Spatial Variations in Archaeal Lipids of Surface Water and Core-Top Sediments in the South China Sea and Their Implications for Paleoclimate Studies

Yuli Wei, Jinxiang Wang, Jie Liu, Liang Dong, Li Li, Hui Wang, Peng Wang, Meixun Zhao, and Chuanlun L. Zhang

State Key Laboratory of Marine Geology, Tongji University, Shanghai 200092, China; School of Earth Resources, China University of Geosciences-Wuhan, Wuhan 430074, China; Institute of Marine Organic Geochemistry, Ocean University of China, Qingdao 266100, China; and Department of Marine Sciences, University of Georgia, Athens, Georgia 30602

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The South China Sea (SCS) is the largest marginal sea of the western Pacific Ocean, yet little is known about archaeal distributions and TEX$_{86}$-based temperatures in this unique oceanic setting. Here we report findings of abundances in both core lipids (CL) and intact polar lipids (IPL) of Archaea from surface water (CL only) and core-top sediments from different regions of the SCS. TEX$_{86}$-derived temperatures were also calculated for these samples. The surface water had extremely low abundances of CL (average of 0.05 ± 0.13 ng/liter; n = 75), with higher values present in regions where upwelling is known to occur. The core-top sediments had CL values of 0.1 to 0.9 µg/g, which are on the low end of CL concentrations reported for other marine sediments and may reflect the oligotrophic nature of the open SCS. The IPL of Archaea accounted for 6 to 36.4% of total lipids (CL plus IPL), indicating that the majority of archaeal lipids in core-top sediments were derived from nonliving cells. The TEX$_{86}$-based temperatures of surface water were overall lower than satellite-based sea surface temperatures or CTD-measured in situ temperatures. The core-top sediment samples, however, had TEX$_{86}$ temperatures very close to the mean annual sea surface temperatures, except for samples with water depths of less than 100 m. Our results demonstrated low and heterogeneous distributions of archaeal lipids in surface water and core-top sediments of the SCS, which may reflect local or regional differences in productivity of Archaea. While TEX$_{86}$-based temperatures for core-top marine sediments at deep water depths (>100 m) generally reflected mean annual sea surface temperatures, TEX$_{86}$ temperatures in surface water varied basin wide and underestimated sea surface temperatures in most locations for the season when surface water samples were collected.

The climatic system of the SCS is affected by the proximity to the Tibetan Plateau and Pacific warm pool and characterized by the East Asian monsoons. As a result, the SCS is one of the best places for paleoclimate studies. Furthermore, the SCS has the most suitable conditions for high-resolution paleoceanographic studies because of high sedimentation rates and good carbonate preservation. The SCS is also highly suitable for examining the relationships between continental weathering, productivity, and climate, as three of the largest rivers in the world (from north to south, the Pearl River, the Red River, and the Mekong River) provide detrital fluxes to the basin of the SCS.

Numerous paleoclimate studies have been conducted in the SCS, which are commonly based on temperature proxies such as oxygen isotope ratios and Mg/Ca ratios of foraminifera, foraminiferal transfer function, or the U$_{37}^{K}$ methods. It has been realized that individual temperature proxies all can suffer from some biases, and the ideal approach would be the integration of multiple proxies for addressing the same question. The TEX$_{86}$ proxies have been developed only recently and most successfully used for marine systems (see, e.g., references 5, 7, 11, and 43). In terrestrial environments, the TEX$_{86}$ proxies have been successfully applied to paleoclimate studies of some large lakes.

Despite the importance of the SCS in studies of primary
production and paleoclimate, little research has been done regarding the abundance and community structure of Archaea and the application of archaeal lipids as temperature proxies in the SCS. In this study, we performed archaeal and bacterial glycerol dibiphytanyl glycerol tetraether (GDGT) analyses of both the core lipids (CL) and intact polar lipids (IPL) from both surface water and core-top sediments of the SCS. Our data for the core-top sediments from water depths of greater than 100 m showed that TEX86-derived sea surface temperatures (SST) based on CL matched annual mean sea surface temperatures from the satellite data, whereas TEX86-derived sea surface temperatures based on surface water samples collected in April and May 2010 were lower than satellite-based or CTD-determined sea surface temperatures for those months. This study is the first calibration between satellite sea surface temperatures and TEX86-derived temperatures in the SCS, which may provide a reference for studies of paleoclimate changes in the SCS using these proxies.

MATERIALS AND METHODS

Sample collections. (i) Water column sampling. A cruise in the SCS was made on 23 April to 26 May 2010 by using the R/V Shiyan No. 3 of the South China Sea Institute of Oceanology, Chinese Academy of Sciences. A total of 89 sampling stations were visited (Fig. 1), among which 78 stations were sampled for archaeal lipids from the surface water (5- to 10-m water depths). At each location, filtration of seawater was conducted using a submersible pump, which was connected to a filtration system that contained three parallel and identical glass fiber filters (142-mm diameter) with the same pore size (0.7 μm). The total volume of water for all three filters was recorded, and the filters were collected using sterile stainless steel forceps into 50-ml sterile Falcon tubes. The tubes were immediately stored in a −20°C freezer on board the R/V Shiyan No. 3 after collection, transported under ambient temperature within 3 h, and stored at −80°C until further analysis.

(ii) Core-top sediment sampling. Sediment samples were collected using coring devices during three cruises in the SCS (Fig. 1). Cores A9, A7, and A5 were retrieved in July 2009 using the R/V Dongfanghong No. 2, core HQ08-48PC was collected in 2008 using the R/V Haiyang No. 4, and cores MD05-2894 to MD05-2905 were obtained during the Chinese-French joint Marco Polo/Images 147 cruise in 2005 using the R/V Marion-Dufresne. The lengths of these cores were less than 10 m. On board, the cores were opened and subsamples for lipid and microbiological studies were taken from the centers of the cores under sterile
Lipid analyses. (i) Lipid extraction and fractionation. Three methods were used for extraction of total lipids. In all three methods, the original sample was spined with an internal standard (C_{80}H_{74}O_{8}N_{8}S_{8}, 97.04 ng) before the extraction procedure began. Method A was used for core HQ08-48PC. In this method, the freeze-dried sediment sample spined with the internal standard was extracted ultrasonically five times with a mixture of dichloromethane (DCM) and methanol (MeOH) (3:1, vol/vol). The total extract was transferred into a KOH-MeOH solution (6%), left overnight, and then extracted with n-hexane five times. Method B was used for cores A9, AT, and AS. The freeze-dried sediment sample was ultrasonically extracted three times with MeOH, three times with DCM-MeOH (1:1, vol/vol), and three times with DCM, and all extracts were combined. Method C was used for all filter samples, which produced core lipid only. In this method, the freeze-dried filter material was cut into small pieces using sterilized scissors and then put into a 40-ml tube. MeOH, MeOH-DCM (1:1, vol/vol), and DCM were then used to extract lipids from the filter material sequentially, with each step repeated at least once. Extract from each step was collected, and the total extract was transferred into a KOH-MeOH solution (6%), left overnight, and extracted with n-hexane five times (22).

The final extract obtained from each method was fractionated into apolar and polar fractions using the same procedure. Briefly, the total extract was poured into a glass pipette column filled with activated silica gel and sequentially eluted with hexane-DCM (9:1, vol/vol) to obtain the apolar fraction and with DCM-MeOH (1:1, vol/vol) to obtain the polar fraction. To obtain the core GDGTs (C-GDGTs), the polar fraction was filtered through a 0.45-μm polytetrafluoroethylene (PTFE) filter and directly injected into a liquid chromatograph-mass spectrometer (LC-MS). The intact polar GDGTs (IP-GDGTs) were indirectly obtained as described by Huguet et al. (22). Briefly, half of the polar fraction was dried under N2 and hydrolyzed with 5% (vol/vol) HCl in MeOH for 4 h at 70°C. The hydrolyzed GDGT fractions were sequentially extracted four times with DCM-Milli-Q water (1:1) and four times with Milli-Q water after hydrolysis was complete. Each extraction was followed by centrifugation, and all extracts were pooled into one sample. The extracts were dried under N2 and dissolved in 300 μL n-hexane-isopropanol (99:1, vol/vol) before analysis by LC-MS. The IPL were calculated as the difference between the yields after and before hydrolysis (22).

(ii) GDGT analysis and quantification. Analyses of GDGTs were performed at the University of Hawaii. A slightly modified method of Schouten et al. (56). Separation was performed using an Agilent 1200 liquid chromatograph equipped with an automatic injector and a Prevail Cyano column (2.1 by 150 mm, 3 μm). Separation was determined only for the HQ core. The concentration of total organic carbon (TOC) ranged from 0.18% to 1.36%, with an average value of 0.94% ± 0.33% (n = 11). The δ^{13}C of TOC ranged from −19.54‰ to −24.22‰, with an average value of −21.21‰ ± 0.33‰ (n = 11), which is indicative of marine primary production (26, 46).

Abundances and distributions of archaeal lipids (CL and IPL). (i) Surface water samples. At each station, 200 to 1,100 liters of water was filtered. The abundances of total archaeal CL were all above the detection limit of the instrument (0.8 pg). However, 21 out of the 78 total filter samples gave very low yields based on the examination of the internal standard; these samples were eliminated from further analysis. The remaining samples showed total archaeal CL concentrations ranging from 0.001 ng/liter to 0.894 ng/liter of seawater (see Table S1 in the supplemental material). High values (concentrations above 0.1 ng/liter) were observed near Hainan Island and the east coast of Vietnam and in the central basin of the Bashi Strait between Taiwan and the Philippines; on the other hand, low archaeal CL concentrations commonly occurred in the southeast side of the SCS (Fig. 2). Overall, there is no correlation between concentrations of total archaeal CL and water column depths, as demonstrated by the presence of high values in waters of all
TABLE 1. General physical/chemical properties, total core lipids, and intact polar lipids, of archaea and bacteria of surface sediment samples from the South China Sea.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MD05-2894</th>
<th>MD05-2896</th>
<th>MD05-2898</th>
<th>MD05-2900</th>
<th>MD05-2902</th>
<th>MD05-2903</th>
<th>MD05-2905</th>
<th>HQ08-48PC</th>
<th>A5</th>
<th>A7</th>
<th>A9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude (N)</td>
<td>07°02.25’</td>
<td>08°49.50’</td>
<td>13°47.39’</td>
<td>14°23.33’</td>
<td>17°57.70’</td>
<td>19°27.32’</td>
<td>20°08.17’</td>
<td>16°57.5134’</td>
<td>20°59.746’</td>
<td>21°30.199’</td>
<td>22°00.50’</td>
</tr>
<tr>
<td>Longitude (E)</td>
<td>111°26.47’</td>
<td>112°26.47’</td>
<td>112°11.03’</td>
<td>110°41.74’</td>
<td>114°57.33’</td>
<td>116°15.15’</td>
<td>117°21.61’</td>
<td>119°31.5809’</td>
<td>114°58.784’</td>
<td>114°30.040’</td>
<td>113°59.963’</td>
</tr>
<tr>
<td>Water depth (m)</td>
<td>1,982</td>
<td>1,657</td>
<td>2,395</td>
<td>1,455</td>
<td>3,697</td>
<td>2,066</td>
<td>1,647</td>
<td>1,474</td>
<td>102</td>
<td>73</td>
<td>33</td>
</tr>
<tr>
<td>Sand content (%)</td>
<td>0.3</td>
<td>0.0</td>
<td>0.6</td>
<td>0.0</td>
<td>5.8</td>
<td>0.4</td>
<td>0.7</td>
<td>0.0</td>
<td>10.7</td>
<td>3.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Silt content (%)</td>
<td>70.2</td>
<td>70.7</td>
<td>74.3</td>
<td>73.3</td>
<td>75.5</td>
<td>76.7</td>
<td>82.4</td>
<td>82.1</td>
<td>79.3</td>
<td>82.0</td>
<td>80.1</td>
</tr>
<tr>
<td>Clay content (%)</td>
<td>29.5</td>
<td>29.3</td>
<td>25.1</td>
<td>22.7</td>
<td>18.7</td>
<td>22.9</td>
<td>16.8</td>
<td>17.8</td>
<td>10.1</td>
<td>14.7</td>
<td>18.3</td>
</tr>
<tr>
<td>Total archaeal CL (ng/g)</td>
<td>0.05</td>
<td>0.02</td>
<td>0.16</td>
<td>0.05</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td>ND</td>
<td>0.06</td>
<td>0.06</td>
<td>ND</td>
</tr>
<tr>
<td>Total archaeal IPL (ng/g)</td>
<td>10.07</td>
<td>8.89</td>
<td>12.68</td>
<td>14.18</td>
<td>3.23</td>
<td>3.14</td>
<td>5.39</td>
<td>38.09</td>
<td>14.43</td>
<td>69.04</td>
<td>73.15</td>
</tr>
<tr>
<td>Total branched CL (ng/g)</td>
<td>2.92</td>
<td>0.88</td>
<td>13.24</td>
<td>3.48</td>
<td>1.09</td>
<td>1.03</td>
<td>1.37</td>
<td>ND</td>
<td>4.41</td>
<td>17.79</td>
<td>ND</td>
</tr>
<tr>
<td>Total branched IPL (ng/g)</td>
<td>0.05</td>
<td>0.02</td>
<td>0.16</td>
<td>0.05</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
<td>ND</td>
<td>0.06</td>
<td>0.06</td>
<td>ND</td>
</tr>
</tbody>
</table>

* ND, not determined.

depths (Fig. 3). The concentrations of branched tetraether lipids indicative of bacteria were generally below the detection limit in the filter samples and thus were not reported.

(ii) Sediment samples. In sediment samples, total archaeal CL ranged from 0.11 µg/g to 0.90 µg/g, with the highest value occurring in the shallow water depth (A7, 73 m) (Fig. 4). Total archaeal IPL ranged from 0.88 ng/g to 13.24 ng/g, with the highest value occurring at MD05-2896 of the deep water (Table 1). Similar to the case for the filter samples, high total archaeal CL occurred in both shallow (<200-m) and deep (>1,000-m) waters, and the highest abundance also occurred in the shallower sediments (Fig. 4).

Total branched CL ranged from 3.14 ng/g to 38.72 ng/g, with the highest value occurring at the shallowest water depth (A9, 33 m) (Table 1). Total branched IPL ranged from 0.88 ng/g to 13.24 ng/g; the highest value occurred at the same location (MD05-2896) where the highest archaeal IPL occurred.

Relative abundances of GDGTs in CL and IPL. (i) Filter samples. GDGTs of archaeal CL were dominated by crenarchaeol (25.1% to 65.0%) and GDGT-0 (4.2 to 45.5%) (see Table S1 in the supplemental material). No archaeol (diether) (see Appendix for an explanation of structures) was detected in filter samples. Cluster analysis of the relative GDGT distributions showed no grouping of filter samples according to depth (Fig. 3), suggesting that water depth is unlikely to be a factor affecting the distribution of archaeal lipids in the surface water of the SCS.

(ii) Sediment samples. The highest abundances of archaeal GDGTs in either CL or IPL were also crenarchaeol (35.12 to 69.73%) and GDGT-0 (16.20 to 31.69%) (7482). For the same sample, crenarchaeol was consistently lower in relative abundance in IPL than in CL, whereas GDGT-0 was consistently higher in IPL than in CL. Archaeol was also higher in IPL than in CL in all but one sample (A7). Other GDGT compounds were either higher or lower in IPL than in CL; however, the majority of GDGT-2 and GDGT-3, and to a less extent, GDGT-1 and GDGT-4, showed higher values in IPL than in CL (Table 2). The ring index had a range of 2.28 to 3.70, with the IPL ring index being 0.20 to 1.37 units higher than the CL ring index (Table 2). However, there was no correlation between CL- and IPL-derived ring indices (data not shown), suggesting different GDGT compositions in the two lipid pools.

Cluster analysis showed that the compositions of the archaeal CL GDGTs at shallower (<100-m) water depths were different from those at water depths of below 1,000 m. Within the deep-water cluster, however, no spatial patterning was observed across the basin (Fig. 4). Comparison of the A9, A7, and...
A5 sediment samples with filter samples at water depths near 100 m or below showed that the shallow-sediment C-GDGTs were more similar to those in water samples in the same region than to those farther away from it (data not shown), suggesting a possible local connection between core-top sediment GDGTs and those of the planktonic Archaea. The BIT was less than 0.2 for both CL and IPL at all water depths (Table 2), indicating minor contributions of terrestrial organic matter in these locations (17).

**TEX86-derived temperatures.** (i) SST derived from surface water filter samples. Because the filter samples were collected during April and May of 2010, satellite-derived sea surface temperatures (SST) of April and May 2009 and CTD temperatures recorded during the sampling period were compared to TEX86-derived temperatures. The satellite and CTD temperature maps were consistent in showing the generally higher sea surface temperature in the southern part (below the 17.5°N line) of the SCS than in the northern part; however, CTD temperatures to the east of Hainan Island were 2 to 4°C higher than the satellite temperatures (Fig. 5).

Comparison of satellite sea surface temperatures and the three calculation methods showed the best match for satellite SST averaged for April and May of 2009 and the calculation based on that described by Kim et al. (32) (see Table S1 in the supplemental material), whereas use of satellite-based mean annual SST showed a poorer correlation (data not shown). The majority of TEX86 temperatures calculated according to the method of Kim et al. (32) were lower than satellite temperatures (Fig. 6A) or CTD temperatures (Fig. 6B). This was particularly evident in the northern SCS (Fig. 5). On average, the difference was 3.0 ± 2.3°C (n = 57) between satellite sea surface temperatures (averaged for April and May 2009) and TEX86-derived temperatures and 3.4 ± 2.9°C (n = 57) between CTD and TEX86 temperatures. The larger differences (e.g., greater than 5.0°C) between satellite sea surface temperatures and TEX86 values occurred mostly outside the central basin and toward the land (e.g., samples 15, 30, 48, 69, 75, 76, and 85) (Fig. 1). The large differences between CTD and TEX86 temperatures also occurred mostly at these stations (data not shown).
SST derived from core-top sediments. In most cases the TEX$_{86}^{IP}$-derived temperatures based on IP-GDGTs were higher than those based on C-GDGTs (Table 2). In some cases, the difference between C-GDGT- and IP-GDGT-derived temperatures could be as large as 18.3°C according to the formula of Schouten et al. (55) (equation 1). This difference decreased when formulas of Kim et al. (31, 32) (equations 2 and 3) were used, and the latter formula (equation 3) gave the smallest difference between the C-GDGT- and IP-GDGT-derived temperatures (Table 2).

The TEX$_{86}$ temperatures determined according to the method of Kim et al. (32) gave the closest match to the mean annual sea surface temperature from the satellite data. In the CL, the difference between satellite and TEX$_{86}$ temperatures (32) was less than 1.0°C in all deep-water core-top sediments except MD05-2902, which had a difference of 1.1°C (Table 2). In core-top sediments from shallower water (A9, A7, and A5), however, the difference was considerably larger (4.3 to 9.2°C), with TEX$_{86}$ temperatures lower than satellite temperatures (Fig. 7). Overall, the mean difference between mean annual satellite and TEX$_{86}$ temperatures was 1.9 ± 2.4°C ($n = 11$), which was much smaller than differences observed for filter samples (note that the uncertainty of the calibration in use is 2.5°C, which is greater than the 1.9°C mean difference observed).

In the IPL of the deep-water samples, the difference between satellite and TEX$_{86}$ temperatures (32) was mostly greater than 0.5°C, and it was up to 9.3°C in MD05-2986 (Table 2). Similar to the case for the CL, the IPL temperatures of the shallow-water core-top sediments gave larger differences from the satellite values than those of the deeper-water core-top sediments (Table 2).

**DISCUSSION**

Abundance and distribution of GDGTs. (i) Filter samples. The average concentration of C-GDGTs (0.05 ± 0.13 ng/liter; $n = 57$) for all filter samples (see Table S1 in the supplemental material) was less than 10% of the average concentrations of C-GDGTs determined in other oceanic water column studies (16, 22, 59, 62, 63). Factors affecting the measured abundance of C-GDGTs in oceanic waters may include difference in methods of lipid extraction and different relative responses in the mass spectrometer, growth stage of the planktonic *Archaea*, seasonal variation in planktonic archaeal productivity, water column depth, and/or other variables. Huguet et al. (22) compared several extraction methods on both a living culture and environmental samples. They observed that the living culture had trace amounts of C-GDGTs, indicating that actively growing cells were composed mostly of IP-GDGTs. Environmental samples (including particles from the water column), on the other hand, had considerable amounts of C-GDGTs relative to IP-GDGTs, suggesting that large proportions of environmental lipids were derived from nonliving cells. Those authors also recommended using sonication or Soxhlet extraction for studies aiming to determine TEX$_{86}$-derived temperatures or to quantify the relative abundances of C- versus IP-GDGTs. Our study followed the sonication extraction method recommended by Huguet et al. (22), and the low concentrations of CL are unlikely to be due to method biases. Although we do not know
TABLE 2. Relative abundances of GDGTs and archaeol in both core lipids and intact polar lipids of surface marine sediments in the South China Sea as well as TEX86-based temperatures calculated according to different formulas, such as mean annual sea surface temperatures, and BIT values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GDGT-0 (m/z 1392)</th>
<th>GDGT-1 (m/z 1394)</th>
<th>GDGT-2 (m/z 1298)</th>
<th>GDGT-3 (m/z 1292)</th>
<th>GDGT-4 (m/z 1290)</th>
<th>GDGT-5 (m/z 1296)</th>
<th>Archaeol</th>
<th>Relative abundance of archaeal lipids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H11002</td>
<td>16.50</td>
<td>5.90</td>
<td>2.91</td>
<td>1.09</td>
<td>0.00</td>
<td>67.65</td>
<td>0.69</td>
<td>1.96</td>
</tr>
<tr>
<td>H11002</td>
<td>0.20</td>
<td>23.78</td>
<td>25.00</td>
<td>25.19</td>
<td>24.82</td>
<td>25.82</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>H11002</td>
<td>0.16</td>
<td>28.66</td>
<td>29.12</td>
<td>28.42</td>
<td>27.47</td>
<td>26.66</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

The growth stage of the planktonic Archaea in the SCS, estimates of lifetimes of planktonic Archaea are on the order of days to weeks (24). In reference to what Huguet et al. (21, 23) have observed, the low concentrations of C-GDGTs in our filter samples may not represent cells that were all active at the time of sampling. Another possible explanation for low GDGT concentrations may be the degradation of these compounds during transportation at ambient temperature. However, degradation, if any, appears not to have affected the calculation of temperatures based on the TEX86 formula, which is consistent with Schouten et al. in that oxic degradation does not affect the TEX86 values within the analytical error (54).

Depth distribution and/or seasonal variation in planktonic Archaea may be better reasons for the low concentrations of C-GDGTs in the surface water of the SCS. Quantification of archaeal biomass using molecular DNA methods has repeatedly shown that Crenarchaeota, which are thought to be the major producers of GDGTs in the ocean, are at low levels in surface water and increase in relative or absolute abundances with depth (see, e.g., references 9, 30, 45, 47, and 65). A study of archaeal abundance in the SCS showed the same pattern, with surface water (5 m) having about 10^7 copies of archaeal 16S rRNA genes per ng of DNA, whereas at 75 m the archaeal abundance was 2 orders of magnitude higher (18). Depth profiles of archaeal lipids in the Black Sea also showed low GDGT concentrations in surface water (10 m) and a maximum at about the 100-m depth, which agrees with the maximum Archaea cell numbers (63). Similarly, in the Gulf of Mexico, GDGTs were detected at depths of 400 m and 509 m but not at 10 m (40). On the other hand, planktonic Archaea also vary in abundance in different seasons, with colder temperatures favoring a higher abundance of Archaea in many oceanic regimes (14, 16, 48, 65). It is possible that the low concentration of C-GDGTs in the SCS surface water resulted from sampling in a nonwinter season. This hypothesis has yet to be tested through seasonal and vertical sampling of the water columns in the SCS, which has been planned for the near future.

High abundances of planktonic Archaea are often found in association with upwelling and the oxygen minimum zone (OMZ) (1, 10, 33, 36). In the SCS, upwelling commonly occurs in regions northwest of Luzon and north of Sunda Shelf in winter and off the east coast of Vietnam in summer (41). The abundances of archaeal CL in surface water resulted from sampling at 10 m (40). On the other hand, planktonic Archaea may also vary in abundance in different seasons, with colder temperatures favoring a higher abundance of Archaea in many oceanic regimes (14, 16, 48, 65). It is possible that the low concentration of C-GDGTs in the SCS surface water resulted from sampling in a nonwinter season. This hypothesis has yet to be tested through seasonal and vertical sampling of the water columns in the SCS, which has been planned for the near future.

(ii) Sediment samples. The C-GDGTs in the sediment samples (Table 2) are at the lower end of the ranges observed in other marine sediment environments (see Table 4 in reference 22). For example, C-GDGTs in the range of 0.09 to 11 μg/g were reported for the Drammensfjord sediment in Norway (20, 23). C-GDGTs in the range of 0.06 to 195 μg/g for the Arabian Sea sediment (20), and C-GDGTs in the range of 0.02 to 7.73
μg/g for Atlantic Ocean sediments (19). Lower C-GDGT abundance has been explained as being a result of an enhanced degradation rate under oxic conditions (19). It is unknown whether in this study differential degradation contributed to the lower C-GDGT concentrations in our surface marine sediments. On the other hand, the low GDGT concentrations may reflect the overall oligotrophic conditions of the South China Sea (41), which is consistent with the low C-GDGT concentrations in the surface water and supported by the relatively low TOC (average = 0.94 ± 0.12%, n = 11) in these samples (Table 1) (39).

IP-GDGTs accounted for 6.0 to 36.4% of total GDGTs (C plus IP). This is consistent with observations reported by others (20, 38, 42) and suggests that the majority of GDGT lipids in marine core-top sediments are derived from nonliving Archaea. The sources of CL and IPL in marine sediments, however, are debated and can come from either in situ production (3, 38, 39, 42) or possibly relict IPL from the water column (57). In particular, benthic archaeal populations seem to be able to recycle fossil GDGTs from planktonic Archaea (37, 42, 60), which can explain the higher TEX$_{86}$ temperatures based on IPL than on CL (42).

![FIG. 5. Maps of satellite-based average sea surface temperatures for the April-May season during which the surface water samples were collected (left), in situ temperatures determined from CTD (middle), and TEX$_{86}$-based temperatures of surface water samples according to reference 32. (Maps generated with Ocean Data View software.)](http://aem.asm.org/)

![FIG. 6. (A) Correlations between satellite-based sea surface temperatures (from Fig. 5) and TEX$_{86}$-based temperatures (32). (B) Correlations between CTD in situ temperatures (from Fig. 5) and TEX$_{86}$-based temperatures (32). In both cases, the correlation is insignificant (P > 0.05).](http://aem.asm.org/)
Our observation of structural changes in CL and IPL (Table 2) agrees with a report for other marine sediments (42). However, Liu et al. (42) also showed significant correlations in the ring index and in the TEX\textsubscript{86}-derived temperatures between C- and IP-GDGTs, which allowed them to explain the overall connections between these two lipid pools with three possibilities: (i) the pool of C-GDGTs is strongly influenced by sedimentary \textit{in situ} production and subsequent hydrolysis of IP-GDGTs, (ii) the pool of IP-GDGTs largely represents molecular fossils derived from planktonic \textit{Archaea}, and (iii) there is partial recycling by benthic \textit{Archaea} of fossil C-GDGTs derived from planktonic \textit{Archaea} (42). Neither our data nor those of Liu et al. (42) allow us to draw a conclusion about the exact sources of CL and IPL in the marine sediments. However, the lack of correlations in the ring index and in the TEX\textsubscript{86}-derived temperatures between C- and IP-GDGTs in our study (data not shown) indicates the presence of other sources of C- and IP-GDGTs in the SCS sediments. Modeling (38, 39, 57) in combination with isotopic measurements of different intramolecular components of the GDGT molecules (37, 58, 60) and measurements of the metabolic status of \textit{Archaea} (22, 24) may be needed to thoroughly evaluate to what extent the IP-GDGTs represent fossil or living archaeal biomass in natural environments.

**TEX\textsubscript{86}-derived temperatures.** The development of the TEX\textsubscript{86} proxies has significantly advanced our understanding of paleoclimate change (12). In the core-top sediments, the TEX\textsubscript{86}-derived temperatures based on the work of Kim et al. (32) agree with satellite-derived mean annual surface temperatures except for the shallow (<100-m) water depths, which show significantly lower temperatures than satellite values (Fig. 5). A similar discrepancy has been observed on the Italian shelf of the Gulf of Taranto by Leider et al. (35), who attributed the lower TEX\textsubscript{86}-based temperatures for the near-shore \textit{Archaea} in most of the filter samples. The distribution of the CL was heterogeneous, with high values occurring in regions where upwelling commonly occurs and low values occurring in the southeast area of the SCS. The CL of \textit{Archaea} in surface marine sediments ranged from 0.11 to 0.90 g/g, which were at the low end of CL concentrations commonly observed for other marine sediments and may reflect the oligotrophic productivity of the SCS. The IPL of \textit{Archaea} represented 6 to 36.4% of total lipids (C plus IP), suggesting that the majority of archaeal lipids in core-top sediments were fossil remains of archaeal cells.
surface temperatures, suggesting that planktonic Archaea might respond to temperature variations at the seasonal scale. Nevertheless, the TEX$_{86}$ temperatures of the surface water were significantly lower than satellite or CTD-derived temperatures; however, our data do not allow conclusions to be drawn about the causes of the discrepancies. TEX$_{86}$ temperatures from surface marine sediments in the open ocean (water depth of >1,000 m) were within 1°C of the mean annual sea surface temperatures, suggesting the applicability of TEX$_{86}$ proxies (32) for paleoclimate studies in at least the central basin of the South China Sea. The much lower TEX$_{86}$ temperatures for marine sediments from depths shallower than 100 m indicated that caution must be exercised in interpretation of paleotemperatures from TEX$_{86}$ values obtained from the shallow continental shelf of the SCS.

APPENDIX

Figure A1 shows the structures of isoprenoidal and branched glycerol dibiphytanyl glycerol tetraether (GDGT) and archaeol.

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