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Note

Archaeal and bacterial glycerol dialkyl glycerol tetraethers in sediments from the Eastern Lau Spreading Center, South Pacific Ocean

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ABSTRACT

The compositions of glycerol dialkyl glycerol tetraethers (GDGTs) in surface sediments and sediment cores from the Eastern Lau Spreading Center (ELSC), South Pacific Ocean, were determined. Isoprenoid GDGTs (isoGDGTs) and branched GDGTs (brGDGTs) are present in all the samples, with archaea and bacteria, respectively, as the sources of these membrane lipids. Greater concentrations of isoGDGTs (0.08–38.0 ng/g dry weight (dw)) than brGDGTs (0.05–27.4 ng/g dw) indicate that archaea made larger contributions to the GDGT pool in the ELSC sediments than bacteria. The relative abundance of brGDGTs and BIT index (the branched vs. isoprenoid tetraether) values are higher in samples taken from the seafloor in the vicinity of or close to hydrothermal vents than in samples taken distant from hydrothermal activity, suggesting that brGDGTs are likely produced in the ELSC hydrothermal vents. Temperature estimates based on TEX_{86} (TetraEther indeX of tetraethers consisting of 86 carbon atoms) appear to reflect local surface water temperatures despite potential in situ hydrothermal input of GDGTs to the ELSC sediments.

1. Introduction

GDGTs are membrane lipids produced by archaea and bacteria (Sinninghe Damsté et al., 2000; Weijers et al., 2006a) and exist in two major forms: isoprenoid (isoGDGTs) and branched (brGDGTs) (Appendix A; see also Kim et al., 2008). IsoGDGTs are produced by a diverse array of archaea, including *Crenarchaeota* and *Euryarchaeota*, and they usually have acyclic or ring-containing biphytanyl chains (De Rosa and Gambacorta, 1988; Koga and Morii, 2006). One isoGDGT, crenarchaeol, is postulated to be specific for *Thaumarchaeota* (Brochier-Armanet et al., 2008) and was originally considered to be synthesized only by non-thermophilic marine members of this phylum (Sinninghe Damsté et al., 2002). However, it has been subsequently detected in a culture of thermophilic nitrifying *Thaumarchaeote* (de la Torre et al., 2008) and in microbial mats in terrigenous geothermal hot springs (Zhang et al., 2006; Schouten et al., 2007b; Pearson et al., 2004, 2008) and in soils adjacent to terrigenous geothermal hot springs (Pitcher et al., 2009). BrGDGTs are generally attributed to soil bacteria (Sinninghe Damsté et al., 2000; Weijers et al., 2006b) possibly *Acidobacteria* (Sinninghe Damsté et al., 2011).

The composition of isoGDGTs in sediments can be used to reconstruct paleotemperature histories of aquatic systems using the proxy TEX_{86} (Schouten et al., 2002). This proxy has been applied to reconstruct both sea surface temperatures (SST: e.g. Huguet et al., 2007; Rueda et al., 2009; Castañeda et al., 2010) and lake surface water paleotemperatures (e.g. Powers et al., 2004, 2005, 2010; Tierney et al., 2007; Blaga et al., 2009). Another GDGT proxy, the BIT (branched/isoprenoid) index, has been proposed and applied to determine the relative inputs of soil organic matter to aquatic environments (Hopmans et al., 2004; Weijers et al., 2007; Walsh et al., 2008). However, Peterse et al. (2009) found evidence of in situ production of at least some of the brGDGTs in marine sediments. Tierney and Russell (2009) also postulate in situ production of brGDGTs in Lake Towuti in addition to a soil bacterial source and Schouten et al. (2007b) and Zhang et al. (personal communication) also found brGDGTs in sediments and microbial mats in hot springs. These findings indicate that brGDGTs can be produced not only in soils but also in aquatic environments.

As a contribution towards assessing the possible importance of hydrothermal activity on the origins of GDGT membrane lipids, we investigated their compositional distributions in sediments from a marine hydrothermal field distant from the potential input of continental organic matter. Our study material consists of surface and short core sediments collected from the Lau Basin in the South Pacific Ocean. The results of our investigation have potentially significant implications to applications and interpretations of the TEX_{86} and BIT index proxies in hydrothermal settings.

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2. Material and methods

2.1. Sites and sample collection

The Lau Basin is an actively spreading back-arc basin that is located at the convergent boundary of the Pacific and Indo-Australian plates (Fig. 1A). The Eastern Lau Spreading Center (ELSC) is located in the Lau back-arc basin, west of the Tonga Trench between ~19° and 22.2°S (Fig. 1B). This location lies under the Southeast Trade Winds and the closest significant upwind land area is South America, some 9000 km to the east. Hydrothermal activity has been identified at multiple locations along the ELSC (Ferrini et al., 2008).

Sediment samples were collected during the April/May 2007 cruise of R/V Dayang Yihao. Surface sediment (0–1 cm) samples were obtained by TV-Grab and sediment cores were taken with a multi-corer. All the sediment samples were lithologically described onboard the ship and then divided into subsamples that were stored at −20 °C until analysis. Eight surface sediment samples and two sediment cores were analyzed in our study (Table 1). Surface samples TVG2, TVG11 and TVG14 were taken from areas distant from known hydrothermal activity (>17 km) and TVG5 and TVG6 were taken from areas close to hydrothermal vent Hine Hina (<1 km). TVG9 and TVG10 were taken from the seafloor in the vicinity of hydrothermal vent Mariner and TVG8 was taken from the seafloor in the vicinity of hydrothermal vent Vai Lili (Fig. 1B). Sediment cores TVMC2 and TVMC8 were also collected distant from known hydrothermal activity (Fig. 1B). Core TVMC2 was sectioned at 1 cm intervals, and core TVMC8 was sectioned at 4 cm intervals for this study.

2.2. Extraction and analytical procedures

The sediments were freeze dried and then homogenized using a mortar and pestle. Subsamples of about 3 g were sequentially extracted by sonication with methanol, a mixture (1:1, v:v) of methanol and dichloromethane (DCM), and DCM (15 min, each three times). After each sonication, the samples were centrifuged and the supernatants were collected. The three supernatants of each sample were combined and concentrated by rotary evaporation at 40 °C. The concentrated extracts were partitioned into the chloroform phase by addition of 5% KCl solution. The total lipid extract soluble in the chloroform phase was fractionated into nonpolar and polar fractions using an activated alumina column and hexane:DCM (9:1, v:v) and DCM:methanol (1:1, v:v) as respective eluents.

The polar fraction was evaporated to dryness and redissolved in hexane:propanol (99:1, v:v). The resulting suspension was filtered through a 0.45 μm PTFE filter. The filtrate was analyzed using high performance liquid chromatography (HPLC) and atmospheric pressure positive ion chemical ionization mass spectrometry (APCI-MS; Agilent 6410 QQQ LC–MS). The LC–MS was equipped with an autoinjection system and Agilent Chemstation software. The detection limit of the method was defined as three times the signal/noise ratio. Normal phase separation was achieved with a Prevail Cyano column (150 mm × 2.1 mm, 3 μm; Altech, USA) maintained at 30 °C. The injection volume was 20 μl, and the flow rate was 0.2 ml/min. GDGTs were first eluted isocratically with a mixture of hexane (99%) and propanol (1%) for 5 min, followed by a linear gradient to 2% propanol for 45 min. After each injection, the column was cleaned with a mixture of hexane (60%) and propanol

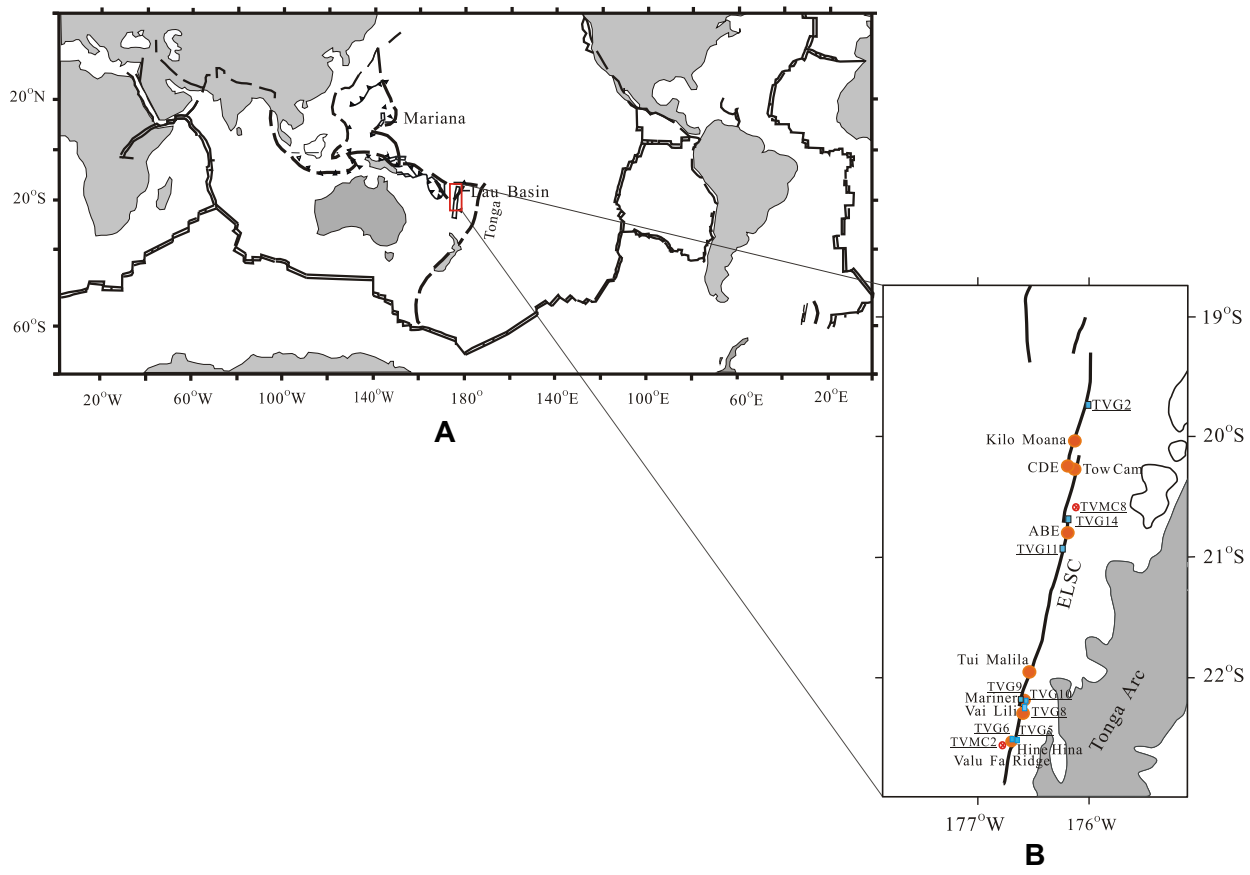

Fig. 1. (A) Location of the Lau Basin in the South Pacific Ocean. Figure adapted from Baker et al. (2008). (B) Sediment sample sites along the Eastern Lau Spreading Center (ELSC) ● marks known hydrothermal vents.

Table 1
Summary of surface sediment sample information and results.

Sample	Latitude (°S)	Longitude (°W)	Water depth (m)	Rough distance from a vent (km)	Total GDGTs (ng/g dw)	isoGDGTs (ng/g dw)	BrGDGTs (ng/g dw)	GDGT-0 (ng/g dw)	Crenarchaeol (ng/g dw)	BrGDGTs (%)	BIT	TEX_{86}	TEX_{86}-T (°C)
TVG2	19.7418	175.956	2350	40 (Kilo Moana)[a]	9.5	8.6	0.9	1.6	3.6	9.0	0.16	0.72	29.9
TVG11	20.9281	176.241	2254	20 (ABE)[a]	2.5	2.1	0.4	0.6	0.7	16.7	0.32	0.69	28.1
TVG14	20.6854	176.185	2249	18 (ABE)[a]	7.9	7.1	0.8	1.9	2.6	10.2	0.18	0.70	28.6
TVG5	22.5338	176.711	1885	0.9 (Hine Hina)[a]	10.1	6.8	3.3	1.1	3.1	32.9	0.44	0.76	32.0
TVG6	22.5318	176.716	1868	0.5 (Hina Hina[a]	42.1	24.5	17.6	5.3	8.8	41.7	0.21	0.69	27.8
TVG8	22.2158	176.607	1744	0.03 (Vai Lili)[a]	65.4	38.0	27.4	12.9	10.5	41.9	0.43	0.73	30.0
TVG9	22.1813	176.602	1922	0.01 (Mariner)[a]	0.1	0.08	0.05	0.03	0.01	41.0	0.76	0.72	29.6
TVG10	22.1811	176.602	1921	0.01 (Mariner)[a]	7.3	6.8	0.5	1.4	2.7	6.7	0.10	0.67	26.7

(40%) for 15 min at 0.2 ml/min. The conditions for APCI-MS were: nebulizer pressure 60 psi, vaporizer temperature 300 °C, drying gas (N_2) flow 5 l/min and temperature 200 °C, capillary voltage −2.5 kV, corona 5 μA. The GDGTs were detected by selected ion monitoring (SIM) mode, following the methods of Hopmans et al. (2000) and Schouten et al. (2007a). Quantification was achieved by integration of the peak area of $[M+H]^+$ ion traces of GDGTs. Each sample was analyzed in duplicate and the data presented are the duplicate means. Absolute amounts of GDGTs are calculated following Huguet et al. (2006). Replicate analysis of samples gave reproducibilities that are ±0.03 for BIT index measurements and ±0.4 °C for the TEX_{86} temperature estimates.

3. Results and discussion

IsoGDGTs and brGDGTs were detected in all the ELSC samples. Fig. 2 shows HPLC-MS base peak chromatograms exhibiting the compositional distributions of GDGTs in the surface sediments. The concentrations of iso- and brGDGTs range from 0.08–38 ng/g and from 0.05–27.4 ng/g dry weight (dw) for the surface sediments (Table 1). The highest GDGT concentrations are found in sediments from the seafloor in the vicinity of or close to the hydrothermal vents (e.g. TVG6 and TVG8). Also, significant differences exist in the relative abundance of brGDGTs in sediment samples from the vicinity of a hydrothermal vent, close to a vent and distant from hydrothermal activity. Abundances are relatively high in samples from the vicinity of or close to hydrothermal vents (33–42% of total GDGTs, except TVG10), and they are relatively low in samples collected distant from the hydrothermal fields (9–17% of total GDGTs; Table 1). BIT values are relatively high (0.21–0.76) in samples from the vicinity of or close to hydrothermal vents and relatively low in samples collected distant from the hydrothermal fields. An exception exists in sample TVG10, which has the minimum BIT value (0.10) which was taken from the vicinity of hydrothermal vent.

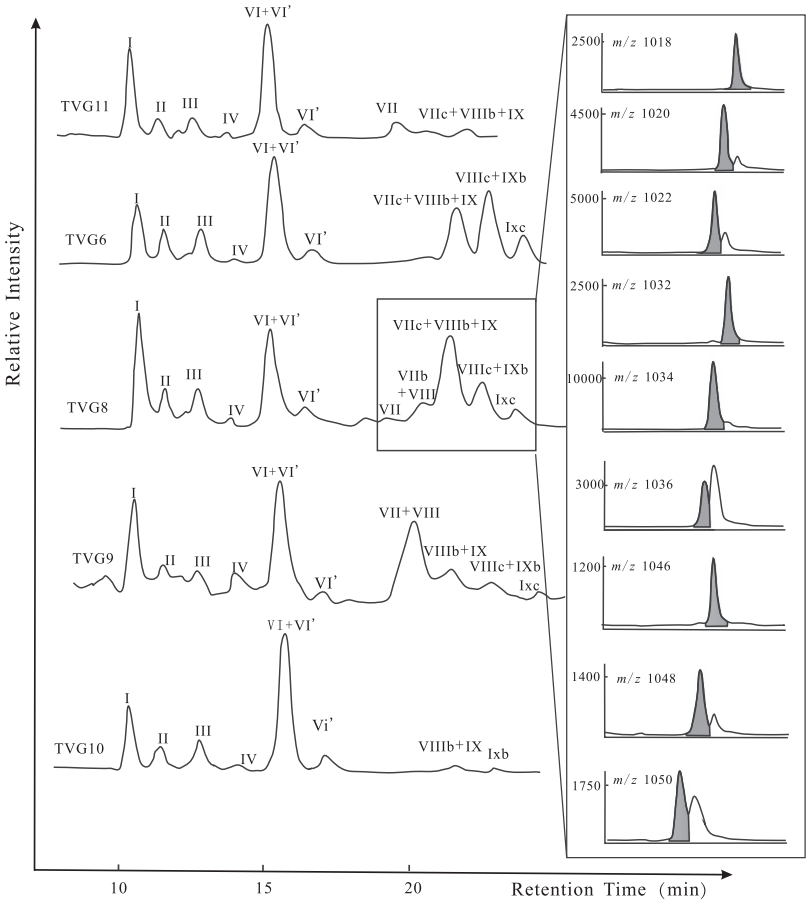

Fig. 2. Total ion and selected ion chromatograms (HPLC–APCI-MS) of GDGTs in surface sediments. Peak numbers refer to GDGT numbers of the structures in Appendix A.

IsoGDGT and brGDGT concentrations range from 0.16–26.9 ng/g and from 0.02–2.4 ng/g dw for core TVMC2 and from 1.7–14.9 ng/g and from 0.14–0.82 ng/g dw for core TVMC8 (Table 2). The concentrations of brGDGTs are generally low for the two sediment cores, both of which were collected at some distance from the hydrothermal fields. The relative abundance of isoGDGTs is 84–93% of total GDGTs for core TVMC2 and 92–95% of total GDGTs for core TVMC8. BIT values are 0.08–0.22 for core TVMC2 and are relatively low (0.10–0.14) for core TVMC8 (Table 2 and Fig. 3). The GDGT concentrations decrease with depth in both cores and this trend is more obvious in the shorter core TVMC2 (Fig. 3). However, a systematically significant change is absent in any of the GDGT proxies, including the proportions of brGDGT and isoGDGT components despite the large decrease in the absolute concentrations. Given the isolated deep sea location of the two cores, which is under a part of the ocean that has not experienced major glacial–interglacial changes in conditions, the concentration decreases in the two cores are most likely caused by the diagenetic degradation of GDGT compounds. However, our data cannot rule out a progressive change in GDGT delivery to the two core locations over time.

The compositional distributions of isoGDGTs in all samples show a characteristic marine archaeal GDGT profile: relatively abundant crenarchaeol and GDGT-0 and smaller amounts of GDGT-1, GDGT-2, and GDGT-3, and the crenarchaeol regio-isomer (Wuchter et al., 2005). IsoGDGTs are relatively more abundant (from 58–94% of total GDGTs) in the sediments compared to brGDGTs, suggesting that archaea make a relatively more important contribution to the GDGT pool in the ELSC sediments than bacteria. For the two sediment cores, the relatively higher abundance of isoGDGTs in core TVMC8 than in TVMC2 (Fig. 3) indicates that archaea made relatively greater contributions to the GDGTs in core TVMC8.

BrGDGTs are usually considered to be derived from anaerobic bacteria living in soils and peat bogs (Weijers et al., 2006a). Therefore, the BIT index was developed and has been used to estimate the relative inputs of fluvial soil organic matter in marine environments (e.g. Hopmans et al., 2004; Weijers et al., 2007). On this basis, the presence of brGDGTs in the ELSC sediments implies delivery of continental organic matter to this isolated location. However, the *n*-alkane distributions of the ELSC sediment samples range from C_{11} to C_{24} and lack the *n*-C_{27} to *n*-C_{33} homologs diagnostic of land plant waxes (unpublished data), indicating virtually no contribution of terrigenous lipids to the surface sediments. Moreover, the proportion of brGDGTs in the ELSC sediments is variable (Tables 1 and 2). Relatively high BIT indices and abundances of brGDGTs are found in sediments in the vicinity of or close to the hydrothermal vents (e.g., TVG5, TVG6, TVG8 and TVG9), suggesting that a local source may exist for the ELSC brGDGTs. Because of the distributional pattern, this origin is likely in situ production of brGDGTs in the hydrothermal vents. However, exceptions exist to this pattern. TVG10 has the minimum BIT value (0.10), and it was taken from the seafloor in the vicinity of hydrothermal vent Mariner. The absolute brGDGT and crenarchaeol concentrations are 0.49 ng/g and 2.7 ng/g dw, respectively (Table 1), and the relative abundance of crenarchaeol is high (37% of total GDGTs). Therefore, the low BIT index value that is found at TVG10 can be attributed to the increase in the abundance of crenarchaeol. Moreover, the sediment of TVG10 was mainly composed of silt and contained no hydrothermal minerals. Therefore, TVG10 probably did not record the input of organic matter derived from the hydrothermal vent biota. For the two sediment cores collected at some distance from the hydrothermal vents, both the BIT index values and brGDGT concentrations are low (Fig. 3), further supporting the origin of the brGDGTs from in situ production in the hydrothermal vents. Although some changes occur with depth in BIT values and relative abundances of brGDGT and isoGDGTs of the shorter core, they are relatively small. The absolute concentrations in the shorter core are similar to those at the same depths in the longer core, indicating that sediments at both sites record similar depositional conditions and have not been affected by localized unusual events or conditions.

The TEX_{86} is widely used for the reconstruction of SSTs (Schouten et al., 2002). The TEX_{86}-derived temperatures are 27–32 °C in the surface ELSC sediments (Table 1). In the study area, the average annual, summer and winter SSTs from 1960 to 2007 were ~28.5 °C, 30.5 °C and 27 °C, respectively (Llewellyn, 2010). The observed annual mean SST from 1950 to 2001 was 28 °C (Zhang and McPhaden, 2006). Therefore, it seems that the ELSC sediment TEX_{86} values reasonably reflect local SST in the Eastern Lau Basin, taking into account analytical error and possible seasonal influences. At the same time, hydrothermal input of GDGTs might change the

Table 2
Summary of core sediment sample information and results.

Sample	Total GDGTs (ng/g dw)	isoGDGTs (ng/g dw)	BrGDGTs (ng/g dw)	GDGT-0 (ng/g dw)	Crenarchaeol (ng/g dw)	BrGDGTs (%)	BIT	TEX_{86}	TEX_{86}-*T* (°C)
TVMC2 (22.5354°S, 176.800°W), water depth 2726 m									
0–1 cm	29.0	26.9	2.1	6.6	9.3	7.2	0.08	0.73	30.5
1–2 cm	19.6	17.2	2.4	3.8	6.0	12.4	0.13	0.69	28.0
3–4 cm	16.3	15.0	1.3	3.4	5.5	7.7	0.12	0.67	27.1
5–6 cm	9.6	8.9	0.7	2.4	2.9	7.7	0.13	0.64	25.5
7–8 cm	10.3	9.4	0.9	2.5	3.1	9.0	0.16	0.64	25.3
9–10 cm	3.4	3.0	0.4	0.8	1.1	12.6	0.18	0.63	24.7
11–12 cm	6.5	5.7	0.8	1.5	1.8	12.4	0.20	0.65	25.6
13–14 cm	6.0	5.1	0.9	1.4	1.6	15.7	0.20	0.79	33.8
15–16 cm	5.2	4.5	0.7	1.3	1.30	13.0	0.22	0.65	25.6
16–17 cm	0.2	0.17	0.03	0.04	0.06	11.1	0.19	0.68	27.7
TVMC8 (20.6660°S, 176.128°W), water depth 2457 m									
2–3 cm	15.7	14.9	0.8	3.0	5.8	5.2	0.10	0.72	30.0
6–7 cm	11.9	11.1	0.8	3.0	3.7	6.4	0.13	0.71	29.1
10–11 cm	9.5	8.7	0.8	2.6	2.8	8.2	0.14	0.70	28.7
12–13 cm	1.9	1.7	0.2	0.5	0.6	7.6	0.14	0.78	33.1
14–15 cm	8.0	7.6	0.4	1.8	2.6	5.4	0.12	0.71	29.3
18–19 cm	6.6	6.1	0.5	1.1	2.4	8.0	0.14	0.73	30.0
22–23 cm	8.1	7.5	0.6	1.6	2.7	7.8	0.14	0.73	30.5
26–27 cm	9.2	8.7	0.5	1.8	3.3	5.3	0.12	0.73	30.2
30–31 cm	6.8	6.4	0.4	1.4	2.3	6.8	0.11	0.72	29.7
32–34 cm	4.7	4.4	0.3	0.8	1.7	6.2	0.11	0.74	30.6

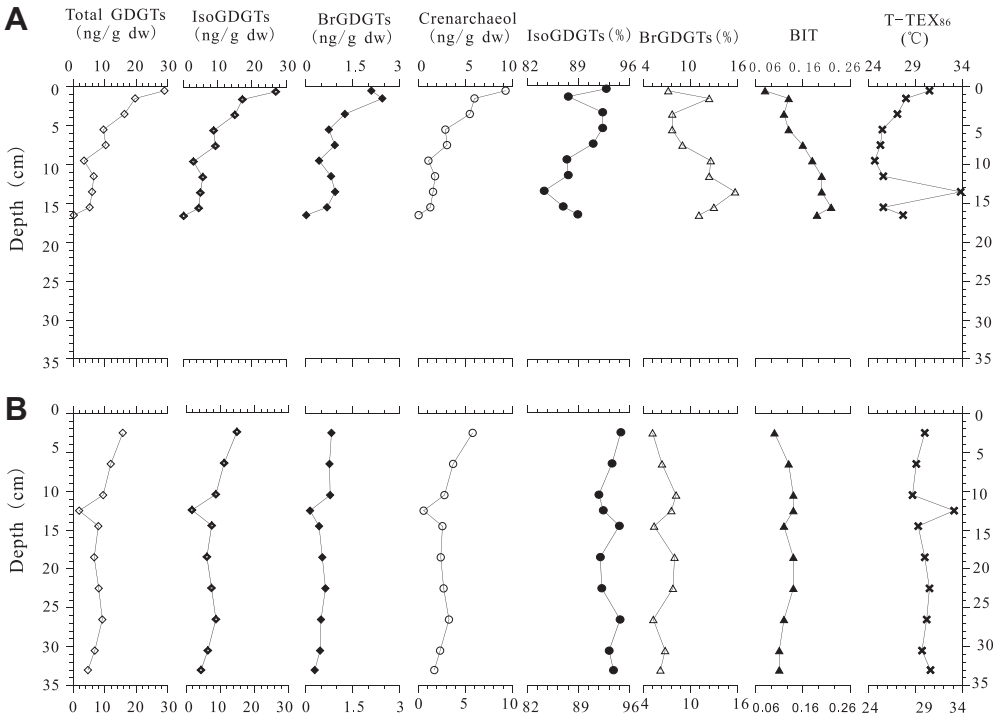

Fig. 3. Down-core sediment profiles of GDGT composition. (A) Core TVMC2, (B) core TVMC8.

recorded TEX_{86} temperature. The relatively higher TEX_{86}-derived temperatures in samples collected in the vicinity of or close to the hydrothermal vents (e.g. TVG5 and TVG8) are possibly due to additional input of related GDGTs by thermophilic and hyperthermophilic archaea that are adapted to conditions close to hydrothermal vents.

The TEX_{86}-derived temperatures are 24.7–33.8 °C and 28.7–33.1 °C for cores TVMC2 and TVMC8, respectively. At the depth of 12.5–13.5 cm, the TEX_{86}-based temperatures reach their maxima in both cores (Fig. 3). At the same time, the relative concentrations of branched GDGTs and the BIT values are also relatively high (Fig. 3). Therefore, this depositional layer perhaps records a past episode of more intense hydrothermal activity and greater in situ production of brGDGTs.

4. Conclusions

BrGDGT concentrations in sediment samples taken from the seafloor in the Eastern Lau Basin Spreading Center (ELSC) in the vicinity of or close to (<1 km) hydrothermal vents are high, which is not likely due to terrigenous GDGT inputs because land areas are too distant (>3200 km) to be important sources. High BIT index values and relatively high abundances of brGDGTs in samples collected from the seafloor in the vicinity of or close to hydrothermal vents in the ELSC suggest that brGDGTs are locally produced in the hydrothermal vents. The TEX_{86}-derived temperature estimates from the ELSC sediments are 26.7–32.0 °C and are similar to modern SSTs, which suggests that TEX_{86} can reflect local SST in areas like the ELSC despite potential GDGT hydrothermal input at the seafloor.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orggeochem.2011.10.012.

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References

Baker, E.T., Embley, R.W., Walker, S.L., Resing, J.A., Lupton, J.E., Nakamura, K.-I., de Ronde, C.E.J., Massoth, G.J., 2008. Hydrothermal activity and volcano distribution along the Mariana arc. Journal of Geophysical Research 113, B08S09. doi:10.1029/2007JB005423.

Blaga, C.I., Reichart, G.-J., Heiri, O., Sinninghe Damsté, J.S., 2009. Tetraether membrane lipid distributions in water-column particulate matter and sediments: a study of 47 European lakes along a north-south transect. Journal of Paleolimnology 41, 523–540.

Brochier-Armanet, C., Boussau, B., Gribaldo, S., Forterre, P., 2008. Mesophilic crenarchaeota: proposal for a third archaeal phylum, the Thaumarchaeota. Nature Reviews Microbiology 6, 245–252.

Castañeda, I.S., Schefuß, E., Pätzold, J., Sinninghe Damsté, J.S., Weldeab, S., Schouten, S., 2010. Millennial-scale sea surface temperature changes in the eastern mediterranean (Nile river delta region) over the last 27,000 years. Paleoceanography 25, 1. doi:10.1029/2009PA001740.

de la Torre, J.R., Walker, C.B., Ingalls, A.E., Könneke, M., Stahl, D.A., 2008. Cultivation of a thermophilic ammonia oxidizing archaeon synthesizing crenarchaeol. Environmental Microbiology 10, 810–881.

De Rosa, M., Gambacorta, A., 1988. The lipids of archaebacteria. Progress in Lipid Research 27, 153–175.

Ferrini, V.L., Tivey, M.K., Carbotte, S.M., Martinez, F., Roman, C., 2008. Variable morphologic expression of volcanic, tectonic, and hydrothermal processes at six

hydrothermal vent fields in the Lau back-arc basin. Geochemistry, Geophysics, Geosystems 9, Q07022. doi:10.1029/2008GC002047.

Hopmans, E.C., Schouten, S., Pancost, R.D., van der Meer, M.T.J., Sinninghe Damsté, J.S., 2000. Analysis of intact tetrameter lipids in archaeal cell material and sediments by high performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometry. Rapid Communications in Mass Spectrometry 14, 585–589.

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

Huguet, C., Hopmans, E.C., Febo-Ayala, W., Thompson, D.H., Sinninghe Damsté, J.S., Schouten, S., 2006. An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids. Organic Geochemistry 37, 1036–1041.

Huguet, C., Schimmelmann, A., Thunell, R., Lourens, L.J., Sinninghe Damsté, J.S., Schouten, S., 2007. A study of the TEX paleothermometer in the water column and sediments of the Santa Barbara basin, California. Paleoceanography 22, 3–8454. doi:10.1029/2006PA001310.

Kim, J.-H., Schouten, S., Hopmans, E.C., Donner, B., Sinninghe Damsté, J.S., 2008. Global sediment core-top calibration of the TEX_{86} paleothermometer in the ocean. Geochimica et Cosmochimica Acta 72, 1154–1173.

Koga, Y., Morii, H., 2006. Special methods for the analysis of ether lipid structure and metabolism in archaea. Analytical Biogeochemistry 348, 1–14.

Llewellyn, L.E., 2010. Revisiting the association between sea surface temperature and the epidemiology of fish poisoning in the South Pacific: reassessing the link between ciguatera and climate change. Toxicology 56, 691–697.

Pearson, A., Huang, Z., Ingalls, A., Romanek, C.S., Wiegel, J., Freeman, K.H., Smittenberg, R.H., Zhang, C.L., 2004. Nonmarine crenarchaeol in Nevada hot springs. Applied and Environmental Microbiology 70, 5229–5237.

Pearson, A., Pi, Y., Zhao, W., Li, W., Li, Y., Inskeep, W., 2008. Factors controlling the distribution of archaeal tetraethers in terrestrial hot springs. Applied and Environmental Microbiology 74, 3523–3532.

Peterse, F., Kim, J.-H., Schouten, S., Kristensen, D.K., Koc, N., Sinninghe Damsté, J.S., 2009. Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway). Organic Geochemistry 40, 692–699.

Pitcher, A., Schouten, S., Sinninghe Damsté, J.S., 2009. In situ production of crenarchaeol in two California hot springs. Applied and Environmental Microbiology 75, 4443–4451.

Powers, L.A., Werne, J.P., Johnson, T.C., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2004. Crenarchaeotal membrane lipids in lake sediments: a new paleotemperature proxy for continental paleoclimate reconstruction? Geology 32, 613–616.

Powers, L.A., Johnson, T.C., Werne, J.P., Castaneda, I.S., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2005. Large temperature variability in the southern African tropics since the last glacial maximum. Geophysical Research Letters 32, L08706.

Powers, L.A., Werne, J.P., Vanderwoude, A.J., Sinninghe Damsté, J.S., Hopmans, E.C., Schouten, S., 2010. Applicability and calibration of the TEX_{86} paleothermometer in lakes. Organic Geochemistry 41, 404–413.

Rueda, G., Rosell-Melé, A., Escala, M., Gyllencreutz, R., Backman, J., 2009. Comparison of instrumental and GDGT-based estimates of sea surface and air temperatures from Skagerrak. Organic Geochemistry 40, 287–291.

Schouten, S., Hopmans, E.C., Schefuβ, E., Sinninghe Damsté, J.S., 2002. Distributional variations in marine crenarchaeotal membrane lipids: a new organic proxy for reconstructing ancient sea water temperatures? Earth and Planetary Science Letters 204, 265–274.

Schouten, S., Huguet, C., Hopmans, E.C., Kienhuis, M.V.M., Sinninghe Damsté, J.S., 2007a. Analytical methodology for TEX_{86} paleothermometry by high-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry. Analytical Chemistry 79, 2940–2944.

Schouten, S., van der Meer, M.T.J., Hopmans, E.C., Rijpstra, W.I., Reysenbach, A.-L., Ward, D.M., Sinninghe Damsté, J.S., 2007b. Archaeal and bacterial glycerol dialkyl glycerol tetraether lipids in hot springs of Yellowstone national park. Applied and Environmental Microbiology 73, 6181–6191.

Sinninghe Damsté, J.S., Hopmans, E.C., Pancost, R.D., Schouten, S., Geenevasen, J.A.J., 2000. Newly discovered non-isoprenoid glycerol dialkyl glycerol tetraether lipids in sediments. Journal of the Chemical Society, Chemical Communications, 1683–1684.

Sinninghe Damsté, J.S., Hopmans, E.C., Schouten, S., van Duin, A.C.T., Geenevasen, J.A.J., 2002. Crenarchaeol: the characteristic glycerol dibiphytanyl glycerol tetraether membrane lipid of cosmopolitan pelagic Crenarchaeota. Journal of Lipid Research 43, 1641–1651.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Weijers, J.W.H., Foesel, B.U., Overmann, J., Dedysh, S.N., 2011. 13,16-Dimethyl octacosanedioic acid (*iso*-diabolic acid), a common membrane-spanning lipid of *Acidobacteria* subdivisions 1 and 3. Applied and Environmental Microbiology 77, 4147–4154.

Tierney, J.E., Russell, J.M., Huang, Y., Sinninghe Damsté, J.S., Hopmans, E.C., Cohen, A.S., 2007. Northern hemisphere controls on tropical southeast African climate during the past 16,000 years. Science 322, 252–255.

Tierney, J.E., Russell, J.M., 2009. Distributions of branched GDGT in a tropical lake system: implications for lacustrine application of the MBT/CBT paleoproxy. Organic Geochemistry 40, 1032–1036.

Walsh, E.M., Ingalls, A.E., Keil, R.G., 2008. Sources and transport of terrestrial organic matter in Vancouver Island fjords and the Vancouver-Washington Margin: a multiproxy approach using δ^{13} corg, lignin phenols, and the ether lipid BIT index. Limnology and Oceanography 53, 1054–1063.

Weijers, J.W.H., Schouten, S., Hopmans, E.C., Geenevasen, J.A.J., David, O.R.P., Coleman, J.M., Pancost, R.D., Sinninghe Damsté, J.S., 2006a. Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits. Environmental Microbiology 8, 648–657.

Weijers, J.W.H., Schouten, S., Spaargaren, O.C., Sinninghe Damsté, J.S., 2006b. Occurrence and distribution of tetraether membrane lipids in soils: implications for the use of the TEX_{86} proxy and the BIT index. Organic Geochemistry 37, 1680–1693.

Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S., 2007. Environmental controls on bacterial tetraether membrane lipid distribution in soils. Geochimica et Cosmochimica Acta 71, 703–713.

Wuchter, C., Schouten, S., Wakeham, S.G., Sinninghe Damsté, J.S., 2005. and spatial variation in tetraether membrane lipids of marine Crenarchaeota in particulate organic matter: implications for TEX_{86} paleothermometry. Paleoceanography 20, PA3013. doi:10.1029/2004PA001110.

Zhang, C.L., Pearson, A., Li, Y.L., Mills, G., Wiegel, J., 2006. A thermophilic temperature optimum for crenarchaeol and its implication for archaeal evolution. Applied and Environmental Microbiology 72, 4419–4422.

Zhang, D., McPhaden, M.J., 2006. Decadal variability of the shallow Pacific meridional overturning circulation: relation to tropical sea surface temperatures in observations and climate change models. Ocean Modelling 15, 250–273.