

Extremely high sea-surface temperatures at low latitudes during the middle Cretaceous as revealed by archaeal membrane lipids

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ABSTRACT

The middle Cretaceous (125–88 Ma) greenhouse world was characterized by high atmospheric CO₂ levels, the general absence of polar ice caps, and much higher global temperatures than at present. Both δ¹⁸O-based and model-based temperature reconstructions indicate extremely high sea-surface temperatures (SSTs) at high latitudes. However, there are a number of uncertainties with SST reconstructions based on δ¹⁸O isotope data of foraminifera due to diagenetic overprinting effects and tenuous assumptions with respect to the δ¹⁸O value of Cretaceous seawater, the paleoecology of middle Cretaceous marine organisms and seawater pH. Here we applied a novel SST proxy (i.e., TEX₈₆ [tetraether index of 86 carbon atoms], based on the membrane lipids of marine crenarchaeota) derived from middle Cretaceous sedimentary rocks deposited at low latitudes. The TEX₈₆ proxy indicates that tropical SSTs in the proto-North Atlantic were at 32–36 °C during the early Albian and late Cenomanian–early Turonian. This finding agrees with SST estimates based on δ¹⁸O paleothermometry of well-preserved foraminifera as well as global circulation model calculations. The TEX₈₆ proxy indicates cooler SSTs (27–32 °C) for the equatorial Pacific during the early Aptian, which is in agreement with SST estimates based on δ¹⁸O paleothermometry.

Keywords: Cretaceous, sea-surface temperature, TEX₈₆, tropics.

INTRODUCTION

Numerous lines of evidence—most notably terrestrial and marine faunal and floral distributions, leaf and tree-ring characteristics, sedimentary facies distributions, and the absence of high-latitude glacial deposits—point to a mean middle Cretaceous climate that was significantly warmer with a lower equator-to-pole surface-temperature gradient than at present (see Poulsen et al., 1999). For quantification of middle Cretaceous temperatures we currently rely on δ¹⁸O paleothermometry of carbonate tests (in particular foraminifera). However, determinations of sea-surface temperatures (SSTs) using this method are based on tenuous assumptions with respect to the δ¹⁸O value of Cretaceous seawater, the paleoecology of middle Cretaceous marine organisms (e.g., Price and Hart, 1998), sea-surface salinity (e.g., Poulsen et al., 1999), and seawater pH (e.g., Zeebe, 2001). In addition, diagenetic overprinting and the scattered occurrence of foraminifera in the middle Cretaceous geologic record, especially in the organic-rich sediments deposited during so-called oceanic anoxic events (OAEs), often preclude com-

plete and accurate SST reconstructions (e.g., Norris and Wilson, 1998; Wilson et al., 2002). A number of δ¹⁸O studies (e.g., Kolodny and Raab, 1988; Huber et al., 1995; Wilson and Norris, 2001; Wilson et al., 2002; Norris et al., 2002) have provided data to support the inferred extreme warm middle Cretaceous climate. These studies are in agreement with general circulation models that indicate that the high atmospheric CO₂ levels (2–4 times present-day value) required to explain the middle Cretaceous polar warmth also result in tropical SSTs ~2–5 °C higher than today (e.g., Poulsen et al., 1999, 2001). However, due to the uncertainties associated with δ¹⁸O paleothermometry, there is a strong need for an independent SST proxy to confirm the middle Cretaceous greenhouse hypothesis and the relationship between pCO₂ and SST (see discussion in Bice and Norris, 2002).

We have identified the membrane lipids of marine crenarchaeota, ubiquitous microorganisms that make up 20%–30% of the picoplankton in present-day oceans (Schouten et al., 2000; Sinninghe Damsté et al., 2002). They consist of tetraether membrane lipids with 0–4 cyclopentane rings and, in one case, a cyclohexane ring (for molecular structures, see Fig. 1). A study of marine surface sedi-

ments from all over the globe showed that these organisms adjust the composition of their tetraether membranes lipids in response to SST (Schouten et al., 2002). This response, quantified as the so-called TEX₈₆ (tetraether index of 86 carbon atoms), shows a linear relationship ($r^2 = 0.92$) and can thus be used to determine SST from the tetraether membrane composition preserved in sediments and sedimentary rocks (Schouten et al., 2002). We have also reported the occurrence of tetraether membrane lipids in organic-rich Cretaceous sedimentary rocks (Kuypers et al., 2001), leading us to study the potential of the new paleothermometer to reconstruct SSTs of the middle Cretaceous greenhouse world. Our findings suggest that this new proxy can be applied in immature organic-rich sedimentary rocks to reconstruct middle Cretaceous SSTs.

MATERIAL AND METHODS

The sedimentary samples used in this study (see Table 1) derive from early Aptian (Deep Sea Drilling Project [DSDP] Site 463 in the equatorial Pacific Ocean), early Albian (Ocean Drilling Program [ODP] Hole 1049c off the coast of Florida), and the late Cenomanian–early Turonian (DSDP Site 367 off the coast of Senegal and DSDP Site 603B off the coast of North America). Detailed characteristics of bulk and molecular isotopic geochemistry of DSDP Site 367 and ODP Hole 1049c black shales were described previously (Kuypers et al., 2001, 2002).

For lipid analysis, freeze-dried sedimentary rocks were ultrasonically extracted three times with methanol, three times with dichloromethane (DCM)/methanol (1:1, v/v), and three times with DCM, and all extracts were combined. The bulk of the solvent was removed by rotary evaporation under vacuum. The extracts were further purified by column chromatography using Al₂O₃ as the stationary phase and a DCM/methanol (1:1, v/v) mixture as the eluent. The separated fraction was then dissolved by sonication (5 min) in hexane/propanol (99:1, v/v). The fraction was filtered through a 0.45 μm, 4-mm-diameter Teflon filter prior to analysis by high-performance liquid chromatography–atmospheric-pressure

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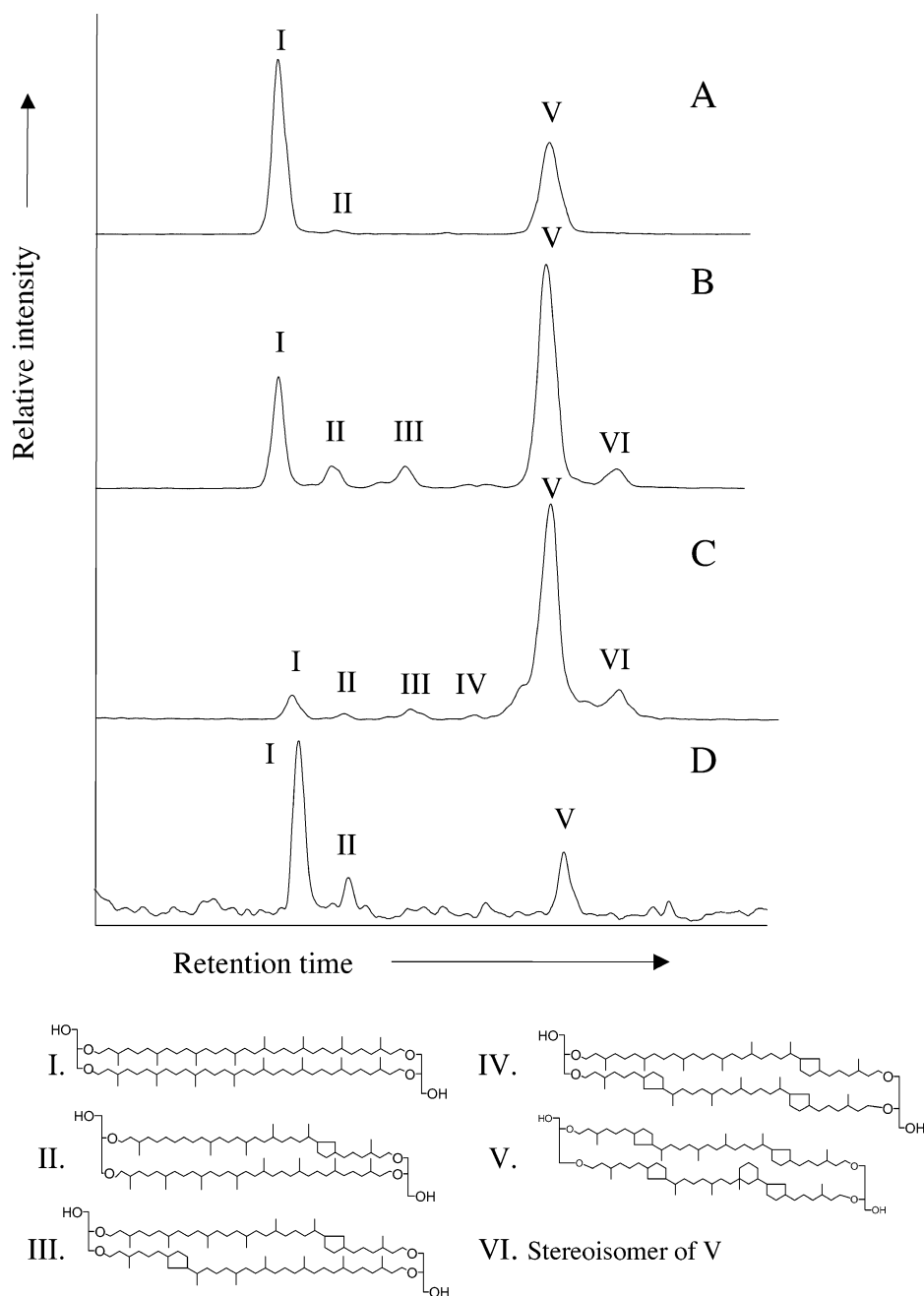


Figure 1. High-performance liquid chromatography base-peak chromatograms showing tetraether lipid composition of sedimentary rocks from (A) present-day Antarctic Ocean, (B) Arabian Sea, (C) Deep Sea Drilling Project (DSDP) Site 367, and (D) DSDP Site 463.

positive-ion chemical-ionization mass spectrometry (HPLC–APCI–MS). Conditions for HPLC–MS analyses of the purified extracts were described by Schouten et al. (2000).

Quantification was achieved by integration of the peak areas in the respective $[M + H]^+$ and $[M + H]^+ + 1$ (i.e., protonated molecule and isotope peak) traces of tetraether lipids. The

TEX₈₆ values were determined according to the formula given by Schouten et al. (2002).

RESULTS AND DISCUSSION

Archaeal Lipid Distribution

For this study a number of black shales from different time periods, covering three different OAEs, were analyzed for archaeal lipids (Table 1). The black shales were deposited between paleolatitudes 20°S and 30°N and contained immature organic matter, as revealed by the relatively high amounts of thermally labile 17β,21β(H)-hopanes (Kuypers, 2001; Kuypers et al., 2001, 2002). Although archaeal lipids I–VII could be found in varying abundance, their relative distribution in nearly all of the Cretaceous sedimentary rocks was strikingly similar (e.g., Fig. 1C): a high abundance of crenarchaeol (V), relatively lower amounts of an isomer of crenarchaeol (VI) and tetraether lipids with 2–3 cyclopentane rings, and very low amounts of tetraether lipids with 0–1 cyclopentane rings. As shown by Schouten et al. (2002), the relative distribution pattern of tetraether lipids correlates with SST—i.e., with higher temperatures, crenarchaeol and tetraether lipids III–VI increase in abundance relative to tetraether lipids I–II (see Figs. 1A and 1B as an example from a polar [Antarctica; ~2 °C] and a tropical ocean [Arabian Sea; ~27 °C], respectively). The extreme low abundance of tetraether lipids I–II observed in Cretaceous sedimentary rocks (e.g., Fig. 1C) is striking, because at present, even surface sediments from the tropical oceans (e.g., Arabian Sea; Fig. 1B) contain substantial amounts of tetraether lipids I–II compared to III–VI. This result strongly suggests that low-latitude SSTs in the middle Cretaceous were substantially higher than they are today. The lone exception is the distribution of tetraether lipid isomers in a black shale deposited during the early Aptian (OAE 1a) in the Pacific Ocean (DSDP Site 463; paleolatitude ~20°S) (Fig. 1D). The distribution shows that, in contrast to the already discussed black shales, tetraether lipids I–II are in much higher relative abundance compared to tetraether lipids III–VI. This finding suggests cooler SSTs at this location than during deposition of the other middle Cretaceous sedimentary rocks.

TABLE 1. LOCATIONS OF ANALYZED MIDDLE CRETACEOUS SEDIMENTARY ROCKS

| Site | Location | Paleo-latitude | Depth (mbsf) | Age | Event | TOC (%) | Reference |
|-----------|----------------|----------------|--------------|---------------------|--------|---------|-----------------------|
| DSDP 603B | North Atlantic | ~30°N | 1128–1134 | Cenomanian-Turonian | OAE 2 | 0.2–9 | Kuypers (2001) |
| DSDP 367 | North Atlantic | ~5°N | 636–644 | Late Cenomanian | OAE 2 | 2–46 | Kuypers et al. (2002) |
| ODP 1049C | North Atlantic | ~30°N | 142.3–143.8 | Early Albian | OAE 1b | 4–6 | Kuypers et al. (2001) |
| DSDP 463 | Pacific Ocean | ~20°S | 614–626 | Early Aptian | OAE 1a | 0.1–4 | Price et al. (1998) |

Note: DSDP—Deep Sea Drilling Project; ODP—Ocean Drilling Program; OAE—oceanic anoxic event; mbsf—meters below seafloor.

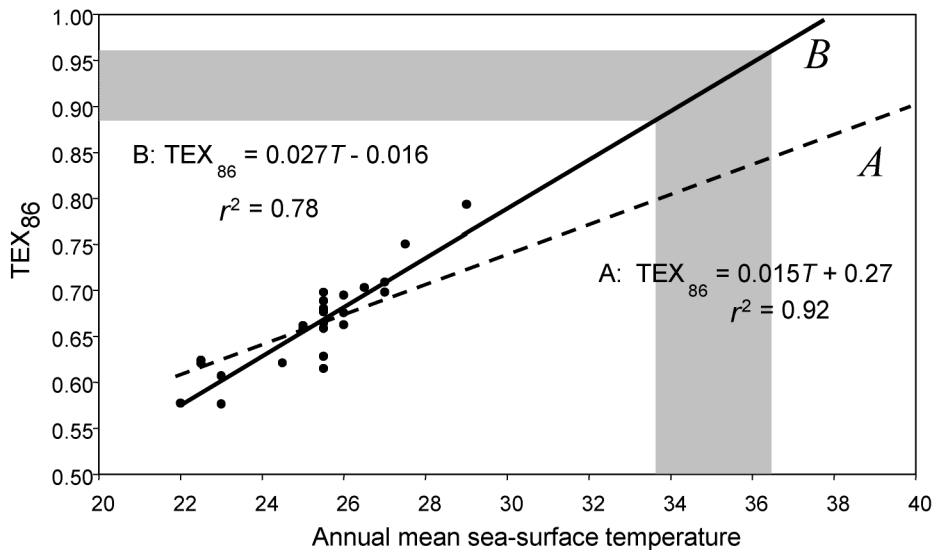


Figure 2. Global correlation of TEX_{86} (tetraether index of 86 carbon atoms) values with temperature (T) in Holocene surface sediments for $T > 0^\circ\text{C}$ (dashed line A; after Schouten et al., 2002) and correlation of TEX_{86} values with temperature in selected Holocene surface sediments for $T > 20^\circ\text{C}$ (solid line B). Gray band indicates range of TEX_{86} values in most middle Cretaceous sedimentary rocks.

Temperature Reconstructions Using the TEX_{86}

The relative distribution of crenarchaeotal tetraether lipids can be quantified by using the TEX_{86} (Schouten et al., 2002). Values for the TEX_{86} range from 0.69 to 0.84 in samples

from the early Aptian (OAE 1a) to 0.96 in samples from the Cenomanian–Turonian (OAE 2). These values are substantially higher than those found in surface sediments in present-day tropical oceans such as the Arabian Sea (0.70–0.71; $\text{SST} \approx 27^\circ\text{C}$) or equa-

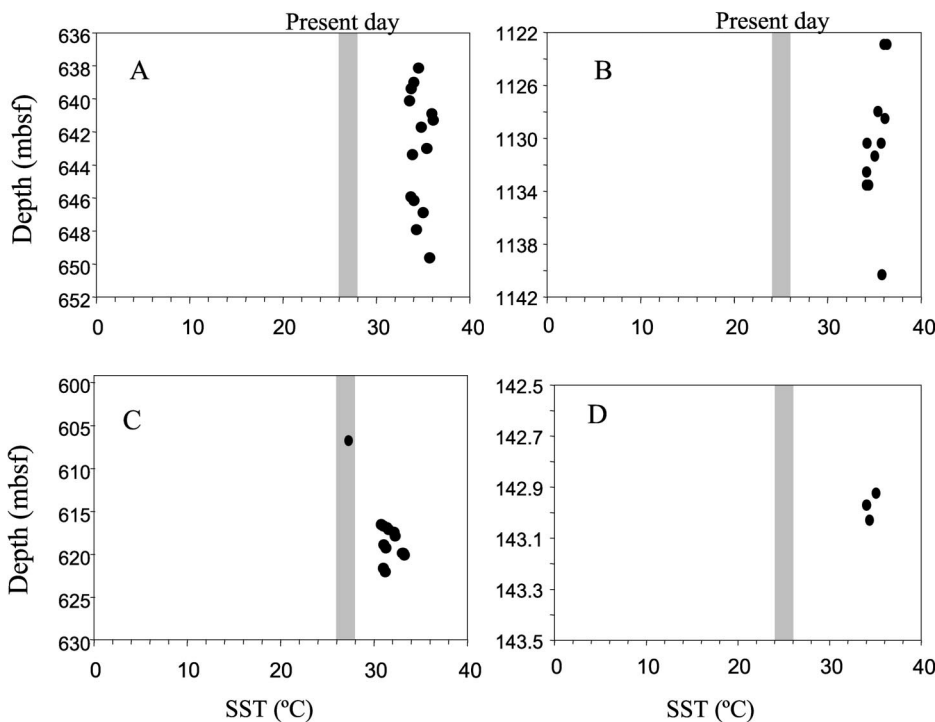


Figure 3. Sea-surface temperatures (SST) reconstructed by using TEX_{86} (tetraether index of 86 carbon atoms) values of (A) Cenomanian–Turonian (C-T) section from Deep Sea Drilling Project (DSDP) Site 367 in proto–North Atlantic at equator (mbsf—m below seafloor), (B) C-T section from DSDP Site 603 in proto–North Atlantic at paleolatitude 30°N , (C) early Aptian section from DSDP Site 463 in Pacific at equator, and (D) late Albian section from Ocean Drilling Program Site 1049 in proto–North Atlantic at paleolatitude 30°N .

torial Atlantic (0.68–0.69; $\text{SST} \approx 26^\circ\text{C}$), again suggesting that SSTs were substantially higher at low latitudes during the middle Cretaceous.

A problem arises when the TEX_{86} values are converted to SSTs by using the global correlation established by Schouten et al. (2002). Although the best fit through the data points is a linear relationship with an $r^2 = 0.92$, there is a tendency that at higher SSTs, the TEX_{86} is higher than predicted by the linear correlation line (dashed line A, Fig. 2). This deviation has implications for our attempt to reconstruct Cretaceous SSTs on the basis of the TEX_{86} values because we are forced to extrapolate the global TEX_{86} correlation line to higher SST and TEX_{86} values owing to a lack of present-day open-ocean systems with high temperatures (i.e., $>29^\circ\text{C}$). In order to provide the most representative extrapolation line, we established a new relationship by using only data from surface sediments with annual SSTs $> 20^\circ\text{C}$ (solid line B, Fig. 2). Again the best fit was a linear correlation relationship ($r^2 = 0.78$), but with a significantly steeper slope (0.027T vs. 0.015T [$T = \text{temperature}$] in the original calibration line). The result is that SST estimates using this revised calibration line will yield lower temperatures than estimates using the previously published global correlation line. This deviation may be due to a different population of crenarchaeota living in tropical oceans compared to temperate and polar oceans. Preliminary laboratory experiments using large-scale mesocosms show shifts in crenarchaeotal populations when temperatures are increased (C. Wuchter, 2003, personal commun.). At this point it seems likely that this revised calibration line will give the best SST estimates for the Cretaceous. When the TEX_{86} values are converted into SST values by using the high-temperature calibration line, SST estimates range from 27 to 32°C in the equatorial Pacific Ocean in the late Aptian to $32\text{--}36^\circ\text{C}$ during the Cenomanian–Turonian (Fig. 3).

Comparison With Other Paleotemperature Estimates

The SSTs calculated from the TEX_{86} values for DSDP Site 367 ($33\text{--}36^\circ\text{C}$) are in the range of the peak temperatures ($33\text{--}34 \pm 2^\circ\text{C}$) calculated by $\delta^{18}\text{O}$ paleothermometry (corrected for salinity and pH) of exceptionally well preserved late Cenomanian foraminifera from DSDP Site 144 (Norris et al., 2002), which was located on the Demerara Rise (off northeast South America) in a climatic setting comparable to that of DSDP Site 367 (Kuypers et al., 2002). The TEX_{86} -based SSTs for the northern part of the proto–North Atlantic (DSDP Site 603B; paleolatitude 30°N) are

nearly identical to the SSTs for the southern part of the proto-North Atlantic (DSDP Site 367; 5°N). The TEX₈₆-based SSTs for Site 603B are comparable to the temperatures (32–33 ± 3 °C) calculated by δ¹⁸O paleothermometry (corrected for salinity only) of exceptionally well preserved early Cenomanian foraminifera at nearby ODP Site 1052 (Wilson and Norris, 2001). Hence, SSTs calculated from the TEX₈₆ values are in excellent agreement with δ¹⁸O SST estimates. Furthermore, the high TEX₈₆-based SSTs are in agreement with global circulation model calculations. Poulsen et al. (1999) calculated an annual SST of 34 °C for DSDP Site 144, in excellent agreement with our results for nearby DSDP Site 367. Both the TEX₈₆ values and δ¹⁸O paleothermometry indicate slightly higher SSTs for the northern proto-North Atlantic than the model-based annual SST of 29 °C for the early Cenomanian (Poulsen et al., 1999).

Analysis of black shales deposited during the early Albian (OAE 1b) at paleolatitude 30°N in the proto-Northern Atlantic (Site ODP 1049) revealed high SSTs similar to those during the Cenomanian–Turonian, i.e., 33–35 °C. The TEX₈₆-based SSTs are somewhat higher than those estimated by general circulation models (29 °C; Poulsen et al., 1999), but much higher than the estimates of 20–22 °C by Erbacher et al. (2001), although these values were not corrected for salinity and pH. SSTs calculated from TEX₈₆ values for black shales deposited during the early Aptian (OAE 1a) in the Pacific Ocean (DSDP Site 463; paleolatitude ~20°S) range between 30 and 32 °C. These SSTs are consistent with general circulation models, which estimate annual SSTs of 30 °C at Site DSDP 463 (Poulsen et al., 1999), but are higher than the inferred SST of 26 °C (as recalculated by Poulsen et al., 1999, from Price et al., 1998) from δ¹⁸O paleothermometry at Site DSDP 463. It is interesting to note that there seems to be a drop to ~27 °C at the end of OAE 1a, although this cooling is only represented by a single data point. Weissert and Lini (1991) suggested that during the early Aptian the warm greenhouse climate was interrupted by a cooling event in which temperatures returned to present-day values. Further studies into this time interval using the TEX₈₆ proxy may now reveal the frequency and magnitude of such periods in the middle Cretaceous.

CONCLUSIONS AND IMPLICATIONS

Our results show the potential to apply the new SST proxy, the TEX₈₆, to estimate middle Cretaceous SSTs. Notably, this proxy can be applied in organic-rich sediments and sedimentary rocks where foraminifera are often lacking, and thus can provide an SST record

complementary to δ¹⁸O paleothermometry. First results of the TEX₈₆ proxy indicate that low-latitude SSTs were extremely high, much higher than at present, during the middle Cretaceous greenhouse world. The TEX₈₆-based SSTs are in agreement with δ¹⁸O studies on excellently preserved foraminifera (Wilson et al., 2002; Norris et al., 2002) and SST estimates based on general circulation models (Poulsen et al., 1999). Our results indicate that open-ocean SSTs are not restricted by feedback mechanisms to an upper limit, but that the “tropical thermostat” was set much higher during the Cretaceous (Norris et al., 2002). General circulation models use high atmospheric CO₂ concentrations (e.g., Bice and Norris, 2002) to induce high polar warmth, thereby yielding high tropical SSTs. Our confirmation of these high tropical SSTs thus suggests that CO₂, in combination with tectonic forcing (Leckie et al., 2002; Poulsen et al., 2003), may have been a driving force for the middle Cretaceous hothouse.

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