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The influence of near surface sediment hydrothermalism on the TEX_{86} tetraether lipid-based proxy and a new correction for ocean bottom lipid overprinting

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Key Points

- High *i*GDGTs turnover in shallow sediments is shown to be non-selective and does not impact TEX_{86} paleoclimate ratios.
- The proxy nonetheless can be overprinted by addition of sediment sourced lipids when geothermal temperatures rise above ~60–70 °C.
- A universally applicable, diagenetic correction model is presented to remove overprinting artifacts in the TEX_{86} proxy.

Abstract

The diversity and relative abundances of tetraether lipids produced by Thaumarchaeota in soils and sediments increasingly is used to assess environmental change. For instance, the TetraEther indeX of 86 carbon atoms (TEX_{86}), based on archaeal isoprenoidal glycerol dialkyl glycerol tetraether (*i*GDGT) lipids, is frequently applied to reconstruct past sea-surface temperatures (SST). Yet, it is unknown how the ratio fully responds to environmental and or geochemical variations and if the produced signals are the adaptive response by Thaumarchaeota to climate driven temperature changes in the upper water column. We present the results of a four push-core transect study of surface sediments collected along an environmental gradient at the Cathedral Hill hydrothermal vent system in Guaymas Basin, Gulf of California. The transect crosses a region where advecting

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hydrothermal fluids reach 155 °C within the upper 21cm below the seafloor (cmbsf) close to the vent center to near ambient conditions at the vent periphery. The recovered *i*GDGTs closest to the vent center experienced high rates of turnover with up to 94% of lipid pool being lost within the upper 21 cmbsf. Here, we show that turnover is non-selective across TEX_{86} GDGT lipid classes and does not independently affect the ratio. However, as evident by TEX_{86} ratios being highly correlated to the Cathedral Hill vent sediment porewater temperatures ($R^2 = 0.84$), the ratio can be strongly impacted by the combination of severe lipid loss when it is coupled to the addition of *in situ i*GDGT production from archaeal communities living in the vent sediments. The resulting signal overprint produces absolute temperature offsets of up to 4 °C based on the TEX_{86}^{H} -calibration relative to modern climate records of the region. The overprint is also striking given the flux of GDGTs from the upper water column that is estimated to represent ~93% of the combined intact polar lipid (IPL) and core GDGT lipid pool initially deposited on the seafloor. A model to correct the overprint signal using IPLs is therefore presented that can similarly be applied to all near-surface marine sediment systems where calibration models or climate reconstructions are made based on the TEX_{86} measure.

1. Introduction

Archaeal and bacterial tetraether cellular membrane lipids mark common and structurally diverse compounds that are frequently used to track the presence of living and dead microorganisms in the geosphere (e.g. Schouten et al., 2002, 2004; Hopmans et al., 2004; Weijers et al., 2007; Lipp et al., 2008). The proportional abundances of these lipids forms various prominent proxies for assessing environmental change through time. For example, TEX_{86} (TetraEther indeX with 86 carbon atoms (Schouten et al. (2002) is the most widely used archaeal lipid-based paleotemperature proxy for marine environments (Table 1; Eq. 1). This proxy measures variations in the number of cyclopentyl rings within the hydrocarbon skeleton of a select range of archaeal core lipid (CL) classes (Supplementary Figure A-1) following the initial assumption that cyclization of the biphytanyl moiety is an organismal response to changing sea surface temperatures (SSTs). The proxy is therefore used in paleo-oceanographic studies in many different regions around the world (Huguet et al., 2006; Kim et al., 2008; McClymont et al., 2012) with TEX_{86} values typically ranging from 0.2–0.9 in both marine and lake sediment (Sinninghe Damsté et al., 2009; Powers et al., 2010; Zhang et al., 2016 Morrissey et al., 2018; Yao et al., 2019; Kumar et al., 2019). The utility of TEX_{86} rests on the premise that *i*GDGTs found in ocean bottom sediments are almost exclusively produced by marine planktonic Thaumarchaeota that inhabit the epipelagic zone (Wakeham et al., 2003; Tierney, 2014).TEX_{86}-based lipids are therefore required to be efficiently and continually transported from the upper water column to the underlying ocean floor sediments to produce a chemostratigraphic record of microbial response to changing SST conditions (Wuchter et al., 2005).

Since its introduction, the reliability of TEX_{86} to accurately track paleoclimate variations has been questioned. For example, over the past decade, considerable effort has been made to reconstruct the early Paleogene greenhouse climate with a variety of paleoclimate proxies (Hollis et al., 2012). However, TEX_{86} appears to significantly over-estimate reconstructed SSTs relative to other proxies such as Mg/Ca, clumped isotopic compositions

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of foraminiferal calcite, as well as various climate models based on partial pressure of carbon dioxide (pCO_2) predictions (Lunt et al., 2012; Naafs et al., 2018). The apparent high SST reconstructions have been attributed to proxy complications including ocean subsurface sediments origin of lipids (Ho and Laepple, 2016). For late Neogene climate reconstructions, the proxy has been shown to underestimate warming trends relative to $U_{37}^{k'}$-derived temperatures (Lawrence et al., 2020). In this regard, the debate largely centers on a lack of understanding of how the proxy's associated lipids precisely change in relation to their environment and if these changes are regulated by internal adaptations within the archaeon or by community succession (Elling et al., 2015; Qin et al., 2015).

Additionally, most Thaumarchaeota are found below the photic and epipelagic zone and should therefore not produce a direct response to changing SSTs. Studies from the Pacific Ocean have shown that peak archaeal abundances occur at 100–350 m depth (Karner et al., 2001; Pearson et al 2013). To address the impact of depth habitat, Schouten *et al.* (2013) further proposed a calibration based on suspended particulate matter and *in situ* water temperature from the upper 100 m of the global ocean. In this regard, if these deeper sourced lipids are deposited on the seafloor than the sedimentary GDGT used to generate sea surface temperatures are mixed with significant contributions from much colder waters potentially impacting the reconstructed values providing much lower SSTs. As TEX_{86} may become disproportionality impacted by the collection of mixed source inputs; the location of lipid loading from the water column to the ocean floor sediments seems to be an factor as strong positive relationship between water depth and differences in TEX_{86}^{H} values are observed in both surface sediments and suspended particulate organic matter from the Mediterranean Sea (Kim et al., 2015). The differences appear to be driven by increase relative abundances of TEX_{86} lipids GDGT-2 and the isomers of crenarchaeol (Lui et al., 2018; Damsté et al., 2018) coupled to decreasing abundances of GDGT-1 and GDGT-3 with increasing water depth. The systematic change results in a higher reconstructed SST bias for deep-water surface sediments. Therefore, such sourcing effects have further resulted in speculation that the TEX_{86} ratio of open ocean sediments may actually reflect deeper water column and subsurface rather than SSTs (Huguet et al., 2007; Lopes dos Santos *et al.*, 2010; Kim *et al.*, 2012a,b; Ho & Laepple, 2016; Hurley et al., 2016). To compensate for this, both TEX_{86}^{H} and TEX_{86}^{L} have been re-calibrated against subsurface (0–900 m water depth) temperatures (Kim *et al.*, 2012a,b; Ho & Laepple, 2016).

The GDGT relative abundances recorded in a TEX_{86} measurements may constitute a multi-variable system, having both a component of lipids contributed to the "pool" via *in situ* sources and by depositional processes. TEX_{86}-based SST estimates have been observed to substantially deviate from other temperature proxies (e.g., Huguet et al., 2006; Liu et al., 2009; Rommerskirchen et al., 2011; Hollis et al., 2012; Seki et al., 2012) implying these values can be a response to seasonal biases, non-thermal influences, or other ecological signals. Non-thermal influence result from lipid abundances being brought to marine sediments from non-planktonic Thaumarchaeota origins such as from the deep water or within marine sediments (Liu et al., 2011; Kerou et al. 2020). There are likely other driving forces other than temperature that impact the archaeal GDGT production and relative abundances. Some examples of these drivers include organismal selectivity to specific

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growth phases and growth rates (Elling et al., 2014; Hurley et al., 2016); ammonia oxidation rates (Hurley et al., 2016); and redox conditions (Qin et al., 2015).

By artificially hydrolyzing the headgroups of marine archaeal IPLs harvested from a sediment trap, Lipp and Hinrichs (2009) demonstrated that the production of GDGTs by ocean floor sediment microbial communities may impact TEX_{86} values. Similarly, Elling et al. (2015) confirmed TEX_{86} values can represent a mixed GDGT signal from both active microbial production in shallow sediments and fossil lipids sourced from the water column. These authors further demonstrated that TEX_{86} values from cultures can diverge from the global calibration that forms the basis for most climate reconstructions suggesting that the sedimentary community compositions may exert some controls on the TEX_{86} signal. Besseling et al. (2019) further extended these concerns, suggesting TEX_{86} reflects subsurface temperatures rather than SSTs as the input of GDGTs in marine settings are not exclusive to Thaumarchaeota, because a majority of marine group I (MGI) Archaea also reside in subsurface waters or marine sediments. Collectively, these observations indicate a sub-pelagic zone where microorganisms may mix with the GDGTs from the surface, thus providing mixed signals and inaccurate TEX_{86} values from mixed sources. However, other authors have found that TEX_{86} ratios are not impacted by benthic Archaea due to the low relative turnover rates for the lipids in marine sediments (Lengger et al., 2012, 2014; Omuh et al., 2020). Omuh et al. (2020) found little effect to the TEX_{86} paleoclimate ratio when examining surface sediments near hydrothermal vent sites on the Southeast Indian Ridge in the southern Indian Ocean. Lengger et al. (2012, 2014) reported no significant deviation between the TEX_{86} values in sediment cores collected near the oxygen minimum zone from that of the overlying water column in the Arabian Sea with near linear degradation rates of both IPLs and CLs.

While not an ideal location to create SST reconstructions, hydrothermal vents of sedimented ocean basins do represent an anomalous end-member to the vast expanse of ambient ocean floor sediment where paleoclimate reconstructions are commonly produced. The Guaymas Basin, Gulf of California (Figure 1) is one such site. The basin experiences elevated sedimentation rates ranging between 0.4–0.2 cm/yr. (Curray et al., 1979; Gieskes et al., 1988) due in part to the high productivity of the upper water column. The ocean floor hydrothermally impacted surface sediments are also a location of active and diverse microbial communities with vents that are often covered by Beggiatoa dominated microbial mats (Teske et al., 2016). These sites should in principle enable a high-resolution archaeal lipid-based paleoclimate record that provides optimal conditions for studying potential subsurface lipid overprinting or interferences to common archaeal lipid-based environmental proxies. For this study, we examined near-surface ocean floor sediments from the Cathedral Hill hydrothermal vent complex (Figure 1) in the Guaymas Basin to determine if sea surface paleoclimate proxy signals can be impacted by the presence of subsurface archaeal populations. The distribution of GDGTs and their corresponding environmental proxy signals were measured within the sediments along a transect at the Cathedral Hill hydrothermal vent system. In this regard, this site offers the unique opportunity to evaluate the response of TEX_{86} and other tetraether-lipid proxies within a microbially diverse sedimentary environment that is exposed to high temperature vent fluids.

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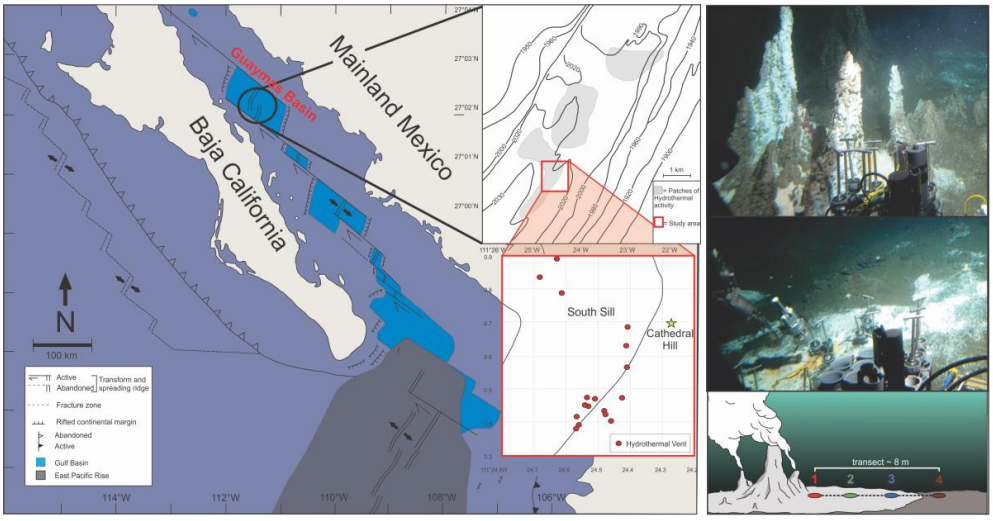

FIGURE 1 A) Location map of Guaymas Basin and the Southern Sill (red outlined box) in the Gulf of California. Cathedral Hill is marked with a yellow star. B) Photo of Cathedral Hill taken via *Alvin*. C) Schematic of the push core transect with a color coding that is consistent for all plots throughout this paper. Maps modified from Teske et al. (2016) and Dazell et al. (2021).

2. Material and methods

2.1. Study location and sampling

Four sediment push cores were collected using HOV *Alvin* (Dive 4462; 10/22/08) at the Cathedral Hill hydrothermal vent site, located at a water depth of 1996 m in the Southern Trough of Guaymas Basin, Gulf of California (27°0.629’ N, 111°24.265’ W) (Figure 1). The push cores, labeled 1 to 4, were taken along a transect with ~ 2 m spacing extending outwards from microbial mat-covered sediments near the sulfide chimney complex to just outside of the microbial mat area in ambient seafloor sediment. Thermal-probe measurements were taken next to each core (Table 1). Once the push cores were brought to the surface, they were subsampled into 2–3 cm-thick intervals, transferred to combusted glass vials and immediately stored at -40 °C (onboard the ship) before being shipped under dry ice to the laboratory and later freeze-dried and stored at -80 °C until being later processed.

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Table 1. Sediment geochemical and lipid proxy data.

Core*a	Depth interval (cmbsf)	Alvin dive # and core ID	Description/lithology*b	Pore water temperature (°C)	Interpolated Pore water temperature (°C)	Sediment weight (g)	TLE µg/g sediment
1	0-2	GB4462-5	Black mud with microbial mat filaments	19	19	2.40	11552.3
1	2-4	GB4462-5	Brownish-green diatomaceous mud	-	67	2.10	7648.2
1	4-6	GB4462-5	Brownish-green diatomaceous mud	85	85	2.04	9266.0
1	6-8	GB4462-5	Brownish-green diatomaceous mud	-	105	2.83	2088.3
1	8-10	GB4462-5	Brownish-green diatomaceous mud	-	117	2.48	4378.1
1	10-12	GB4462-5	Grayish-green mud	121, 124	125	2.52	1972.2
1	12-15	GB4462-5	Brownish-green consolidated mud with clay shards	-	135	2.62	1992.4
1	15-18	GB4462-5	Brownish-green consolidated clay	142	145	3.01	1691.0
1	18-21	GB4462-5	Brownish-green consolidated clay	153	153	2.94	1722.0
2	0-2	GB4462-6	Black mud with microbial mat filaments	9, 13	11	2.12	8476.2
2	2-4	GB4462-6	Black mud with microbial mat filaments	-	22	2.30	8653.5
2	4-6	GB4462-6	Brownish-green diatomaceous mud	20	20	3.30	2509.2
2	6-8	GB4462-6	Brownish-green diatomaceous mud	-	47	2.84	3383.8
2	8-10	GB4462-6	Brownish-green diatomaceous mud	-	60	3.34	1480.5
2	10-12	GB4462-6	Brownish-green diatomaceous mud	69, 77	73	2.39	4185.9
2	12-15	GB4462-6	Brownish-green diatomaceous mud	-	87	3.50	1694.3
2	15-18	GB4462-6	Brownish-green diatomaceous mud	118	105	3.50	2011.6
2	18-21	GB4462-6	Brownish-green diatomaceous mud	109	125	3.48	1382.2
3	0-2	GB4462-3	Black mud with microbial mat filaments	3.2	3.2	2.81	7313.2
3	2-4	GB4462-3	Brownish-green diatomaceous mud	-	8	2.88	3909.7
3	4-6	GB4462-3	Brownish-green diatomaceous mud	15	15	2.45	2864.8
3	6-8	GB4462-3	Brownish-green diatomaceous mud	-	26	2.80	5003.6
3	8-10	GB4462-3	Brownish-green diatomaceous mud	34	34	2.80	2018.0
3	10-12	GB4462-3	Brownish-green diatomaceous mud	-	43	3.15	1863.5
3	12-15	GB4462-3	Brownish-green diatomaceous mud	-	54	3.15	1777.8
3	15-18	GB4462-3	Brownish-green diatomaceous mud	61	66	2.45	1428.6
3	18-21	GB4462-3	Brownish-green diatomaceous mud	83	80	2.80	1982.0
4	0-2	GB4462-8	Black mud	0	0	2.80	3440.4
4	2-4	GB4462-8	Brownish-green diatomaceous mud	1.5	8	2.80	3166.1
4	4-6	GB4462-8	Brownish-green diatomaceous mud	16	16	2.55	4000.0
4	6-8	GB4462-8	Brownish-green diatomaceous mud	-	18	2.80	4185.5
4	8-10	GB4462-8	Brownish-green diatomaceous mud	-	21	3.33	4755.3
4	10-12	GB4462-8	Brownish-green diatomaceous mud	-	23	2.44	4843.6
4	12-15	GB4462-8	Brownish-green diatomaceous mud	-	25	0.32	5741.9
4	15-18	GB4462-8	Sample lost during collection	-	-	-	-
4	18-21	GB4462-8	Sample lost during collection	29	-	-	-

Table 1. Sediment geochemical and lipid proxy data (continued).

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Core[*a]	Depth interval (cmbsf)	Alvin dive # and core ID	TEX_{86} Core GDGT[c]	TEX_{86}^{H} Core GDGT[d]	TEX_{86}^{H} Reconstructed SSTs (Kim et al., 2010)[e]	RI[f]	MI[g]	TEX_{86} 1G-GDGT[c]	TEX_{86} Core GDGT[c]
1	0-2	GB4462-5	0.56	-0.25	21.2	2.44	0.34	0.58	0.56
1	2-4	GB4462-5	0.58	-0.23	22.6	2.45	0.38	0.58	0.58
1	4-6	GB4462-5	0.58	-0.24	22.3	2.48	0.36	0.55	0.58
1	6-8	GB4462-5	0.58	-0.24	22.2	2.55	0.35	0.57	0.58
1	8-10	GB4462-5	0.59	-0.23	22.9	2.60	0.34	0.72	0.59
1	10-12	GB4462-5	0.57	-0.25	21.8	2.63	0.31	0.70	0.57
1	12-15	GB4462-5	0.61	-0.22	23.8	2.65	0.37	0.69	0.61
1	15-18	GB4462-5	0.61	-0.22	23.9	2.66	0.36	-	0.61
1	18-21	GB4462-5	0.63	-0.20	24.9	2.66	0.38	-	0.63
2	0-2	GB4462-6	0.55	-0.26	20.6	2.524	0.32	0.46	0.55
2	2-4	GB4462-6	0.54	-0.27	20.4	2.524	0.32	0.58	0.54
2	4-6	GB4462-6	0.54	-0.27	20.4	2.525	0.33	0.60	0.54
2	6-8	GB4462-6	0.56	-0.25	21.5	2.677	0.29	0.71	0.56
2	8-10	GB4462-6	0.58	-0.25	21.7	2.695	0.29	0.70	0.58
2	10-12	GB4462-6	0.57	-0.24	21.9	2.712	0.28	0.68	0.57
2	12-15	GB4462-6	0.57	-0.24	21.9	2.734	0.28	0.73	0.57
2	15-18	GB4462-6	0.58	-0.23	22.6	2.680	0.31	-	0.58
2	18-21	GB4462-6	0.59	-0.23	22.8	2.738	0.28	-	0.59
3	0-2	GB4462-3	0.54	-0.27	20.2	2.41	0.37	0.53	0.54
3	2-4	GB4462-3	0.53	-0.27	19.8	2.62	0.27	0.49	0.53
3	4-6	GB4462-3	0.53	-0.27	19.9	2.53	0.31	0.56	0.53
3	6-8	GB4462-3	0.54	-0.27	20.3	2.50	0.33	0.54	0.54
3	8-10	GB4462-3	0.53	-0.27	19.9	2.54	0.31	0.61	0.53
3	10-12	GB4462-3	0.54	-0.27	20.3	2.64	0.27	0.74	0.54
3	12-15	GB4462-3	0.56	-0.25	21.5	2.56	0.30	0.69	0.56
3	15-18	GB4462-3	0.55	-0.26	20.9	2.77	0.26	0.74	0.55
3	18-21	GB4462-3	0.57	-0.25	21.6	2.68	0.29	0.66	0.57
4	0-2	GB4462-8	0.54	-0.27	20.4	2.43	0.35	0.54	0.54
4	2-4	GB4462-8	0.53	-0.27	20.0	2.59	0.30	0.37	0.53
4	4-6	GB4462-8	0.54	-0.27	20.2	2.55	0.31	0.43	0.54
4	6-8	GB4462-8	0.52	-0.28	19.3	2.55	0.29	0.45	0.52
4	8-10	GB4462-8	0.53	-0.27	19.9	2.69	0.26	-	0.53
4	10-12	GB4462-8	0.53	-0.27	19.8	2.54	0.30	-	0.53
4	12-15	GB4462-8	0.53	-0.28	19.7	2.90	0.20	-	0.53
4	15-18	GB4462-8	-	-	-	-	-	-	-
4	18-21	GB4462-8	-	-	-	-	-	-	-

[*a] Collected core numbers are relabelled in the sample name to reflect a relative transect position (1-4).
[*b] Sediment lithology based on freeze-dried sediments.
[c] TEX_{86} = (GDGT-2 + GDGT-3 + GDGT-5')/(GDGT-1 + GDGT-2 + GDGT-3 + GDGT-5'), (Schouten et al., 2002) applied to both core GDGTs and 1-glycosyl-GDGTs. (1)
[d] TEX_{86}^{H} = log ((GDGT-2 + GDGT-3 + GDGT-5')/(GDGT-1 + GDGT-2 + GDGT-3 + GDGT-5')), for sediments outside the polar regions (Kim et al., 2010).
[e] Following the mean annual sea surface calibration of 0 m water depth (SST = 68.4 × TEX_{86}^{H} + 38.6) of Kim et al. (2010).
[f] Ring index (RI) = 0×(GDGT-0) + 1×(GDGT-1) + 2×(GDGT-2) + 3×(GDGT-3) + 4×(GDGT-4) + 5×(GDGT-5)/ ΣGDGTs, adapted from Pearson et al. (2004). (2)
[g] Methane index (MI) = (GDGT-1 + GDGT-2 + GDGT-3)/(GDGT-1 + GDGT-2 + GDGT-3 + GDGT-5 + GDGT-5') by Zhang et al. (2011).

2.2. Lipid extraction

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Samples were spiked with a recovery standard (1-alkyl-2-acetoyl-*sn*-glycero-3-phosphocholine (PAF); Avanti Polar Lipids, Inc.) and extracted using a modified Bligh and Dyer protocol after Sturt et al. (2004). The extraction involved six steps using 3 different solvent mixtures. The first four steps involved solvent mixtures of methanol/dichloromethane/buffer [2:1:0.8; v/v]. From this, the first two steps used a phosphate buffer (5.5 g/L Na_2HPO_4; Avantor Performance Materials, LLC.) adjusted to pH of 7.4 with HCl; Anachemia Co.), while the third and fourth steps employed a trichloroacetic acid buffer (50 g/L $C_2HCl_3O_2$; Avantor Performance Materials, LLC. (pH of 2). The final two steps used a solvent mixture of methanol/dichloromethane [5:1; v/v]. Each extraction step consisted of a 6 ml of solvent mixture, sonicated for 5 min. and centrifuged for 5 min. at 1250 rpm. After each extraction step, the solvent was decanted and combined in a separation funnel. The combined extract was purified with milliQ water, heated at ca. 60 °C, and evaporated to dryness under a gentle steam of dry nitrogen. The resulting total lipid extract (TLE) was then spiked with 1, 2-diheneicosanoyl-*sn*-glycero-3-phosphocholine (C_{21}-PC; Avanti Polar Lipids, Inc.) and subsequently stored at -20 °C before it was injected for mass spectral analysis.

2.3. High performance liquid chromatography – mass spectrometry (HPLC-MS)

A reverse phase electrospray ionization method with a scan range from 100–3000 *m/z* was chosen for its ability to simultaneous resolve archaeal IPLs and CLs. An aliquot of each sample representing 1% of the TLE was analyzed using an Agilent Technologies 1260 Infinity II HPLC coupled to an Agilent Technologies 6530 quadruple time-of-flight mass spectrometer (qToF-MS). Separation was achieved following the method described by Zhu et al. (2013) using an Agilent Technologies ZORBAX RRHD Eclipse Plus C_{18} (2.1 mm × 150 mm × 1.8 µm) reverse phase column, fitted with a guard column and maintained at 45 °C. The flow rate was set to 0.25 mL/min. and the gradients were: mobile phase A (methanol/formic acid/ammonium hydroxide [100:0.04:0.10] v:v:v) held at 100% for 10 min., followed by a linear gradient to 24% mixing with mobile phase B (propan-2-ol/formic acid/ammonium hydroxide [100:0.04:0.10] v:v:v) extending for 5 min., a linear gradient to 65% B for 75 min., followed by 70% B for 15 min., that finished by re-equilibrating with 100% A for 15 min. The injection solvent was methanol.

Analyte identification was achieved by accurate mass resolution, mass spectral analysis using Agilent Technology's MassHunter software and by comparison of fragmentation patterns with the literature (e.g., Knappy et al., 2009; Liu et al., 2010; Yoshinaga et al., 2011). Quantification was achieved by summing the integration of peak areas of adducts $[M+H]^+$, $[M+NH_4]^+$, and $[M+Na]^+$ for the respective GDGTs of interest. The signals for these compounds were monitored as $[M+H]^+$ on the *m/z* 1464.38, 1462.36, 1460.34, 1458.33 1456.31, 1454.30 mass chromatograms. Additionally, mass fragments consistent with the loss of a biphytane (*m/z* 743.7) were observed. Once the integrated peak areas were determined for each GDGT, concentration values were obtained relative to the internal C_{21}-PC standard and reported in µg/g dry sediment weight.

Response factors were determined by a series of injections of a standard solution containing; 1,2-diacyl-3-O-(α-D-galactosyl1-6)-β-D-galactosyl-*sn*-glycerol (DGDG), 1,2-

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diacyl-3-O-β-D-galactosyl-*sn*-glycerol (MGDG), 1-alkyl-2-acetoyl-*sn*-glycero-3-phosphocholine (PAF), 1,2-di-O-phytanyl-*sn*-glycerol (Archaeol), 1',3'-bis[1,2-dimyristoyl-*sn*-glycero-3-phospho]-glycerol (14:0 Cardiolipin), 1,2-diheneicosanoyl-*sn*-glycero-3-phosphocholine (C_{21}-PC) from Avanti Polar Lipids, Inc., USA, and 2,2´-di-O-decyl-3,3´-di-O-(1´´,ω´´-eicosanyl)-1,1´-di-(rac-glycerol) (C_{46}-GTGT) from Pandion Laboratories, LLC in amounts ranging from 100 pg to 30 ng. Concentrations of the standard mix were then calculated from peak areas of molecular ions in mass chromatograms. Response factors were calculated relative to the C_{21}-PC, and the appropriate correction factor was applied to the particular lipid class of interest.

A series of samples were re-run to identify or confirm deviations in the data set. The variations between the concentrations of GDGTs in the re-run and the initial runs yielded a maximum difference of ~ ± 4 µg/g per GDGT compound, providing confidence in the initial results and confirming the presence of two outlies in the data set. These outliers are Core 4 at 8-10 cm, with abnormally low concentrations of all compounds that is likely ion suppression from a sample heavily impregnated with oil, and Core 3 at 15–18 cm, which contains relatively high lipid concentrations that are yet to be explained.

3. Results and Discussion

3.1. Archaeal lipid diversity and heterotrophic loss

The Cathedral Hill transect sediments have *i*GDGTs containing 0–4 cyclopentyl (GDGT 0–4) as well as crenarchaeol (Cren) and the isomer of crenarchaeol (Cren') that contains five rings (four cyclopentyl and one cyclohexyl moiety) (Table S1). Branched GDGTs include 1a-c, 2a-c, and 3a were found to have discontinuous and/or low absolute abundances, with some compound classes not being detected (i.e. *br*GDGT-3b). The *br*GDGTs are therefore not further examined in this study. For cores 1 to 3 the concentrations of all *i*GDGT compounds systematically decrease with depth (Figure 2). Bentley et al. (2021) established the sedimentation of archaeal lipids from the upper water column as being uniform both in terms of spatial loading across the length of the transect as well as over the past 52.5–105 yrs. of sedimentation penetrated by the length of the push core. From this, it is estimated that ~70.57 ± 23.5 µg *i*GDGTs/g sed./yr. is being deposited on the seafloor from the upper water column. However, for cores closest to the vent site, lipid abundances exhibited a much sharper decrease with depth, which Bentley et al. (2021) attribute to the turnover of archaeal lipids coupled to, but not directly caused by, hydrothermalism. For cores 1 and 2, losses reach as high as 94% within the upper 21 cmbsf (cm below sea floor). The lipid loss is less severe for core 3 at ~60%. For the ambient core 4, *i*GDGTs have similar down core stratigraphic trends with a near-consistent average of 400 µg/g sediment concentration and no systematic loss of lipids.

Due to the extreme vent conditions at Cathedral Hill, the identified archaeal *i*GDGT-based IPLs within the sediments most likely represent the composition of cellular membrane material from active archaeal communities residing in the sediments. These lipids have exclusively monoglycosyl (1G) or diglycosyl (2G) head groups linked to a 2,3-sn-glycerol. Within the pyrolytic environment the transformation of IPL *i*GDGTs could hypothetically

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add to the core *i*GDGT lipid pool. Similar to CLs, the 1G-GDGTs range from -0 to -4 and include Cren and Cren'. Surface concentrations of these lipids are ~15 µg/g sed. in cores 1 to 3 (residing within the microbial mat) and 11 µg/g sed. for core 4 (Table S2). Also similar to the CLs, the archaeal IPL concentrations decrease down core and are tightly controlled by porewater temperatures (Table S2). For cores 1 and 2 the maximum depths for detectable 1G-GDGTs are 15–18 and 12–15 cmbsf, corresponding to vent porewater temperatures of 145 and 87 °C, respectively. In core 3, 1G-GDGTs persists down core with a consistent lipid depletion that reaches its lowest concentration of 5.22 µg/g sed. in the bottom of the core at 18–21 cmbsf sediment depth where porewater temperatures rise to 80 °C. In core 4, which is most similar to the ambient ocean bottom conditions and falls outside of the area covered by the microbial mat, the lipid concentrations average is ~8 µg/g sed. across the depth of the core. The 2G-GDGTs have 0 to 2 cyclopentyl rings that for cores 1 and 2 are restricted to the upper 4 to 6 cmbsf. These lipids are not further investigated in this study as 2G-GDGTs are of limited abundance (max summed concentrations <7 µg/g sed.) and their structural diversities negligibly effect isoprenoid-based proxies.

Lipid-based proxies for the calibration or reconstruction of paleoclimate records such as TEX_{86}, BIT, CBT, and MBT, are based on environmentally scaled loadings of select GDGT compound classes. These proxies could be negatively impacted should other ocean floor sediment systems experience high rates of lipid turnover (Lengger et al., 2014). To evaluate whether down-core depletions of lipid concentrations impacted tetraether-based proxies, the concentrations of the highly abundant GDGT-0 was plotted relative to the TEX_{86} ratio lipids (*i*GDGT-1, -2, -3, and Cren') (Figure 3A). For figure 3A, straight lines in the logarithmic plot indicate near-equal depletion rates between the paired x- and y-axis lipid classes. Similarly, parallel lines between lipid pairs also indicates near-equal depletion rates, with vertical offsets between pairs marking different initial starting abundances between the paired lipid classes. In this regard, *i*GDGT-0, -1, -2, and Cren' have undergone the same rate of turnover. However, the depletion rate of *i*GDGT-3's is lower than that of other lipid classes for cores 1 and 2. Although, this may represent a distinct resilience to turnover, we suggest it results from overprinting by the subsurface hyperthermophilic archaeal community (see below).

To better track changes across each core, the degradation rate constants (k') of TEX_{86} lipid classes were calculated for each push core (Figure A2; Table A3) using a first-order kinetic model:

$$C_t = C_i \cdot e^{-k't} \tag{5}$$

in which C_t and C_i are concentration at time (t) and the initial concentration, respectively (Schouten et al., 2010). Rearranging Eq. 5, the k' were calculated as

$$k' = (-\ln[C_t / C_i])/t \tag{6}$$

From these data, it is evident that the down core concentrations of each lipid decrease at equivalent rates for all but core 2 (i.e. they have the same slopes for their rates of decay;

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$m_{log\ k'}$). This is consistent with the TEX_{86} *i*GDGT lipid classes being removed from the sediment lipid pool in a non-selective manner.

Lastly, TEX_{86}, RI, and MI values were plotted against their respective summed *i*GDGTs lipid concentrations (Fig 3B–D). For samples located within the habitable zone (having porewaters ranging from 0–123˚C; Kashefi and Lovley, 2003), no correlation is observed between the lipid abundances and proxy ratios of TEX_{86}, RI, or MI (Figure 3B–D). This further suggests these proxies are not affected by turnover in the habitable zone. However, once sediment burial reaches beyond the habitable zone, TEX_{86} ratios trend to higher values (similarly also reflected in GDGT-3 concentration trends of Figure 3A). Collectively, these data strongly indicate that archaeal lipid turnover is largely nonselective of the TEX_{86} lipid classes and will therefore theoretically not in and of itself significantly impact archaeal lipid paleoclimate proxy reconstructions.

Apart from paleoclimate reconstructions, the archaeal lipid data can also be used to resolve some aspects of the local biogeochemical cycles present at the vent site. Maximal anaerobic oxidation of methane (AOM) at Guaymas Basin has been observed at 35 to 90 °C, but generally accounts for less than 5% of sulfate reduction (Kallmeyer and Boetius, 2004). For example, highly ^{13}C-depleted CLs reaching up -70‰ in hydrothermal vent sediments with porewater temperatures as high as 95 °C indicates thermophilic archaea actively engaging in AOM (Schouten et al., 2003). The methane index (MI; Table 1) can be used to differentiate regions of normal marine (values between 0–0.3) and active AOM conditions where values >0.5–1 for gas hydrate impacted sediments and subsurface environments with high levels of AOM (Stadnitskaia et al., 2008, Zhang et al., 2011). When applying the MI to the Cathedral Hill sediments very low values are recorded with no correspondence to thermal controls. Although, it could be considered that this arises from selective degradation; the very low MI values are equally explained by broad loading of *i*GDGTs from the upper water column. As such, the low AOM activities may also indicate microbial ammonia oxidation, which has been shown to influence the TEX_{86} proxy (Hurley et al., 20016) is likely not a significant factor in this setting.

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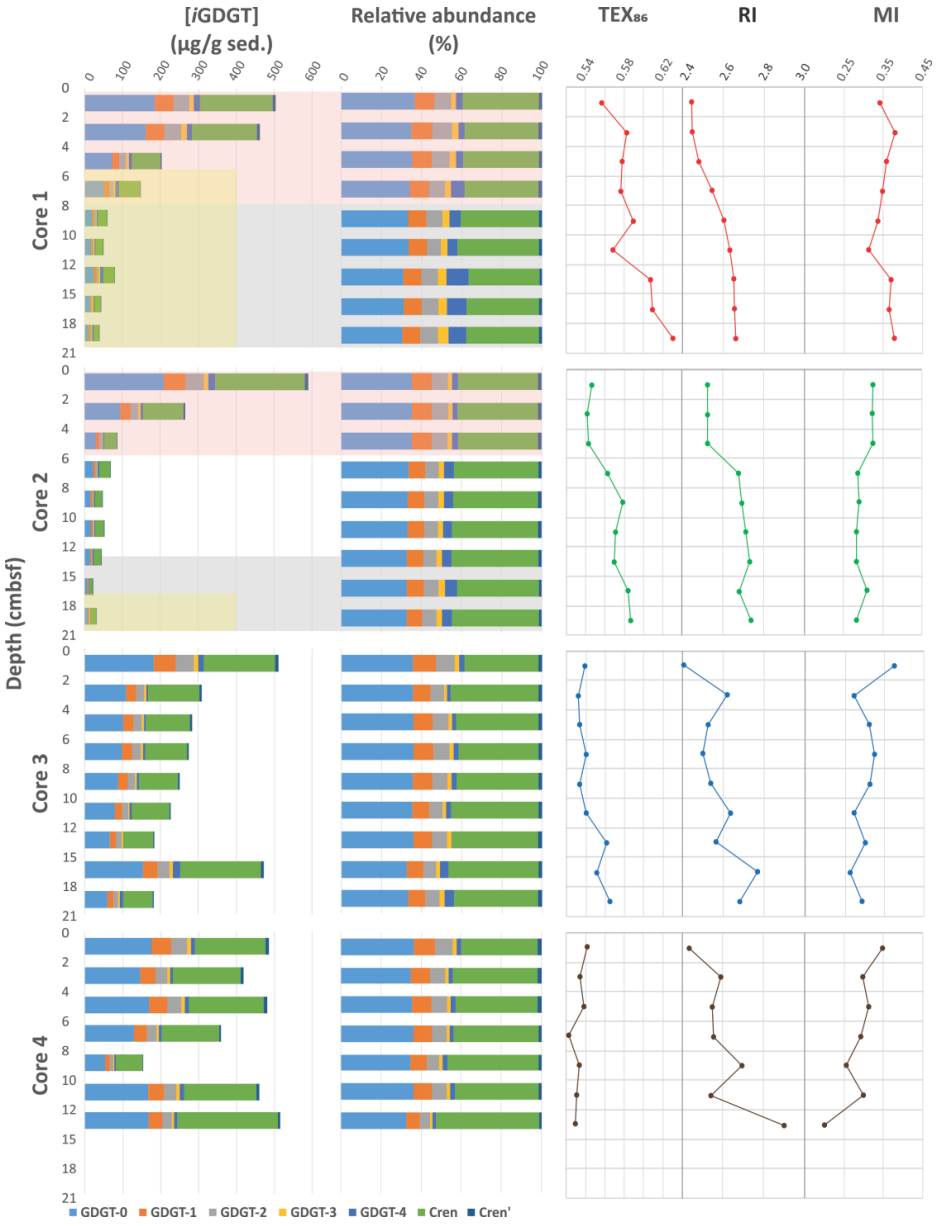

FIGURE 2. Down core profiles of the Cathedral Hill core *i*GDGTs absolute and relative lipid abundances and their generated *i*GDGT proxies: TEX_{86}, RI, and MI. Pink regions indicate transect intervals within zones of active GDGT lipid heterotrophy (Bentley et al., 2021). Grey regions mark regions where porewater temperatures exceed 123 °C marking a zone beyond the upper thermal limit of life. Yellow fields indicate regions where oil generation and hydrocarbon degradation has been noted to occur (Dalzell et al., 2021).

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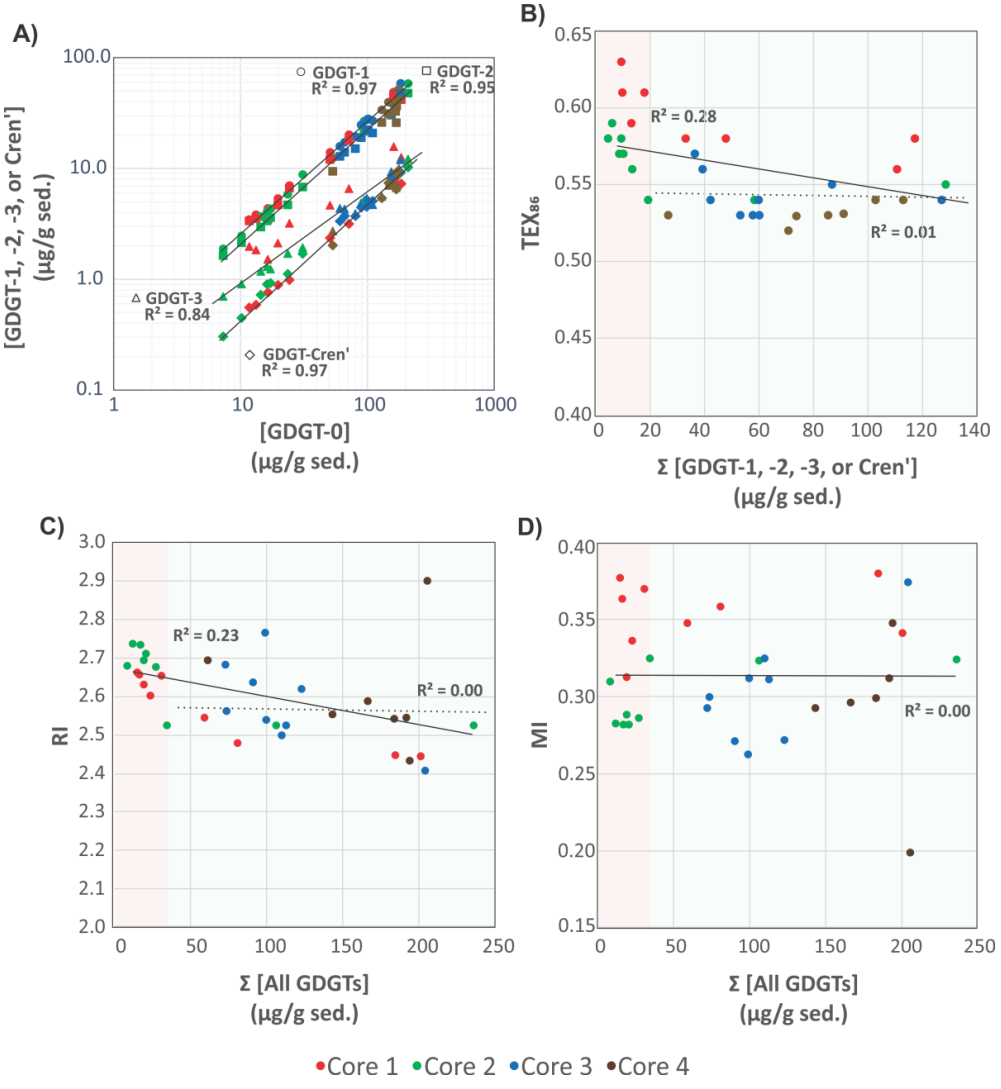

FIGURE 3. A) Comparison of TEX_{86} lipid concentrations GDGT-1 (circles), -2 (squares), -3 (triangles), and Cren' (diamonds) relative to the GDGT-0. Comparison of B) TEX_{86}, C) RI, and D) MI proxy values relative to summed *i*GDGTs abundances of the Cathedral Hill transect cores. Light green and pink regions indicate areas within and outside the habitable zone of life. Solid and dotted regression lines mark the total number of samples investigated for this study (*n*=34) and those that only reside within the habitable zone where up to 94% of the archaeal lipid turnover occurs (*n*=22), respectively.

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3.2. TEX_{86} and reconstructed SSTs

McClymont et al. (2012) reported a GDGT-based reconstructed annual SSTs of 16–18 °C for ambient sediment in the Guaymas Basin during an annual cycle from 1996–1997 following the calibration model for sediments outside of polar regions proposed by Kim et al. (2010). These authors demonstrated the temperatures derived from the TEX_{86} reconstruction were significantly lower than those derived from the closely co-varying $U_{37}^{k\prime}$, an alkenone lipid-based paleoclimate proxy (Brassell et al., 1986), and satellite measured estimates that jointly produced a mean annual sea surface temperature (MASST) of 23 °C. The longer 21-year (1982–2004) satellite-derived MASST is also reported to be higher at 24 °C (Herrera-Cervantes et al., 2007). Although the sites and time frames of these surveys do not match that of the Cathedral Hill survey, they do provide context to what our reconstructed TEX_{86} values should record.

The high sedimentation rate at Cathedral Hill has resulted in near homogenous inputs of organic matter from the upper water column across the transect area (Dalzell et al., 2021; Bentley et al., 2021). Therefore, TEX_{86} reconstructions should produce equivalent cross-transect trends with sediment depth. Nonetheless, as with changes in the archaeal lipid concentrations, the profiles of *i*GDGT proxies TEX_{86} and RI of the transect similarly have down core trends (Figure 2; Bentley et al., 2021). For core 4, TEX_{86} span a narrow range of values (n=7; 0.52–0.54, avg. 0.53 ± 0.01; Figure 4A) across a period of ~ 37.5 to 75 yrs. To a slightly lesser degree, the shallow-surface samples (0-2 cmbsf) across the transect also display near-equal values to core 4 (n=4; 0.56–0.54; avg. 0.55 ± 0.01). These values mark a TEX_{86}^{H} reconstructed mean annual SST of 19.3–20.4 °C following the Kim et al. (2010) calibration model (Table 1). However, the TEX_{86} values recorded in cores 1 to 3 at Cathedral Hill have considerably larger ranges that systematically increase with rising porewater temperatures (R^2 = 0.83; Table 1; Figure 2 and 4A). This increase is most noticeable in core 1 where the highest TEX_{86} values are obtained from the bottom core sediments (10–21 cmbsf) where TEX_{86} values span 0.57–0.63 (Table 1; Fig 4A) corresponding to a TEX_{86}^{H} reconstructed SST change of 3.1 °C marking a range from 21.8 to 24.9 °C (Table 1). Since the Cathedral Hill transect only spans ~8 m, the fundamental driver for the proxy's increases must be exposure to *in situ* vent fluid temperatures (Figure 4).

Two mechanisms are considered for the observed proxy variations. The first is that progressive ring-loss due to carbon-carbon bond cleavage of pentacyclic rings moieties by exposure to the sharp geothermal gradient at Cathedral Hill acts to systematically attenuate the *i*GDGT lipid pool. Hydrous pyrolysis experiments conducted by Schouten et al. (2004) demonstrated that at extreme temperatures (ca. >160 °C), TEX_{86} values become negatively impacted by the preferential destruction of polycyclic GDGTs. Such losses produce progressively lower ratio values. Although, the transect sediment porewaters do not reach the pyrolytic temperatures of the Schouten et al. (2004) experiment, they are high enough to generate hydrocarbons (Dalzell et al., 2021) and thermochemically degrade *i*GDGTs in the hottest regions of the transect. However, the observed stratigraphic TEX_{86} trends do not match those of predicted ring loss as the values increase rather than decrease in relation to

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elevated porewater condition. Nonetheless, the thermochemical oxidative loss of GDGTs and its effect on the TEX_{86} ratio is further explored below (section 3.4).

The second mechanism is that subsurface microbial communities donate enough core GDGTs to overprint the detrital signal source. The RI (Figure 4B) values were similarly compared to recorded porewater temperatures to better interpret the TEX_{86} trends and to ensure that the Cathedral Hill reconstructed temperatures are influenced by the subsurface microbial community. In this regard, RI is used to monitor the adaptive response of an archaeal community at the hydrothermal vent site. Lipid cyclization is an adaptive response to changing environmental temperature or acidity in which an archaeon increases its rigidity by decreasing the fluidity and permeability of its cellular membrane that, therefore, also further regulates the flow of solutes and nutrients in and out of the cell (Gliozzi et al., 1983; De Rosa and Gambacorta, 1988; Uda et al., 2001; Schouten et al., 2002; Macalady et al., 2004; Boyd et al., 2013). Both cores 1 and 2 have RI values highly correlated to temperature (R^2 = 0.87 and 0.75, respectively) consistent with heat stress adaption. As such, a significant proportion of the measured *i*GDGTs likely emanate from archaeal communities living in the shallow sediments of Cathedral Hill. In this regard, the lipid cyclization pattern may reflect stratigraphically discrete thermophilic to hyperthermophilic communities that are selectively adapted to more extreme temperature conditions.

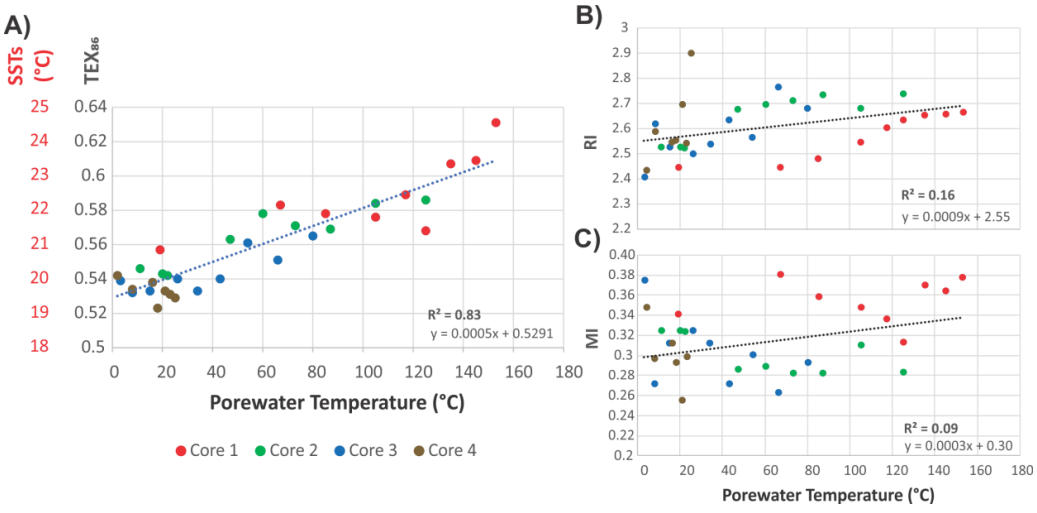

FIGURE 4. Cross plots of A) TEX_{86}, B) RI, and C) MI, *i*GDGT proxies versus porewater temperature. TEX_{86}^{H}reconstructed MASSTs are based on Kim et al. (2010).

3.3. Lipid signal sourcing

To evaluate the sources of measured archaeal lipids, core and $_{IPL}TEX_{86}$ indices were compared as signal response loadings from their respective pools of living and dead cellular

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debris (Figure 5). For cores 1, 2, and 3 the 1G-*i*GDGT $_{IPL}TEX_{86}$ measures are correlated with temperature (R^2 = 0.46, 0.74, and 0.66, respectively; Figure 5A). In this regard, 1G-*i*GDGT $_{IPL}TEX_{86}$ ratio appears to also measure *in situ* porewater temperatures. Factors such as community composition and adaptation may further impact the $_{IPL}TEX_{86}$ ratio as the rates of changes between cores 1–3 are not the same. Similar to the CL TEX_{86} values, the $_{IPL}TEX_{86}$ are not correlated to their summed TEX_{86} lipid abundances (Figure 5B). Such a condition is consistent with the living lipid pool being modified by the archaeal community's response to thermal stress and not by subsequent thermal oxidative transformation occurring shortly after cell death.

The IPL and CL lipids of transect samples can be further grouped into three clusters (A, B, C), suggesting a mixed signal for the sourcing of archaeal GDGTs from both the living and dead pools of archaea (Figure 5C). In this plot, we assume that clusters falling on the 1:1 line indicate the living biota can equally contribute to the dead pool of total recovered GDGTs. Those off-axis contribute either less or more to one or the other lipid pool. The three clusters mark unique thermal zones within the transect area with cluster A being composed of the ambient core 2 to 4 seafloor surface samples; cluster B marking a mix of intermediate temperature samples from all cores; and cluster C being composed of high temperatures samples. The lipid groups likely mark distinct archaeal communities. As cluster B resides on the 1:1 line, the TEX_{86} core lipids likely have a mixed of detrital and *in situ* inputs. Cluster C, however, appears likely dominated by *in situ* lipid production. The hyperthermophilic *Methanopyrus kandleri,* recovered from other Guaymas Basin sites (Teske et al., 2014), may represent one such archaeon contributing to the cluster C lipid pool. The thermal zonation and equivalent directionality of the resulting ratios (i.e. both CL and IPL TEX_{86} ratios increase with porewater temperature) further supports overprinting of the original CL TEX_{86} sea surface signal by the ocean bottom sediment archaeal community as a mechanism for the observed CL TEX_{86} trends.

Collectively, these results suggest the source of the archaeal core lipids measured in the TEX_{86} and RI indices progressively become more dominated by subsurface microbial communities adapted to the hotter hydrothermal vent fluids. Our results also indicate that in select natural environments, such as hydrothermal vent complexes, the TEX_{86} SST-proxy may entirely record ocean bottom sediment porewater temperatures. To our knowledge, a clear case of overprinting to this level has not yet been demonstrated.

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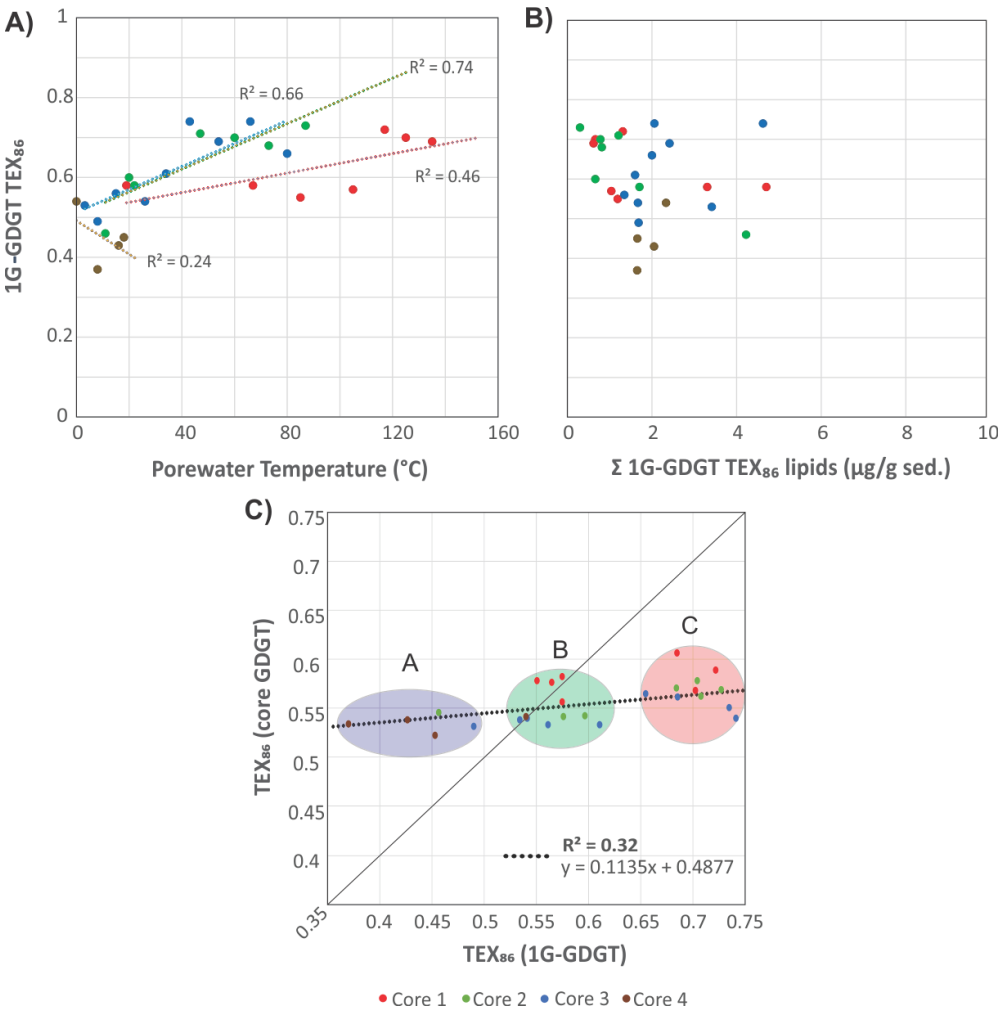

FIGURE 5. Cross plots of 1G-*i*GDGTs $_{IPL}TEX_{86}$ versus (A) porewater temperatures and (B) the concentration of 1G-*i*GDGTs in the sediments. C) TEX_{86} proxy of core GDGTs vs 1G-GDGTs. Clusters A–C may represent differernt archeal communities that are providing varying inputs of *i*GDGT to the core GDGT lipid pool. The dotted trendline is the particial least square regression of the complete core lipid TEX_{86} data set. The solid line marks the 1:1 CL to IPL proxy correspondance indicating both allochthonous and autochthonous sources contribute equally to the core GDGT lipid pool.

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3.4. TEX_{86} overprint corrections

The measured TEX_{86} ($_{M}TEX_{86}$) value of the Cathedral Hill sediments is herein considered to be a weighted sum of a sea surface TEX_{86} ($_{SS}TEX_{86}$) value acquired from lipids sourced in the upper water column that is further modified by a component of water column sourced core lipids ($_{WC}TEX_{86}$) as well as by additions of archaeal lipids from the benthic and subsurface microbial communities ($_{Sed}TEX_{86}$). These ratio loadings are potentially further modified by diagenetic influences in the ocean bottom sediments. Over the cumulative sediment burial period and measured porewater temperatures of the Cathedral Hill push core sediments, these influences include the selective loss of lipids by their binding into protokerogen (K) and potential changes due to the loss of lipid by turnover (φ; section 3.1). Additional catagenetic effects from thermochemical alteration of lipids (θ) may also attenuate the sum of sedimentary core lipids by their exposure to high temperature vent fluids. Collectively, these effects are considered to form the following relationship:

$$ {}_{M}\mathrm{TEX}_{86} = \frac{a_{SS}\mathrm{TEX}_{86} + b_{WC}\mathrm{TEX}_{86} + c(d_{0\text{-}n})_{Sed}\mathrm{TEX}_{86}}{\varphi + K + \theta} \tag{7} $$

where a, b, and c, are measured scaling parameters for lipid loading and φ, K, and θ are diagenetic and catagenetic alteration parameters. Solving for $_{SS}TEX_{86}$:

$$ {}_{SS}\mathrm{TEX}_{86} = \frac{{}_{M}\mathrm{TEX}_{86}(\varphi + K + \theta)}{a} - \frac{b_{WC}\mathrm{TEX}_{86} + c(d_{0\text{-}n})_{Sed}\mathrm{TEX}_{86}}{a} \tag{8} $$

In this regard, a portion of the archaeal community from the deeper water column, presumably initially sourced of IPLs, and an additional community inhabiting the ocean floor sediments are assumed to eventually die with their respective IPLs gradually becoming converted to CLs that further contribute to the observed $_{M}TEX_{86}$ value. For this study, no data were collected to calculate $b_{WC}TEX_{86}$ and its potential impact on $_{M}TEX_{86}$ is not further considered. However, it is highly likely, given the longer residence times for glycosidic-based headgroups of the identified archaeal IPLs and their relatively short settling time through the water column that a component of this lipid source could already be mixed with the $_{Sed}TEX_{86}$ value (Lengger et al., 2012). For this study, $_{Sed}TEX_{86}$ is an IPL-TEX_{86} ratio based on detected 1G-GDGT-1, -2, -3, and Cren' as present in the original paleoclimate proxy (Eq. 1; Table 1; Figure 6). The 2G-GDGT lipids are excluded from the calculation due to their low absolute concentrations (<2 µg/g sed.), their limited number of detected TEX_{86} core lipid configurations (comprising only of GDGT-1 and GDGT-2; Table A2), and their short stratigraphic zones of occurrence (section 3.1). The $_{Sed}TEX_{86}$ is further scaled by the summed concentrations of these lipids as they increasingly accumulate with sediment depth ($d_{0\text{-}n}$). For Cathedral Hill, the sum of allochthonous TEX_{86} lipids (Σ[GDGTs $_{CL\text{-}TEX_{86}\ lipids}$]$_{0\text{-}2}$) is estimated to be 120 µg/g sed. based on an average surface lipid concentration (0-2 cmbsf) measured across the four core transect. As such,

$$ c(d_{0\text{-}n}) = \sum_{i=0}^{n} \left(\frac{[\mathrm{GDGTs}_{IPL\text{-}TEX_{86}\ lipids}]_{n}}{[\mathrm{GDGTs}_{CL\text{-}TEX_{86}\ lipids}]_{0\text{-}2cm}} \right) \tag{9} $$

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where n is the deepest point of sediment burial.

Selective lipid removal by digenetic and catagenetic processes theoretically may also affect the TEX_{86} value; however, their perspective impact on the directionality and magnitude of the ratio are difficult to predict and equally hard to discretely measure. For Cathedral Hill, although the loss of GDGTs to protokerogen formation could potentially impact the ratio, it has been proven to be very low for the analyze sediments (Bentley et al., 2021). As such, the selectivity of lipid classes being adsorbed to a protokerogen is undeterminable. More importantly, for this site it is insignificant, and the K parameter in Eqs. 7 and 8 is therefore assigned a value of 0.

The degradation rates of each TEX_{86} lipid class were independently measured for the four push cores (Eq. 6; Fig. A2). Given the high geothermal gradient at Cathedral Hill, some of the transect push core sediments resided within zones of active catagenesis (Fig. 2; Dalzell et al., 2021). As the abundance of both CLs and IPLs differentially decreases through the various core sediment profiles with turnover rates that appear to be constrained by porewater temperature changes (section 3.1), the degradation rates must also record the effects of thermochemical oxidative weathering (Fig. 3B). In this case, φ and θ are therefore treated as a grouped parameter.

To determine if individual lipid classes were selectively removed during degradation, the variance (s^2) of the rate change as measured from its respective regression slope (i.e. $m_{logk'}$) of the TEX_{86} lipid classes (Fig. A2; Supplemental Table A3 from Eq. 6) were calculated. For the Cathedral Hill transect, the calculated $m_{logk'}$ s^2 is 0.11, which suggests near equal degradation rates for all TEX_{86} lipid classes. Therefore, lipid turnover and the concomitant thermochemical oxidation of these lipid classes is also similarly non-selective. A weighing function for the degree of lipid class selectivity during turnover is nonetheless proposed:

$$\varphi+\theta = 1/{}_{M}TEX_{86}^{0.11} \tag{10}$$

When applied to Eq. 8 minor changes to the reconstructed lumped ${}_{SS}+{}_{WC}TEX_{86}$ ratio are observed consistent with the absence of a comparative relationship between iGDGT down core lipid depletions and the respective ${}_{M}TEX_{86}$ ratios across the biologically active zone of the transect sediments (section 3.1; Figure 3B).

Equation 7 predicts an average transect ${}_{SS}+{}_{WC}TEX_{86}^{H}$ reconstructed SST of 21.92 ±0.66 °C with no elevated trends for increasing porewater temperatures across each of the transect cores (Table 2; Figure 6A). If the φ, K, and θ scaling parameters are removed from the calculation the average temperature shifts 2.08 °C lower to 19.69 ±0.39 °C (Table 2; Figure 6B). The marginal change is likely due to only a few sediment samples displaying evidence of *in situ* hydrocarbon generation associated with thermochemical oxidation (Dalzell et al., 2021). Irrespective of approach, but particularly the case for the more simplified expression, all measures produce values closer to the expected SST of 19.3–20.4 °C that is based on the range of values recorded for core 4 and the three transect surface sediments (section 3.2). These values are ~3 °C lower than the 23–24 °C obtained for the 21-year (1982–2004) satellite-derived MASST data for the Guaymas Basin region (Herrera-

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Cervantes et al., 2007). Nonetheless, nearly all $_{M}TEX_{86}$ attenuation can therefore be attributed to sediment microbial overprinting. The high degree of influence is striking given that the upper water flux of GDGTs is estimated to represents up to 93% of the total intact polar and core GDGT lipid pool within these sediments. In this regard, it demonstrated that microbial community influences TEX_{86} measurements.

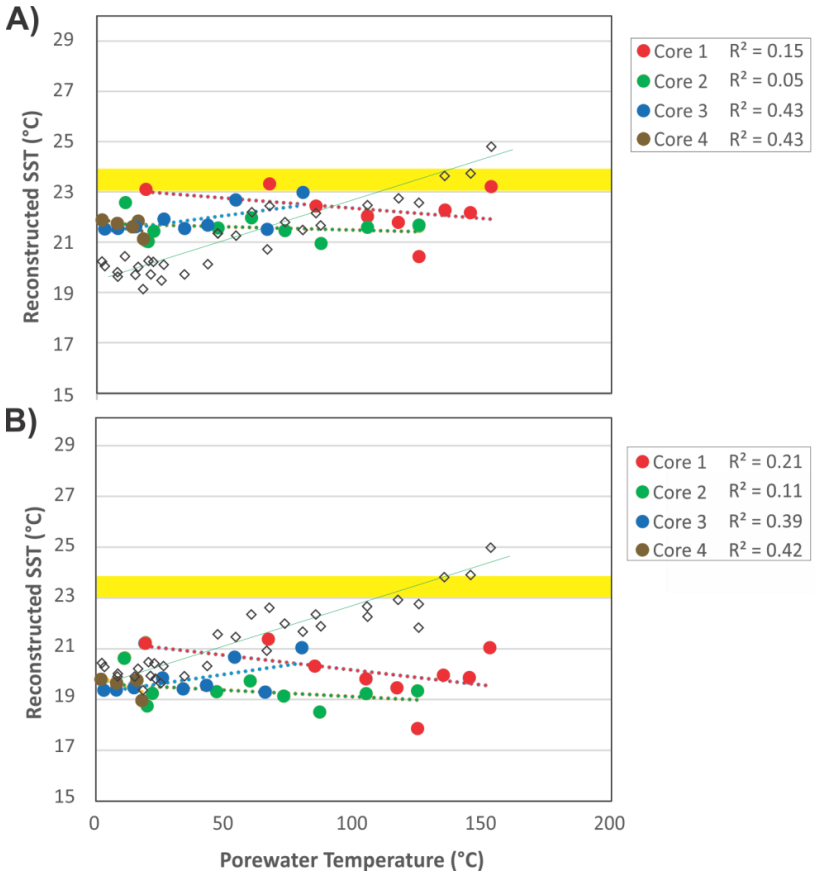

FIGURE 6. Reconstructed $_{SS}TEX_{86}$ SSTs from (A) Eq. 8 and (B) Eq. 8 without φ, *K*, and θ scaling parameters compared to measured porewater temperatures. $_{M}TEX_{86}$ values are also plotted for reference (open green circles). Yellow field is the 23–24 °C range observed for the 21-year (1982–2004) satellite-derived MASST data (Herrera-Cervantes et al., 2007). The corrected data series show a lack of correlation suggesting that model can back-out the original SST signal.

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Table 2. Reconstructed sea surface temperatures.

Sample	Depth (cmbsf)	Porewater Temp. (°C)	*t* Time (yrs.)	$_{M}TEX_{86}$ (Measured *i*GDGT TEX_{86})	Reconstructed SST (°C)	TEX_{86} 1G-GDGT IPLs (µg/g)	Cumulative 1G-GDGTs Loading with Depth (µg/g)	$_{Sed}TEX_{86}$ (i.e. 1G-GDGT $_{IPL}TEX_{86}$)	$c(d_{0\text{-}n})$ Cumulative Weighted IPL Loading (Eq. 9)
Core 1 (0-2cm)	1	19	10	0.56	21.2	4.80	0	0.58	0.00
Core 1 (2-4cm)	3	67	20	0.58	22.6	3.41	4.80	0.58	0.04
Core 1 (4-6cm)	5	85	30	0.58	22.3	1.29	8.21	0.55	0.07
Core 1 (6-8cm)	7	105	40	0.58	22.2	1.14	9.50	0.57	0.08
Core 1 (8-10cm)	9	117	50	0.59	22.9	1.41	10.64	0.72	0.09
Core 1 (10-12cm)	11	125	60	0.57	21.8	0.76	12.05	0.70	0.10
Core 1 (12-15cm)	13	135	70	0.61	23.8	0.72	12.81	0.69	0.11
Core 1 (15-18cm)	17	145	80	0.61	23.9	0.00	13.53	0.69	0.11
Core 1 (18-21cm)	20	153	90	0.63	24.9	0.00	13.53	0.69	0.11
Avg.				**0.59**	**22.84**				
Std. Dev.				**0.02**	**1.16**				
Core 2 (0-2cm)	1	11	10	0.55	20.6	4.33	0	0.46	0.00
Core 2 (2-4cm)	3	22	20	0.54	20.4	1.80	4.33	0.58	0.04
Core 2 (4-6cm)	5	20	30	0.54	20.5	0.76	6.13	0.60	0.05
Core 2 (6-8cm)	7	47	40	0.56	21.5	1.31	6.89	0.71	0.06
Core 2 (8-10cm)	9	60	50	0.58	22.3	0.88	8.20	0.70	0.07
Core 2 (10-12cm)	11	73	60	0.57	22.0	0.92	9.08	0.68	0.08
Core 2 (12-15cm)	13	87	70	0.57	21.8	0.40	10.00	0.73	0.08
Core 2 (15-18cm)	17	105	80	0.58	22.6	0.00	10.40	0.73	0.09
Core 2 (18-21cm)	20	125	90	0.59	22.7	0.00	10.40	0.73	0.09
Avg.				**0.56**	**21.61**				
Std. Dev.				**0.02**	**0.91**				
Core 3 (0-2cm)	1	3.2	10	0.54	20.2	3.51	0	0.53	0.03
Core 3 (2-4cm)	3	8	20	0.53	19.9	1.79	3.51	0.49	0.01
Core 3 (4-6cm)	5	15	30	0.53	19.9	1.45	5.30	0.56	0.01
Core 3 (6-8cm)	7	26	40	0.54	20.3	1.77	6.74	0.54	0.01
Core 3 (8-10cm)	9	34	50	0.53	19.9	1.70	8.51	0.61	0.01
Core 3 (10-12cm)	11	43	60	0.54	20.3	2.16	10.21	0.74	0.02
Core 3 (12-15cm)	13	54	70	0.56	21.4	2.52	12.37	0.69	0.02
Core 3 (15-18cm)	17	66	80	0.55	20.9	4.72	14.89	0.74	0.04
Core3 (18-21cm)	20	80	90	0.57	21.6	2.10	19.61	0.66	0.02

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Avg.				**0.54**	**20.50**				
Std. Dev.				**0.01**	**0.67**				
Core 4 (0-2cm)	1	2	10	0.54	20.4	2.43	0	0.54	0.02
Core 4 (2-4cm)	3	8	20	0.53	20.0	1.75	2.43	0.37	0.01
Core 4 (4-6cm)	5	16	30	0.54	20.2	2.15	4.18	0.43	0.02
Core 4 (6-8cm)	7	18	40	0.52	19.3	1.76	6.34	0.45	0.01
Core 4 (8-10cm)	9	21	50	0.53	19.9	0.44	8.09	-	-
Core 4 (10-12cm)	11	23	60	0.53	19.8	2.20	8.54	-	-
Core 4 (12-15cm)	13	25	70	0.53	19.7	0.00	10.74	-	-
Avg.				**0.53**	**19.90**				
Std. Dev.				**0.01**	**0.34**				
Avg.									
Std. Dev.									

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Table 2. Reconstructed sea surface temperatures (continued).

Sample	Eq. 8 excluding φ+θ+*K*			Eq. 8 including φ+θ+*K*		
	$_{SS+WC}TEX_{86}$ ($_{M}TEX_{86}$ - $c(d_{0\text{-}n})*_{Sed}TEX_{86}$)	$_{SS+WC}TEX_{86}^{H}$ (after Kim et al., 2010)	$_{SS+WC}TEX_{86}^{H}$ Reconstructed SST (°C)	φ+θ (Eq. 10) (where s^2 = 0.11; Table A3)	$_{SS+WC}TEX_{86}$	$_{SS+WC}TEX_{86}^{H}$ Reconstructed SST (°C) (after Kim et al., 2010)
Core 1 (0-2cm)	0.56	-0.25	21.2	1.07	0.59	23.1
Core 1 (2-4cm)	0.56	-0.25	21.4	1.07	0.60	23.3
Core 1 (4-6cm)	0.54	-0.27	20.3	1.07	0.58	22.5
Core 1 (6-8cm)	0.53	-0.27	19.8	1.07	0.57	22.0
Core 1 (8-10cm)	0.52	-0.28	19.5	1.07	0.57	21.8
Core 1 (10-12cm)	0.50	-0.30	17.9	1.08	0.54	20.5
Core 1 (12-15cm)	0.53	-0.27	20.0	1.07	0.58	22.3
Core 1 (15-18cm)	0.53	-0.27	19.8	1.07	0.58	22.2
Core 1 (18-21cm)	0.55	-0.26	21.0	1.07	0.60	23.2
Avg.	**0.54**	**-0.27**	**20.10**	**1.07**	**0.58**	**22.33**
Std. Dev.	**0.02**	**0.02**	**1.08**	**0.00**	**0.02**	**0.89**
Core 2 (0-2cm)	0.55	-0.26	20.6	1.07	0.58	22.6
Core 2 (2-4cm)	0.52	-0.28	19.2	1.07	0.56	21.5
Core 2 (4-6cm)	0.51	-0.29	18.7	1.08	0.55	21.1
Core 2 (6-8cm)	0.52	-0.28	19.3	1.07	0.56	21.6
Core 2 (8-10cm)	0.53	-0.28	19.7	1.07	0.57	22.0
Core 2 (10-12cm)	0.52	-0.28	19.1	1.07	0.56	21.5
Core 2 (12-15cm)	0.51	-0.29	18.5	1.08	0.55	21.0
Core 2 (15-18cm)	0.52	-0.28	19.2	1.07	0.56	21.6
Core 2 (18-21cm)	0.52	-0.28	19.3	1.07	0.57	21.7
Avg.	**0.52**	**-0.28**	**19.32**	**1.07**	**0.56**	**21.61**
Std. Dev.	**0.01**	**0.01**	**0.60**	**0.00**	**0.01**	**0.49**
Core 3 (0-2cm)	0.52	-0.28	19.4	1.07	0.56	21.5
Core 3 (2-4cm)	0.52	-0.28	19.4	1.07	0.56	21.6
Core 3 (4-6cm)	0.53	-0.28	19.5	1.07	0.57	21.7
Core 3 (6-8cm)	0.53	-0.27	19.9	1.07	0.57	21.9
Core 3 (8-10cm)	0.52	-0.28	19.4	1.07	0.56	21.6
Core 3 (10-12cm)	0.53	-0.28	19.6	1.07	0.57	21.7
Core 3 (12-15cm)	0.55	-0.26	20.7	1.07	0.59	22.7
Core 3 (15-18cm)	0.52	-0.28	19.3	1.07	0.56	21.5
Core3 (18-21cm)	0.55	-0.26	21.0	1.07	0.59	23.0
Avg.	**0.53**	**-0.27**	**19.79**	**1.07**	**0.57**	**21.91**
Std. Dev.	**0.01**	**0.01**	**0.62**	**0.00**	**0.01**	**0.55**
Core 4 (0-2cm)	0.53	-0.27	19.8	1.07	0.57	21.9
Core 4 (2-4cm)	0.53	-0.28	19.7	1.07	0.57	21.8

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Core 4 (4-6cm)	0.53	-0.28	19.8	1.07	0.57	21.9
Core 4 (6-8cm)	0.52	-0.29	19.0	1.08	0.56	21.2
Core 4 (8-10cm)	-	-	-			
Core 4 (10-12cm)	-	-	-			
Core 4 (12-15cm)	-	-	-			
Avg.	**0.53**	**-0.28**	**19.55**	**1.07**	**0.65**	**21.67**
Std. Dev.	**0.01**	**0.01**	**0.39**	**0.00**	**0.01**	**0.35**
			19.71			**21.92**
			0.79			**0.66**

4. Conclusions

For this study, we demonstrate the commonly used TEX_{86} paleoclimate proxy can become heavily impacted by the ocean floor archaeal community. For the Cathedral Hill vent site at Guaymas Basin, the lipids sourced from these sediments resulted in TEX_{86} reconstructed temperatures that record conditions of the advecting porewaters. However, the impact appears to result from a combination of source inputs, their diagenetic and catagenetic alteration, and further overprint by the additions of lipids from the ocean floor sedimentary archaeal community that has adapted to the high-temperature conditions of the vent fluids by producing more cyclized ring moieties to rigidify their cellular membranes. Together, these processes resulted in absolute TEX_{86}^{H} temperature offsets of up to 4 °C based on calibrations closely suited to the latitudinal position of Guaymas Basin. Such large offsets could be meaningful to paleoclimate reconstructions (i.e. global changes by 2–4 °C mean completed deglaciation). As such, we further present a method to correct the overprints by both water column and subsurface archaeal community's using IPLs extracted from both of these sources. Although, we have not been able to test this model with lipid inputs from the overlying water column, we have demonstrated its effectiveness at removing sediment sourced overprints, which may not be unique to hydrothermal systems. This approach should be capable of being extended to all near-surface marine sediment systems and may improve the quality of calibration models or climate reconstructions that are based on TEX_{86} measures.

Conflicts of Interest

The authors declare no conflict of interest.

Supplementary information

Supplementary material related to this article can be found on-line at https://doi.org/.....

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