increased heat storage in the upper ocean on an annual basis. The Gulf of Mexico is in the path of, or the birthplace for, a large number of Atlantic tropical cyclones, and thus,

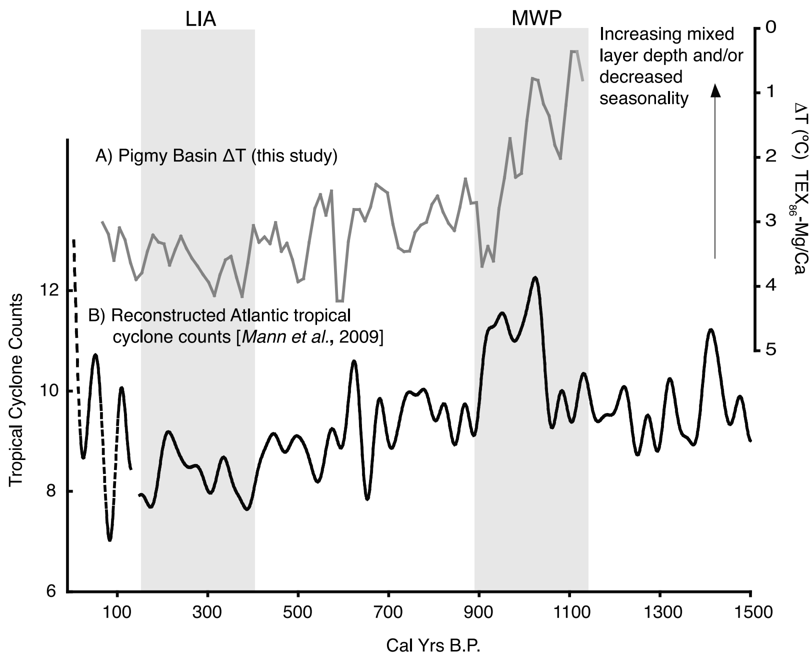

Figure 9. Comparison of ΔT (TEX_{86}-Mg/Ca) from the Pigmy Basin with a reconstruction of tropical cyclone counts from *Mann et al.* [2009]. (a) Grey curve is a three-point running mean of the ΔT record from the Pigmy Basin. We interpret decreasing ΔT in terms of increasing mixed layer depth and/or decreased seasonality. (b) Dashed line is a multidecadal-smoothed record of Atlantic tropical cyclone counts over the past 150 years. The solid black line is the proxy reconstructed Atlantic tropical cyclone counts based on statistical model from *Mann et al.* [2009]. The LIA is indicated by the shaded bar and highlights a minimum in reconstructed tropical cyclone counts and a maximum ΔT. The MWP, indicated with a shaded bar, can be characterized by a maximum in reconstructed tropical cyclone counts and a minimum in ΔT.

it follows that a persistent annual buildup of heat in the upper water column may have been a factor in enhancing tropical cyclone activity in the past.

[31] The MWP (circa 1100–900 years B.P.) is marked by the smallest ΔT for the past 1000 years in the Pigmy Basin, suggesting a centennial-scale period in which more heat was being stored in the upper ocean. Greater heat storage in the GOM via a warm mixed layer that is thicker and/or more seasonally persistent is consistent with reconstructions of greater tropical cyclone frequency in the Atlantic basin during the MWP (Figure 9) [*Mann et al.*, 2009]. Maximum ΔT in the Pigmy Basin record is observed during the LIA, suggesting a period of enhanced seasonality and/or a decreased mixed layer depth. This observation is also consistent with a minimum in reconstructed tropical cyclone frequency during the LIA by *Mann et al.* [2009].

5. Conclusions

[32] We present the first comparison of a decadal resolution TEX_{86}-based SST record with a foraminiferal Mg/Ca-based SST record for the past 1000 years from marine sediments. There are similarities in the magnitude and pattern of SST variability recorded by TEX_{86} and Mg/Ca in co-occurring sediments of the Pigmy basin box core, especially over the past four centuries. Both the TEX_{86} and Mg/Ca records indicate a substantially cooler LIA (by 1°C and 2°C, respectively), followed by a rapid warming over the past 150 years (0.7°C/100 years and 1.0°C/100 years, respectively). There are however, significant differences in the two SST records that can most likely be attributed to changes in the seasonal and/or depth distribution of crenarchaeota versus *G. ruber* (white). The core top TEX_{86}-SST suggests that TEX_{86} in the Gulf of Mexico is a summer weighted, upper mixed layer signal, while the Mg/Ca-SST indicates that *G. ruber* are most likely living throughout the year, and/or deeper in the water column. The difference (ΔT) between the two proxy records indicates changes in seasonality and/or mixed layer depth over the past millennium with the LIA characterized by enhanced seasonality and/or a shallow mixed layer whereas the MWP was recognized by a decrease in the seasonal temperature gradient and/or a deeper mixed layer. See Table S1 in the auxiliary material for the downcore TEX86 and BIT data from the Pigmy Basin (PBBC-1F) in the Gulf of Mexico.[1]

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[1]Auxiliary materials are available in the HTML. doi:10.1029/2010PA002000.

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