

Mingqiu Hou, Guangsheng Zhuang, Brooks B. Ellwood, Xiao-lei Liu, and Minghao Wu, 2022, Enhanced precipitation in the Gulf of Mexico during the Eocene–Oligocene transition driven by interhemispherical temperature asymmetry: GSA Bulletin, <https://doi.org/10.1130/B36103.1>.

Supplemental Material

Table S1. Leaf wax isotopic records in the Gulf of Mexico

Table S2. Reconstructions of mean annual precipitation based on leaf wax carbon isotopic records

Table S3. Sea surface temperature reconstructions

Table S4. Leaf wax isotopic records of modern trees

SUPPLEMENTAL INFORMATION

Evaluation of TEX₈₆ based SSTs

TEX₈₆ (TetraEther indeX with 86 carbon atoms) paleothermometry is based on the cyclicity of membrane lipids in marine archaea - glycerol dialkyl glycerol tetraethers (GDGTs) that can be converted to SST (Schouten et al., 2002). TEX₈₆ has been extensively used for paleoclimatic reconstruction because of its ubiquitous occurrence in marine sediments and robustness to diagenesis (Huguet et al., 2009; Kim et al., 2009). Reconstruction of SST from TEX₈₆ requires tests to justify that temperature is a primary control on GDGT distribution. Non-thermal factors, including input of terrigenous organic matter and methanogenic archaeal communities and growth phases of archaea, can influence GDGT distribution and lead to a considerable error in SST estimation (Hopmans et al., 2004; Liu et al., 2011; Elling et al., 2014). To validate the reliability of TEX₈₆^H – based SST reconstruction, we use the Branched and Isoprenoid Tetraethers (BIT) index (Hopmans et al., 2004), Methane Index (MI) (Zhang et al., 2011), ΔRing Index (ΔRI) (Zhang et al., 2016), and %GDGT-0 (Inglis et al., 2015) to evaluate the potential impacts of non-thermal factors and applicability of the TEX₈₆ – SST relationship.

The BIT index is based on the relative abundance of terrestrially derived tetraether lipids (branched GDGTs) versus the *crenarchaeol* (isoprenoid GDGT) produced by marine or lacustrine organic matter (Hopmans et al., 2004). A BIT value of 0.4 is recommended as the limit to differentiate a marine source with soil bacteria-derived GDGTs (Weijers et al., 2006). Samples with high BIT values (BIT > 0.4) are possibly influenced by substantial input of terrestrial organic matter and thus are not used for SST reconstruction. The BIT index is calculated using the following equation:

$$\text{BIT} = \frac{[\text{GDGT - I}] + [\text{GDGT - II}] + [\text{GDGT - III}]}{[\text{GDGT - I}] + [\text{GDGT - II}] + [\text{GDGT - III}] + [\text{Crenl}]} \#(1)$$

Methanotrophic archaea *Euryarchaeota* that live in both moderate and extreme environments, in terms of temperature and salinity, also produce GDGTs. The methane index is used to differentiate the input of methanotrophic archaea from normal marine communities

(Zhang et al., 2011). An MI value < 0.3–0.5 indicates a normal marine setting, while an MI value of > 0.5 suggests a methane hydrate-impacted setting. The methane index is calculated using the following equation:

$$MI = \frac{[GDGT - 1] + [GDGT - 2] + [GDGT - 3]}{[GDGT - 1] + [GDGT - 2] + [GDGT - 3] + [Cren] + [Cren']} \#(2),$$

where RI is defined as the weighted average of ring (cyclopentane) numbers in the GDGTs. Modern marine measurements indicate a significant correlation between RI and TEX₈₆. A deviation (ΔRI) from the modern TEX₈₆-RI relationship can be used to detect non-thermal factors that are incorporated in the TEX₈₆ index. Samples with $\Delta RI > 0.3$ are likely to be influenced by additional tetraether input. ΔRI is expressed as follows:

$$RI = 0 \times [GDGT - 0] + 1 \times [GDGT - 1] + 2 \times [GDGT - 2] + 3 \times [GDGT - 3] + 4 \times [Cren] + 4 \times [Cren'] \#(3)$$

$$RI_{TEX} = -0.77(\pm 0.38) \times TEX_{86} + 3.32(\pm 0.34) \times (TEX_{86})^2 + 1.59(\pm 0.10) \#(4)$$

$$\Delta RI = RI_{TEX} - RI \#(5),$$

where ΔRI stands for the offset between samples (RI) and modern TEX₈₆-RI relationship. The quadratic regression between RI_{TEX} and TEX₈₆ is derived from the global ocean data set (Zhang et al., 2016).

The %GDGT-0 index was used to evaluate the contribution of methanogenic archaea to the sedimentary GDGTs. Samples with %GDGT-0 values higher than 67% are potentially influenced by additional organic sources from methanogenic *Euryarchaeota* (Inglis et al., 2015). The %GDGT-0 index is calculated as,

$$\%GDGT - 0 = (GDGT - 0 / (GDGT - 0 + Crenarchaeol)) \times 100 \#(6)$$

The GDGTs distribution from the HIW core shows a wide range of BIT values (0.17–0.88). The age of 33.85 Ma is a cut-off for separating GDGT distribution from high BIT values (mean BIT = 0.75) in the early Oligocene to relative low BIT values (mean BIT = 0.43) from the late Eocene (Fig. S1). This major increase in BIT values tracks the decrease in P_{aq} values (Fig. S1), and we infer that the samples with high BIT values are most likely the result of a eustatic sea-level fall and thus a landward shift of organic source. The substantial high BIT values (>0.7) during the late Oligocene indicate that these samples are less reliable for SST reconstruction due to this significant terrigenous input. Investigation of modern soil branched GDGTs distribution shows that temperature deviation can be greater than 2 °C when BIT values exceed 0.4 (Weijers et al., 2006). However, further study found that in some localities (e.g., ODP sites 925 and 929), samples with high BIT values (>0.4) show similar SST estimation as those with low BIT values (<0.1) (Inglis et al., 2015). In the HIW core, while the early Oligocene samples exhibit relatively high BIT values (mean BIT = 0.75), the late Eocene samples have mean BIT values of 0.43, close to the threshold of 0.4 for a conservative SST reconstruction. We have compared SST values between samples with BIT < 0.4 and samples with 0.4 < BIT < 0.5. The result shows that SSTs from samples with high BIT values did not exhibit resolvable deviation (exceeding the

analytical error of ± 1 °C) from SSTs from samples with low BIT values (Fig. S1). In addition, there is no correlation between the BIT values and SSTs when the BIT values are smaller than 0.5 (Fig. S2). This implies that the higher-than-threshold BIT values ($0.4 < \text{BIT} < 0.5$) may not bias the SSTs reconstruction from TEX_{86} . Thus, we have concluded that the late Eocene samples with $0.4 < \text{BIT} < 0.5$ can be used for SST reconstruction. In addition, we further evaluated the potential influence of methanogenic *Euryarchaeota* on the GDGTs distribution by examining the ΔRI , %GDGT-0, and MI values. For late Eocene samples, the average ΔRI (0.38) is close to the threshold of 0.3, and the average MI value (0.39) reaches the upper limit for normal marine settings (0.3–0.5). However, the mean %GDGT-0 (40%) is much smaller than the threshold of 67%. Hence, we argue that the impact of methanogens is negligible.

REFERENCES CITED

- Elling, F.J., Könneke, M., Lipp, J.S., Becker, K.W., Gagen, E.J., and Hinrichs, K.-U., 2014, Effects of growth phase on the membrane lipid composition of the thaumarchaeon *Nitrosopumilus maritimus* and their implications for archaeal lipid distributions in the marine environment: *Geochimica et Cosmochimica Acta*, v. 141, p. 579–597, <https://doi.org/10.1016/j.gca.2014.07.005>.
- Hopmans, E.C., Weijers, J.W.H., Schefuss, E., Herfort, L., Damste, J.S.S., and Schouten, S., 2004, A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids: *Earth and Planetary Science Letters*, v. 224, no. 1–2, p. 107–116, <https://doi.org/10.1016/j.epsl.2004.05.012>.
- Huguet, C., Kim, J.-H., de Lange, G.J., Sinninghe Damsté, J.S., and Schouten, S., 2009, Effects of long term oxic degradation on the, TEX_{86} and BIT organic proxies: *Organic Geochemistry*, v. 40, no. 12, p. 1188–1194, <https://doi.org/10.1016/j.orggeochem.2009.09.003>.
- Inglis, G.N., Farnsworth, A., Lunt, D., Foster, G.L., Hollis, C.J., Pagani, M., Jardine, P.E., Pearson, P.N., Markwick, P., Galsworthy, A.M.J., Raynham, L., Taylor, K.W.R., and Pancost, R.D., 2015, Descent toward the Icehouse: Eocene sea surface cooling inferred from GDGT distributions: *Paleoceanography*, v. 30, no. 7, p. 1000–1020, <https://doi.org/10.1002/2014PA002723>.
- Kim, J.-H., Huguet, C., Zonneveld, K.A.F., Versteegh, G.J.M., Roeder, W., Sinninghe Damsté, J.S., and Schouten, S., 2009, An experimental field study to test the stability of lipids used for the TEX_{86} and palaeothermometers: *Geochimica et Cosmochimica Acta*, v. 73, no. 10, p. 2888–2898, <https://doi.org/10.1016/j.gca.2009.02.030>.
- Liu, X., Lipp, J.S., and Hinrichs, K.-U., 2011, Distribution of intact and core GDGTs in marine sediments: *Organic Geochemistry*, v. 42, no. 4, p. 368–375, <https://doi.org/10.1016/j.orggeochem.2011.02.003>.
- Schouten, S., Hopmans, E.C., Schefuss, E., and Damste, J.S.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, no. 1–2, p. 265–274, [https://doi.org/10.1016/S0012-821X\(02\)00979-2](https://doi.org/10.1016/S0012-821X(02)00979-2).
- Weijers, J.W.H., Schouten, S., Spaargaren, O.C., and Damste, J.S.S., 2006, Occurrence and distribution of tetraether membrane lipids in soils: Implications for the use of the TEX_{86} proxy and the BIT index: *Organic Geochemistry*, v. 37, no. 12, p. 1680–1693, <https://doi.org/10.1016/j.orggeochem.2006.07.018>.

Zhang, Y.G., Pagani, M., and Wang, Z., 2016, Ring Index: A new strategy to evaluate the integrity of TEX₈₆paleothermometry: *Paleoceanography*, v. 31, no. 2, p. 220–232, <https://doi.org/10.1002/2015PA002848>.

Zhang, Y.G., Zhang, C.L.L., Liu, X.L., Li, L., Hinrichs, K.U., and Noakes, J.E., 2011, Methane Index: A tetraether archaeal lipid biomarker indicator for detecting the instability of marine gas hydrates: *Earth and Planetary Science Letters*, v. 307, no. 3–4, p. 525–534, <https://doi.org/10.1016/j.epsl.2011.05.031>.

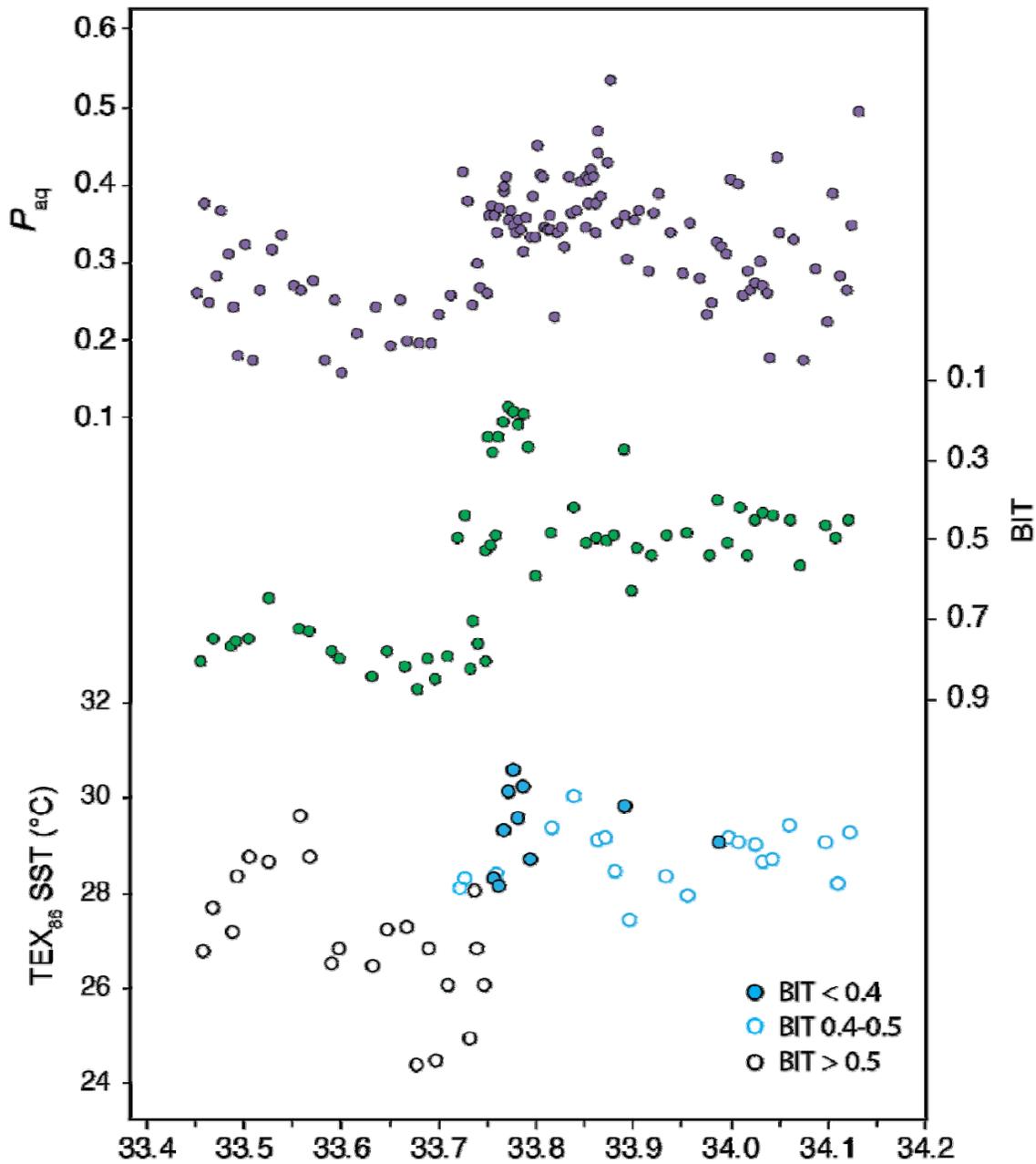


Figure S1 Comparison among TEX₈₆ SSTs, BIT, and P_{aq} values.

