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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For submission to *Biogeosciences*

Number of pages: 27
Number of Figures: 6
Number of Tables: 2
Supplementary pages: 6

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 can be overprinted by 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 archaea and bacteria in soils and sediments are increasingly 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 largely the adaptive response by Thaumarchaeota to oceanographic effects associated with climate or seasonal 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 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 the lipid pool being lost within the upper 21 cmbsf. Here, we show that the turnover is non-selective across TEX_{86} GDGT lipids and does not affect the ratio independently. 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 coupled with the addition of *in situ i*GDGT production from archaeal communities living in the vent sediments. The resulting 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 *i*GDGTs from the upper water column is estimated to be ~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 represent a group of common and structurally diverse compounds frequently used to track the presence of living and dead microorganisms as well as geochemical and physical conditions within present-day and paleoenvironments (e.g., Schouten et al., 2002, 2004; 2013; Hopmans et al., 2004; Weijers et al., 2007, 2014; Hollis et al., 2012; O'Brien, et al., 2017; Stuart et al., 2017). In this regard, the proportional abundances of these lipids form various prominent proxies for assessing environmental change through time. For example, TEX_{86} (TetraEther indeX with 86 carbon atoms; Schouten et al., 2002) is a widely used archaeal lipid-based paleotemperature proxy for marine environments. The ratio measures variations in the number of cyclopentyl rings for a select group of archaeal core lipids (CLs) (Supplementary Figure S1) following the assumption that biphytanyl cyclization is an organismal response to changing sea surface temperatures (SSTs). The proxy is therefore used in many regions around the world with TEX_{86} values typically ranging from 0.2–0.9 in marine settings (e.g. Huguet et al., 2006; Kim et al., 2008; McClymont et al., 2012; Tierney, 2014). The utility of TEX_{86} rests on the premise that *i*GDGTs found in ocean bottom sediments are almost exclusively produced by marine planktonic archaea that inhabit the epipelagic zone (Wakeham et al., 2003; Tierney, 2014; Besseling et al., 2019, 2020). Lipids are therefore required to be efficiently and continually transported from the upper water column to the underlying ocean floor to produce a fossil chemostratigraphic record of microbial response to changing SST conditions with time (Wuchter et al., 2005).

Since its introduction, the reliability of TEX_{86} to accurately track paleoclimate variations has been questioned. TEX_{86}-based SST estimates have been observed to substantially deviate from other temperature proxies (e.g. Huguet et al., 2006; Rommerskirchen et al., 2011; Seki et al., 2012). For example, over the past decade, considerable effort has been made to reconstruct the early Paleogene greenhouse climate system. However, TEX_{86} appears to significantly over-estimate reconstructed SSTs (Hollis et al., 2012) relative to other proxies such as Mg/Ca, or clumped isotopic compositions 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). For late Neogene climate reconstructions, TEX_{86} has been shown to underestimate warming trends relative to the $U^{k'}_{37}$ alkenone-index (Brassell et al., 1986) derived temperatures (Lawrence et al., 2020). The apparent SST offsets have been attributed to how the proxy's associated lipids change in relation to their environment and if these changes are regulated by internal adaptations within the archaeon or by an overarching community succession. In this regard, the debate surrounding these discrepancies largely centers on establishing responses to seasonal biases (e.g. Herford et al., 2006; Wuchter et al., 2006; Huguet et al., 2011); the development of adequate calibration methods (e.g. Kim et al., 2010; Pearson et al., 2013; Tierney et al. 2014); identifying lipid sourcing effects – including subsurface sediments origins for those used with the calculation of TEX_{86} (e.g. Lipp and Hinrichs, 2009); as well as physical, chemical, and ecological controls for archaeon *i*GDGTs cyclization (e.g. Elling et al., 2015; Qin et al., 2015; Hurley et al., 2016).

For non-thermal influences, the primary concern is what archaeal taxa produce *i*GDGTs and where they are sourced. To this end, most TEX_{86} lipids are thought to be produced by Marine Group I (MGI) planktonic Thaumarchaeota (Brochier-Armanet et al., 2008), which are most abundant below the photic and epipelagic zone (e.g., Karner et al., 2001). Some inputs from Marine Group II (MGII), Euryarchaeota, that live in the upper 100 m of the water column, may also contribute to the sediment pool (Lincoln et al., 2014; Wang et al., 2015; Ma et al., 2020). Within this context, many regions of the ocean floor may become highly impacted by colder, deeper water column inputs. For example, a strong positive correlation was shown to exist between ocean depth and differences in TEX^{H}_{86} values for both surface sediments and suspended particulate organic matter in the Mediterranean Sea (Kim et al., 2015). Here TEX_{86} dissimilarities appear to be driven by increases in the relative abundances of the GDGT-2 and isomers of crenarchaeol (see Lui et al., 2018; Sinninghe Damsté et al., 2018) coupled with decreasing abundances of GDGT-1 and GDGT-3 below the thermocline and the ammonium maxima of the water column, which produces a systematic reconstructed SST bias for deep-water surface sediments. Similar conditions have been observed for the

Pacific Ocean (Karner et al., 2001; Pearson et al., 2013) and Southern Atlantic (Hurley et al., 2016) where peak archaeal abundances occur at 100–350 m depth. For these regions, the TEX_{86} lipids should not produce a direct response to changing SSTs. These sourcing effects have led to speculation that the TEX_{86} ratio of open ocean sediments may actually reflect deeper water column and subsurface conditions 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 address this, Schouten et al. (2013) proposed a calibration based on suspended particulate matter and *in situ* water temperature from the upper 100 m of the global ocean. Both TEX_{86}^{H} and TEX_{86}^{L} (Kim et al., 2012a,b) have also been re-calibrated against subsurface (0–900 m water depth) temperatures.

Other non-thermogenic driving forces impacting the production, cyclization, and relative abundance of TEX_{86}-based lipids include organismal selectivity to specific growth phases and growth rates (Elling et al., 2014; Hurley et al., 2016); redox conditions (Qin et al., 2015); and the incorporation of *i*GDGT from archaeal communities living in the ocean floor sediments. With respect to the latter, Lipp and Hinrichs (2009) demonstrated that the production of intact polar lipid GDGTs (IPL-GDGTs) by ocean floor sediment microbial communities collected in the Peru Margin were distinctly different from upper water column sourced CLs and that the conversion of this living pool to fossil lipids would shift TEX_{86} ratios to higher values. However, the overall impact may now be substantial as Umoh 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) also 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. All together, the *i*GDGT relative abundances recorded in a sediment TEX_{86} measurement may ultimately constitute a multi-variable datapoint, mixing lipid components that are themselves responses to temperature, organismal substrate and metabolism dynamics, and biozone niche partitioning that spans from the ocean surface to *in situ* shallow sediment community pools lastly further attenuated by depositional and diagenetic processes.

While not an ideal location to create SST reconstructions, hydrothermal vents of sedimented ocean basins do represent an anomalous endmember to the vast expanse of ambient ocean floor sediment where paleoclimate reconstructions are commonly produced. The sedimented vent systems of Guaymas Basin, Gulf of California (Figure 1) is one such site. The basin experiences high sedimentation rates ranging from 0.4–0.2 cm yr^{-1} (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 (e.g. McKay et al., 2012; Meyer et al., 2013; Teske et al., 2016). These sites should in principle, enable a high-resolution archaeal lipid stratigraphic record that provides optimal conditions for studying potential shallow diagenetic and subseafloor interferences to common archaeal lipid-based environmental proxies. The region further offers an ideal setting to compare TEX_{86} proxy responses to *in situ* lipid production from thermophilic sedimentary archaea that differ from the pelagic background communities (e.g. Schouten et al., 2003). Recently, Bentley et al. (2022) produced a survey of the source and diagenetic and catagenetic alteration of archaeal lipids from the Cathedral Hill hydrothermal vent complex (Figure 1) in the Guaymas Basin, Gulf of California. Within the investigation, it was observed that most *i*GDGTs are sourced from the overlying water column. Building on the results of Schouten et al. (2003), it was observed that these lipids can become heavily turned over in the hotter portions of the vent site where they rarely survive long enough to become cracked into hydrocarbon biomarkers such as biphytanes and derivatives of biphytanes. For this study, we further examine the *i*GDGT lipid distributions in these near-surface ocean floor sediments to determine if paleoclimate proxy signals can be impacted by the presence of subsurface archaeal populations. The distribution of *i*GDGTs and their corresponding environmental proxy signals were measured within the sediments along a transect at the complex. 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.

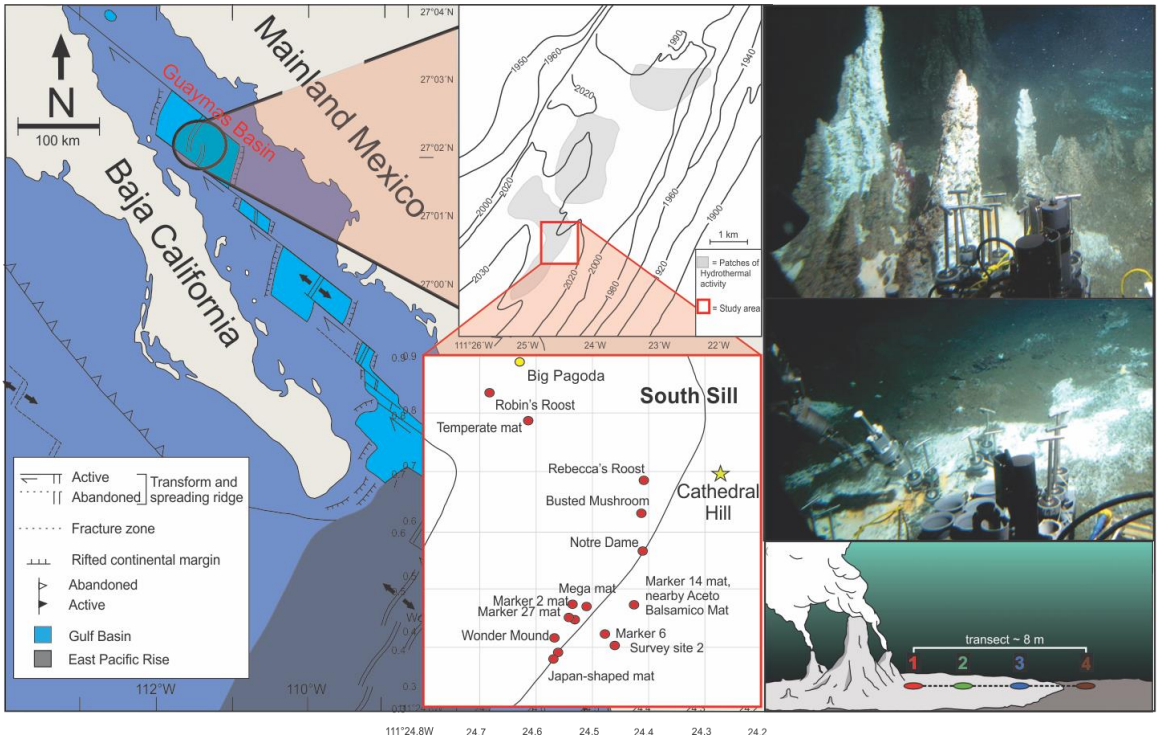

FIGURE 1 A) Location map of Guaymas Basin and the Southern Sill (red outlined box) in the Gulf of California. Cathedral Hill is marked with a yellow star. B) Photo of Cathedral Hill taken via *Alvin*. C) Schematic of the push core transect with a color-coding that is consistent for all plots throughout this paper. Maps modified from Teske et al. (2016), Dalzell et al. (2021), and Bentley et al. (2022).

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 sequentially taken beside each core (Table 1). Once the push cores were brought to the surface, the sediments were subsampled into 2–3 cm-thick depth 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.

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 (mg g sed^{-1})[*]	Sum of IPL *i*GDGT (µg g^{-1})[†]	Sum of *i*GDGT (µg g^{-1})[‡]
1	0-2	GB4462-5	Black mud with microbial mat filaments	19	19	1.97	11.5	16.7	503.1
1	2-4	GB4462-5	Brownish-green diatomaceous mud	-	67	2.04	7.65	14.6	461.7
1	4-6	GB4462-5	Brownish-green diatomaceous mud	85	85	2.03	9.37	6.0	203.3
1	6-8	GB4462-5	Brownish-green diatomaceous mud	-	105	1.99	2.09	4.3	148.6
1	8-10	GB4462-5	Brownish-green diatomaceous mud	-	117	2.01	4.38	3.2	59.0
1	10-12	GB4462-5	Grayish-green mud	121, 124	125	2.01	1.97	1.7	48.8
1	12-15	GB4462-5	Brownish-green consolidated mud with clay shards	-	135	1.98	1.99	1.4	78.7
1	15-18	GB4462-5	Brownish-green consolidated clay	142	145	1.96	1.69	0.0	42.6
1	18-21	GB4462-5	Brownish-green consolidated clay	153	153	1.98	1.72	0.0	38.4
2	0-2	GB4462-6	Black mud with microbial mat filaments	9, 13	11	2.02	8.48	17.8	591.0
2	2-4	GB4462-6	Black mud with microbial mat filaments	-	22	1.97	8.65	7.5	266.3
2	4-6	GB4462-6	Brownish-green diatomaceous mud	20	20	1.95	2.51	2.5	87.4
2	6-8	GB4462-6	Brownish-green diatomaceous mud	-	47	1.95	3.38	3.4	69.7
2	8-10	GB4462-6	Brownish-green diatomaceous mud	-	60	1.95	1.48	2.0	48.4
2	10-12	GB4462-6	Brownish-green diatomaceous mud	69, 77	73	1.94	4.19	2.0	52.1
2	12-15	GB4462-6	Brownish-green diatomaceous mud	-	87	2.02	1.69	1.0	44.2
2	15-18	GB4462-6	Brownish-green diatomaceous mud	118	105	1.95	2.01	0.0	22.3
2	18-21	GB4462-6	Brownish-green diatomaceous mud	109	125	1.94	1.38	0.0	31.2
3	0-2	GB4462-3	Black mud with microbial mat filaments	3.2	3.2	1.96	7.31	15.3	511.3
3	2-4	GB4462-3	Brownish-green diatomaceous mud	-	8	1.96	3.91	8.3	308.9
3	4-6	GB4462-3	Brownish-green diatomaceous mud	15	15	2.00	2.86	7.0	283.5
3	6-8	GB4462-3	Brownish-green diatomaceous mud	-	26	2.02	5.00	7.5	275.3
3	8-10	GB4462-3	Brownish-green diatomaceous mud	34	34	1.97	2.02	5.7	251.1
3	10-12	GB4462-3	Brownish-green diatomaceous mud	-	43	2.01	1.86	5.8	227.7
3	12-15	GB4462-3	Brownish-green diatomaceous mud	-	54	1.94	1.78	6.5	184.6
3	15-18	GB4462-3	Brownish-green diatomaceous mud	61	66	2.01	1.43	12.3	473.1
3	18-21	GB4462-3	Brownish-green diatomaceous mud	83	80	1.96	1.98	5.2	182.3
4	0-2	GB4462-8	Black mud	0	0	1.93	3.44	16.7	485.4
4	2-4	GB4462-8	Brownish-green diatomaceous mud	1.5	8	2.01	3.17	14.6	417.8
4	4-6	GB4462-8	Brownish-green diatomaceous mud	16	16	1.95	4.00	6.0	480.6
4	6-8	GB4462-8	Brownish-green diatomaceous mud	-	18	2.02	4.19	4.3	359.7
4	8-10	GB4462-8	Brownish-green diatomaceous mud	-	21	2.02	4.76	3.2	153.5
4	10-12	GB4462-8	Brownish-green diatomaceous mud	-	23	1.95	4.84	1.7	459.5
4	12-15	GB4462-8	Brownish-green diatomaceous mud	-	25	1.95	5.74	1.4	515.2
4	15-18	GB4462-8	Sample lost during collection	-	-	-	-	0.0	503.1
4	18-21	GB4462-8	Sample lost during collection	29	-	-	-	0.0	461.7

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

Core[*a]	Depth interval (cmbsf)	Alvin dive # and core ID	SUM of TEX_{86} *c*GDGT[c] (μg g^{-1})	TEX_{86} *c*GDGT[c]	TEX_{86}^{H} *c*GDGT[d]	TEX_{86}^{H} Reconstructed SSTs (Kim et al., 2010)[e]	RI[f]	MI[g]	TEX_{86} $_{IPL}$GDGT[c]
1	0-2	GB4462-5	110.7	0.56	-0.25	21.2	2.44	0.34	0.58
1	2-4	GB4462-5	117.1	0.58	-0.23	22.6	2.45	0.38	0.58
1	4-6	GB4462-5	47.7	0.58	-0.24	22.3	2.48	0.36	0.55
1	6-8	GB4462-5	33.0	0.58	-0.24	22.2	2.55	0.35	0.57
1	8-10	GB4462-5	13.0	0.59	-0.23	22.9	2.60	0.34	0.72
1	10-12	GB4462-5	10.1	0.57	-0.25	21.8	2.63	0.31	0.70
1	12-15	GB4462-5	17.8	0.61	-0.22	23.8	2.65	0.37	0.69
1	15-18	GB4462-5	9.8	0.61	-0.22	23.9	2.66	0.36	-
1	18-21	GB4462-5	9.3	0.63	-0.20	24.9	2.66	0.38	-
2	0-2	GB4462-6	128.5	0.55	-0.26	20.6	2.52	0.32	0.46
2	2-4	GB4462-6	58.2	0.54	-0.27	20.4	2.52	0.32	0.58
2	4-6	GB4462-6	19.2	0.54	-0.27	20.4	2.53	0.33	0.60
2	6-8	GB4462-6	13.4	0.56	-0.25	21.5	2.68	0.29	0.71
2	8-10	GB4462-6	9.3	0.58	-0.25	21.7	2.70	0.29	0.70
2	10-12	GB4462-6	10.1	0.57	-0.24	21.9	2.71	0.28	0.68
2	12-15	GB4462-6	8.5	0.57	-0.24	21.9	2.73	0.28	0.73
2	15-18	GB4462-6	4.5	0.58	-0.23	22.6	2.68	0.31	-
2	18-21	GB4462-6	6.0	0.59	-0.23	22.8	2.74	0.28	-
3	0-2	GB4462-3	127.0	0.54	-0.27	20.2	2.41	0.37	0.53
3	2-4	GB4462-3	57.7	0.53	-0.27	19.8	2.62	0.27	0.49
3	4-6	GB4462-3	60.0	0.53	-0.27	19.9	2.53	0.31	0.56
3	6-8	GB4462-3	59.8	0.54	-0.27	20.3	2.50	0.33	0.54
3	8-10	GB4462-3	53.0	0.53	-0.27	19.9	2.54	0.31	0.61
3	10-12	GB4462-3	42.1	0.54	-0.27	20.3	2.64	0.27	0.74
3	12-15	GB4462-3	39.2	0.56	-0.25	21.5	2.56	0.30	0.69
3	15-18	GB4462-3	86.8	0.55	-0.26	20.9	2.77	0.26	0.74
3	18-21	GB4462-3	36.4	0.57	-0.25	21.6	2.68	0.29	0.66
4	0-2	GB4462-8	112.9	0.54	-0.27	20.4	2.43	0.35	0.54
4	2-4	GB4462-8	85.3	0.53	-0.27	20.0	2.59	0.30	0.37
4	4-6	GB4462-8	102.7	0.54	-0.27	20.2	2.55	0.31	0.43
4	6-8	GB4462-8	70.8	0.52	-0.28	19.3	2.55	0.29	0.45
4	8-10	GB4462-8	26.6	0.53	-0.27	19.9	2.69	0.26	-
4	10-12	GB4462-8	91.0	0.53	-0.27	19.8	2.54	0.30	-
4	12-15	GB4462-8	73.7	0.53	-0.28	19.7	2.90	0.20	-
4	15-18	GB4462-8	110.7	-	-	-	-	-	-
4	18-21	GB4462-8	117.1	-	-	-	-	-	-

[*] Also reported in Bentley et al. (2022).

[†] Sum of GDGT-1, -2, -3. -4, -5, and -5' (Table S1).

[‡] Sum of all detected 1G- and 2G-GDGTs (Table S3).

[*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 (also referred to as $_{M}TEX_{86}$ in section 3.4).

[d] TEX_{86}^{H} = log ((GDGT-2 + GDGT-3 + GDGT-5')/(GDGT-1 + GDGT-2 + GDGT-3 + GDGT-5')), for sediments outside low latitudes (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) and promoted by Zeng et al. (2016).

[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

Lipid extractions followed a modified Bligh and Dyer protocol laid out in Bentley et al. (2022) and following Sturt et al. (2004). A subsample of freeze-dried sediment was added to a Teflon© centrifuge tube followed by the addition of 6 ml of mix A solvent solution comprising of 2:1:0.8 v/v/v methanol (MeOH), dichloromethane (DCM), and phosphate buffer (5.5 g L^{-1} Na_2HPO_4; Avantor Performance Materials, LLC. adjusted to pH of 7.4 with HCl; Anachemia Co.). The solvent sediment mixture was further spiked with 1-alkyl-2-acetoyl-*sn*-glycero-3-phosphocholine (PAF) recovery standard purchased from Avanti Polar Lipids, Inc. The slurry was sonicated for 5 min then centrifuged for 5 min at 1250 rpm. The resulting supernatant was added to a separatory funnel. This procedure was performed twice before being joined by two replicate extractions using mix B, a 2:1:0.8; v/v/v solution of MeOH, DCM, and trichloroacetic acid buffer (50 g L^{-1} $C_2HCl_3O_2$; Avantor Performance Materials, LLC. of pH 2) and a final two replicate extractions using mix C, a 5:1 v/v solution of MeOH and DCM. Once complete, the combined A, B, and C. For each step, the organic fraction was collected in a beaker, and the combination of mix A, B, and C were subjected to 10 ml of DCM and H_2O (MilliQ) to achieve separation. The organic phase was drawn off and the water was extracted using 3 DCM washes, drawing off the organic phase after each wash. The organic phase was then back-extracted with H_2O to ensure purity. The resulting organic phase was then evaporated to dryness at 60 °C under dry nitrogen. The resulting total lipid extract (TLE) was transferred to pre-weighed autosampler vials using DCM:MeOH 1:1 v/v, spiked with 1, 2-diheneicosanoyl-*sn*-glycero-3-phosphocholine (C_{21}-PC; Avanti Polar Lipids, Inc.) and stored at -20 °C.

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

Mass spectrometric analyses were performed on an Agilent Technologies 1260 Infinity II HPLC coupled to an Agilent Technologies 6530 quadruple time-of-flight mass spectrometer (qToF-MS) operated in positive mode. Chromatographic separation used a reverse-phase method outlined by Zhu et al. (2013). The HPLC was fitted with an Agilent Technologies ZORBAX RRHD Eclipse Plus C_{18} (2.1 mm × 150 mm × 1.8 μm) reverse phase column and guard column maintained at 45 °C. The sample injection solvent was methanol. An aliquot of each sample representing 1% of the TLE was analyzed. A 0.25 mL min^{-1} flow rate was established with mobile phase A consisting of methanol/formic acid/ammonium hydroxide (100:0.04:0.10 v/v/v) held at 100% for 10 min, thereafter mixed following a linear gradient with mobile phase B (propan-2-ol/formic acid/ammonium hydroxide (100:0.04:0.10 v/v/v) to 24%, 65%, and 70% over 5-, 75-, and 15-min intervals, respectively. Each sample run was finished by re-equilibrating the system with 100% mobile phase A for 15 min The effluent was ionized by an electrospray ionization source with a gas temperature of 300 °C, a 3 L min^{-1} drying gas flow, and a 5.33 μA source current. The mass spectrometer was set to a 100–3000 *m/z* scan range in positive mode in an untargeted method with 10 ppb resolution to simultaneously resolve both archaeal IPLs and CLs.

Analyte identification was achieved by accurate mass resolution, mass spectral analysis using Agilent Technology's MassHunter software, and comparison of fragmentation patterns with the literature (e.g., Knappy et al., 2009; Liu et al., 2010; Yoshinaga et al., 2011 – see Bentley et al., 2022 for further details). Mass fragments consistent with the loss of a biphytane (*m/z* 743.7) were screened for all archaeal lipids. Quantification was achieved by summing the integration peak areas of $[M+H]^+$, $[M+NH_4]^+$, and $[M+Na]^+$ adducts for the respective IPLs and CLs of interest. 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: PAF, C_{21}-PC, 1,2-diacyl-3-O-(α-D-galactosyl1-6)-β-D-galactosyl-*sn*-glycerol (DGDG), 1,2-diacyl-3-O-β-D-galactosyl-*sn*-glycerol (MGDG), 1,2-di-O-phytanyl-*sn*-glycerol (Archaeol), 1',3'-bis[1,2-dimyristoyl-*sn*-glycero-3-phospho]-glycerol (14:0 Cardiolipin) 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. Response factors were calculated relative to the C_{21}-PC, and the appropriate correction factor was then applied to the 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^{-1} per

GDGT compound, providing confidence in the initial results and confirming the presence of two outliers in the data set (Bentley et al., 2022). These outliers are Core 4 at 8-10 cm, with abnormally low concentrations of all compounds that are 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 turnover

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 (*br*GDGTs) including Ia-c, IIa-c, and IIIa were found to have discontinuous and/or low absolute abundances, with some compound classes not being detected (i.e. *br*GDGT-IIIb; Table S2). The *br*GDGTs are therefore not further examined in this study. For cores 1 to 3 the concentrations of nearly all *i*GDGT compounds systematically decrease with depth (Figure 2). Bentley et al. (2022) 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 an inferred 52.5–105 yrs of sedimentation as penetrated by the length of the push core (based on sedimentation rates). From this, it is estimated that ~70.57 ± 23.5 μg *i*GDGTs g^{-1} sed yr^{-1} is being deposited on the seafloor from the overlying water column. However, for cores closest to the vent site, lipid abundances exhibited a much sharper decrease with depth, which Bentley et al. (2022) 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 seafloor). 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^{-1} sediment concentration and no systematic loss of lipids.

Due to the high temperature conditions of the vent fluids at Cathedral Hill, the identified archaeal *i*GDGT-based IPLs within the sediments most likely represent the composition of cellular membrane material from archaeal communities living 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 add to the core *i*GDGT lipid pool. Similar to CLs, the 1G-GDGTs contain 0-4 cyclopentyl moieties and include Cren and Cren'. Surface concentrations of these lipids are ~15 μg g^{-1} sed. in cores 1 to 3 (residing within the microbial mat) and 11 μg g^{-1} sed. for core 4 (Table S2). Also similar to the CLs, the archaeal IPL concentrations decrease down core and are closely coupled to increasing 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 persist down core with a consistent lipid depletion that reaches its lowest concentration of 5.22 μg g^{-1} 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^{-1} 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 <2 μg g^{-1} sed.) and their structural diversities negligibly affect 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 contributions of select GDGT compounds. 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 slopes for the various lipid pairs also indicates near-equal depletion rates, with vertical offsets between pairs marking different initial starting abundances of the compared lipid. 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 instead 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 S2; Table S3) using a first-order kinetic model:

$$C_t = C_i \cdot e^{-k't} \quad (1)$$

in which C_t and C_i are concentration at time (t) and the initial concentration, respectively (e.g. Schouten et al., 2010). Rearranging Eq. 1, the k' were calculated as

$$k' = (-\ln[C_t / C_i])/t \quad (2)$$

From these data, it is evident that the down core concentrations of each lipid decrease at equivalent rates (i.e. they have the same slopes for their rates of decay $s^2 = 0.2$). the exception to this is core 2, which independent of two outliers has different decay paths for GDGT-3 and GDGT-5. This is consistent with the TEX_{86} *i*GDGT lipid classes largely being removed from the sediment lipid pool in a non-selective manner.

Based on these results, the TEX_{86}, ring index (RI), and methane index (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 themselves significantly impact archaeal lipid paleoclimate proxy reconstructions.

Apart from paleoclimate reconstructions, archaeal lipid CLs are sometimes used to resolve aspects of localized biogeochemical cycles within sediments. To this end, the location and degree of anaerobic oxidation of methane (AOM) is determined by methane and archaeal lipid carbon isotope measures (e.g. Boetius et al., 2000; Schouten et al., 2003; Stadnitskaia et al., 2008; Biddle et al., 2012) as well as by the proportional abundances of core GDGTs (*c*GDGTs) in the form of the MI (Zhang et al., 2011; Carr et al., 2018; Petrick et al., 2019). With respect to the latter, the MI proxy is used to differentiate regions of normal marine (with values between 0–0.3) and active AOM conditions in and around cold seeps (where values >0.5–1 are reported for gas hydrate impacted sediments and subsurface environments with high AOM levels). To our knowledge, the use of this proxy for hydrothermal vent systems has not been thoroughly investigated even though this microbial process has been well documented at Guaymas Basin. For example, highly ^{13}C-depleted CLs reaching up to -70‰ in hydrothermal vent sediments with porewater temperatures as high as 95 °C indicates thermophilic archaea actively engaging in AOM (Schouten et al., 2003). Biddle et al. (2012) through the detection of relevant archaeal communities by 16S RNA in conjunction with highly depleted methane carbon isotope values determined active AOM spanning 35 to 90 °C porewater conditions. AOM is not likely to be the dominant form of carbon and sulfur metabolism as it generally accounts for less than 5% of sulfate reduction (Kallmeyer and Boetius, 2004). When applying the MI to the Cathedral Hill push core transect survey low values (ranging from 0.2–0.38; Table 1) are recorded with no correspondence to thermal controls across the vent transect (Figure 4). Although, it could be considered that the low values arise from a lack of AOM within these sediments the low MI values are consistent with a high upper water column *i*GDGTs loading as estimated by Bentley et al. (2022).

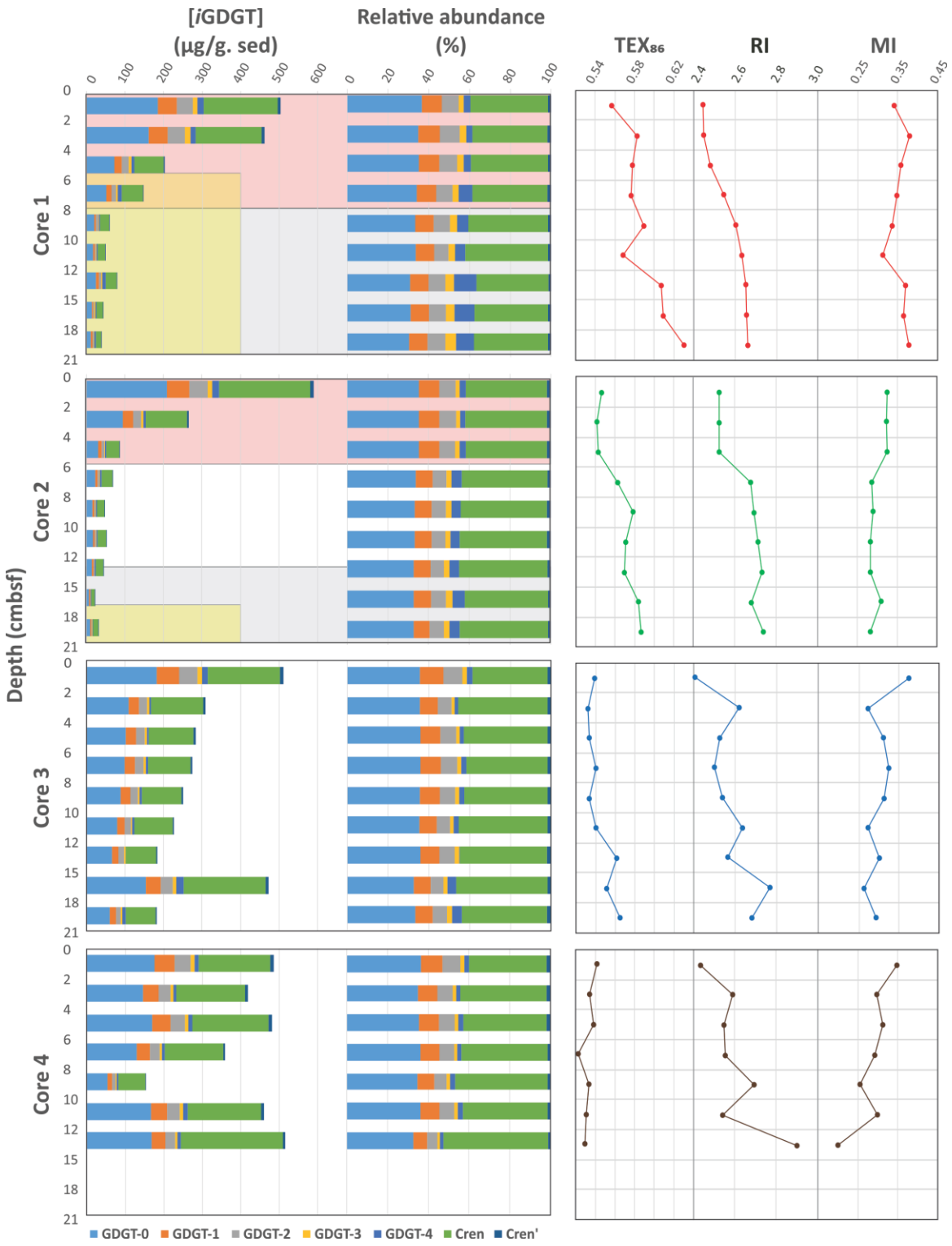

FIGURE 2. Down core profiles of the Cathedral Hill core *i*GDGTs absolute and relative lipid abundances and their generated *i*GDGT proxies: TEX_{86}, RI, and MI. Pink regions indicate transect intervals within zones of active GDGT lipid heterotrophy (Bentley et al., 2022). Grey regions mark regions where porewater temperatures exceed 123 °C marking a zone beyond the known upper thermal limit of life (Kashefi and Lovley, 2003). Yellow fields indicate regions where oil generation and hydrocarbon degradation have been noted to occur (Dalzell et al., 2021).

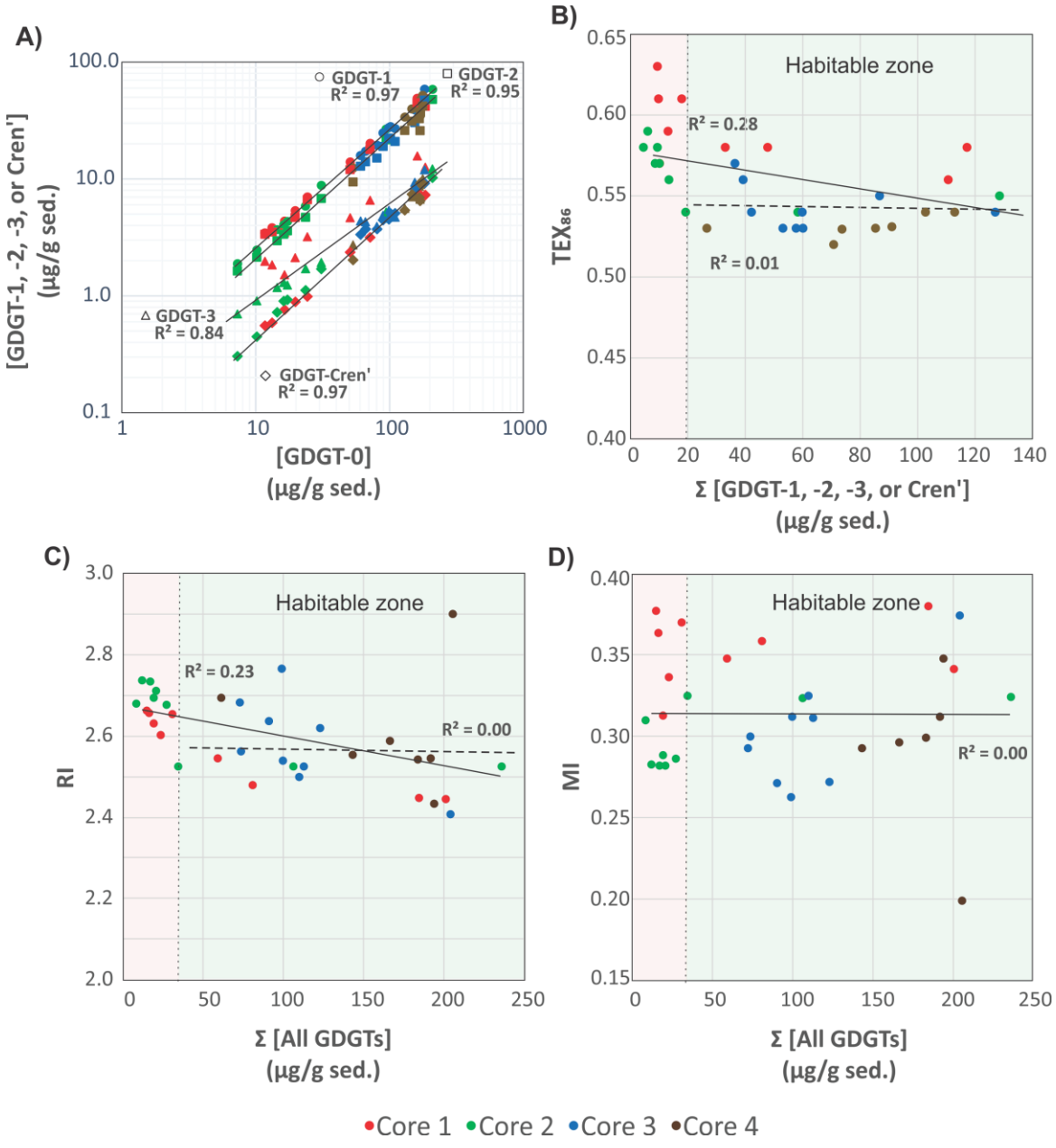

FIGURE 3. A) Comparison of TEX_{86} lipid concentrations GDGT-1 (circles), -2 (squares), -3 (triangles), and Cren' (diamonds) relative to the GDGT-0. Comparison of B) TEX_{86}, C) RI, and D) MI proxy values relative to summed *i*GDGTs abundances of the Cathedral Hill transect cores. Light green and pink 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.

3.2. TEX_{86} and reconstructed SSTs

McClymont et al. (2012) reported a GDGT-based reconstructed annual SSTs of 16–18 °C from particulate organic matter collected in ambient sediment traps in the Guaymas Basin during an annual cycle from 1996–1997. The reconstructed temperatures followed 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 produced by the closely co-varying $U^{k\prime}_{37}$ paleoclimate proxy, and satellite measured estimates that jointly estimated 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., 2022). 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., 2022). 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. corresponding to the depth of the cores. To a slightly lesser degree, the core top (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^{H}_{86} 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 with values spanning from 0.53 to 0.63 (Table 1) 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; marking the non-habitable zone) where TEX_{86} values span 0.57–0.63 (Table 1; Fig 4A) corresponding to a TEX^{H}_{86} reconstructed SST change of 3.1 °C marking a range from 21.8 to 24.9 °C (Table 1). The fundamental driver for the proxy's is likely influenced by the archaeal community composition that is responding to their 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 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 they are also more long-lived than what is produced from a laboratory experiment. 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 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. This same was also observed in the Guaymas Basin by Schouten et al. (2003) who reported an increase in the RI of core lipid GDGTs with in situ temperature. As such, a significant

proportion of the measured *i*GDGTs likely emanates from archaeal communities living in the shallow sediments of Cathedral Hill. As such, the lipid cyclization pattern may reflect stratigraphically discrete thermophilic to hyperthermophilic communities that are selectively adapted to more extreme temperature conditions (see Bentley et al., 2022 for further discussion on the lipid-based taxonomic make-up of the vent site).

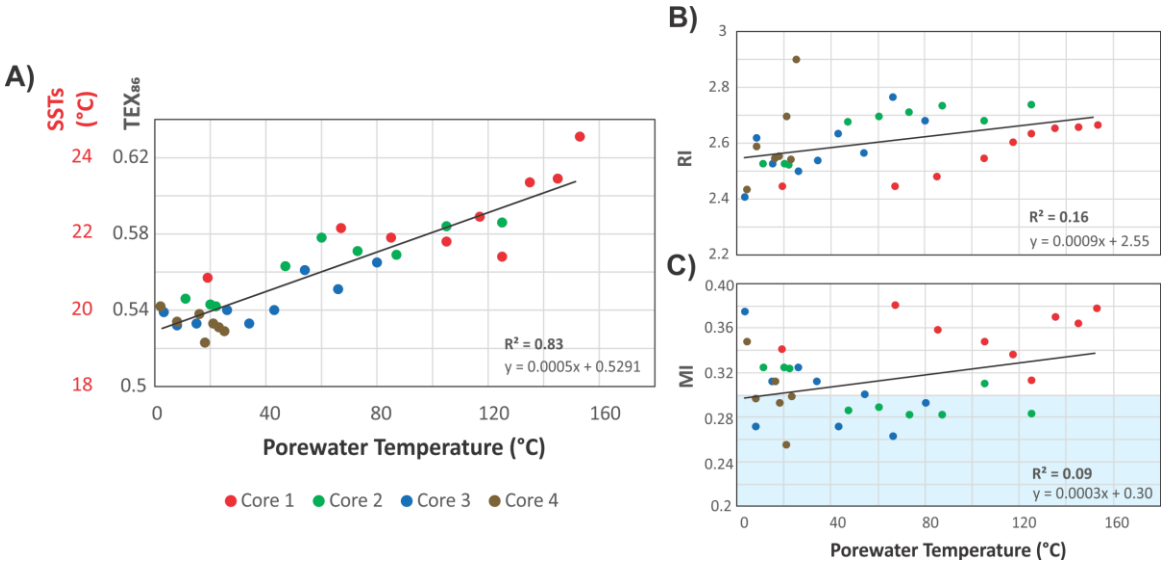

FIGURE 4. Cross plots of A) TEX_{86}, B) RI, and C) MI, *i*GDGT proxies versus porewater temperature. TEX_{86}^{H}reconstructed MASSTs are based on Kim et al. (2010). Blue field indicates MI values for normal marine conditions (Zang et al., 2011).

3.3. Lipid signal sourcing

To evaluate the sources of measured archaeal lipids, CL and $_{IPL}TEX_{86}$ (the ratio applied to IPLs that contain equivalent core lipids) indices were compared as signal responses from their respective pools of living and dead cellular debris (Figure 5). For cores 1, 2, and 3 the 1G-*i*GDGT $_{IPL}TEX_{86}$ measures are positively 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 be largely influenced by *in situ* porewater temperatures as well as may by the archaeal community ecology of the vent system. 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 $_{IPL}TEX_{86}$ is not correlated to their summed TEX_{86} lipid abundances (Figure 5B). Such a condition is largely 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 mix 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 CLs 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.

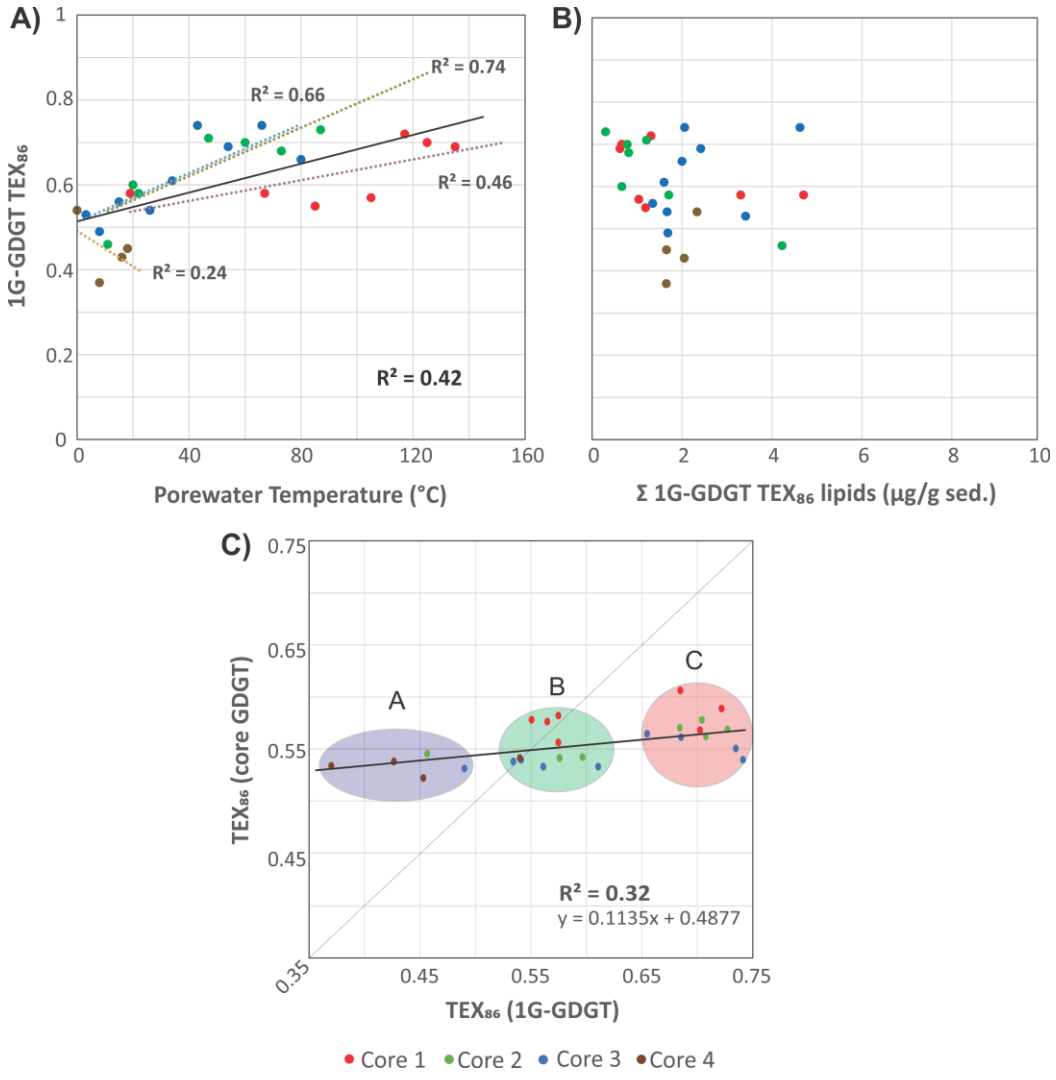

FIGURE 5. Cross plots of 1G-*i*GDGTs $_{IPL}TEX_{86}$ versus (A) porewater temperatures and (B) the concentration of 1G-*i*GDGTs in the sediments. C) TEX_{86} proxy of core GDGTs vs 1G-GDGTs. Clusters A–C may represent different archeal communities that are providing varying inputs of *i*GDGT to the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

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 the deeper 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 collectively also potentially further modified by diagenetic influences in the ocean bottom sediments. Over the cumulative sediment burial period and in consideration of the 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 by 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:

$$ {}_{M}TEX_{86} = \frac{a_{SS}TEX_{86} + b_{WC}TEX_{86} + c(d_{0\text{-}n})_{Sed}TEX_{86}}{\varphi + K + \theta} \quad (3) $$

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 $_{SS}TEX_{86}$:

$$ {}_{SS}TEX_{86} = \frac{{}_{M}TEX_{86}(\varphi + K + \theta)}{a} - \frac{b_{WC}TEX_{86} + c(d_{0\text{-}n})_{Sed}TEX_{86}}{a} \quad (4) $$

In this regard, a portion of the archaeal community from the upper water column, presumably initially sourced of IPLs, and an additional community inhabiting the ocean floor sediments were assumed to eventually die with their respective IPLs gradually hydrolyze, joining the CL pool where they further contribute to the observed $_{M}TEX_{86}$ value. For this study, no data was collected to calculate $b_{WC}TEX_{86}$ and its potential impact on $_{M}TEX_{86}$ cannot be further considered in this study. 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 (Lengger et al., 2012; Xie et al., 2013) that a component of this lipid source was already mixed with the $_{Sed}TEX_{86}$ contribution. For this study, $_{Sed}TEX_{86}$ is an $_{IPL}TEX_{86}$ ratio based on detected 1G-GDGT-1, -2, -3, Cren' and 2G-GDGT-1, -2, as present in the original paleoclimate proxy (Table 1; Figure 6). Testing the removal of 2G-GDGTs lipids, which have a low absolute concentration (<2 μg g^{-1} sed.) and shallow stratigraphic zones of occurrence (section 3.1; Table S2), yielded a negligible <1 °C change in the summed average reconstructed SST.

The $c(d_{0\text{-}n})$ measured scaling parameter was calculated as

$$ c(d_{0\text{-}n}) = \sum_{i=0}^{n} \left(\frac{[\text{GDGTs}_{IPL\text{-}TEX_{86}\ \text{lipids}}]_{n}}{[\text{GDGTs}_{CL\text{-}TEX_{86}\ \text{lipids}}]_{0\text{-}2cm}} \right) \quad 5) $$

using the summed concentrations of 1G- and 2G-GDGTs that have the potential to become converted to *c*GDGTs by progressive burial diagenesis and $d_{0\text{-}n}$ marking the range of sampled sediment depths, with 0 being the 0-2cmbsf core top and *n* the deepest point of sediment burial. These intervals are divided by the water column input of TEX_{86} lipids ($[\text{GDGTs}_{CL\text{-}TEX86\ \text{lipids}}]_{0\text{-}2cm}$) estimated to be 120 μg g^{-1} sed. based on their average measured concentration across the four-core transect. The function assumes the surface sediment does not hydrolyze its IPL-GDGTs to CLs (Table 2). When applied to Eq. 4 and further excluding φ, *K*, and θ, the $_{SS+WC}TEX_{86}^{H}$ reconstructed SSTs average 19.68 ±0.79 °C (Table 2; Figure 6A) with the total samples having an unchanging depth profile that mirrors the range of values measured in the ambient sediments of core 4 (Figure 2).

The selective lipid removal by diagenetic 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. Although the loss of GDGTs to protokerogen formation

could potentially impact the ratio, it was shown to be a negligible sink for the lipids (Bentley et al., 2022). As such, the *K* parameter in Eqs. 3 and 4 was therefore assigned a 0 value. Due to 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). The degradation rates of each TEX_{86} lipid were independently measured for the four push cores (Eq. 2; Fig. S2). 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 treated as grouped parameters. 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. $m_{logk'}$) from the TEX_{86} lipids (Figure S2; Table S4 from Eq. 2) were calculated. For the Cathedral Hill transect, the calculated $m_{logk'}$ s^2 is 0.20, which is due to accelerated degradation rates for higher ring lipids, GDGT-3 and Cren', in samples from cores 1 and 2, where high vent temperatures resulted in hydrocarbon generation of the sediments (Dalzell et al., 2021). A weighing function for the degree of lipid class selectivity during turnover is proposed:

$$\varphi+\theta = 1/_{M}TEX_{86}^{0.2} \quad (6)$$

When applied to Eq. 4, the corrected data series produces an average transect $_{SS}+_{WC}TEX_{86}^{H}$ reconstructed SST of 23.66 ±0.59 °C with a near-zero partial least squares regression slope (Table 2; Figure 6B). As these modeled values are within the 23–24 °C obtained for the 21-year (1982–2004) satellite-derived MASST data for the Guaymas Basin region (Herrera-Cervantes et al., 2007). Based on these calculations, nearly all $_{M}TEX_{86}$ attenuation can be attributed to sediment microbial overprinting coupled to diagenetic and catagentic loss of lipids consistent with prior observations at Guaymas Basin (Schouten et al., 2003; Zhang et al., 2011). The high degree of influence this has on the TEX_{86} proxy is striking given that the upper water flux of GDGTs at Cathedral Hill is estimated to represents up to 93% of the total intact polar and core GDGT lipid pool within these sediments. In this regard, this study demonstrates the benthic microbial community can influence TEX_{86} measurements.

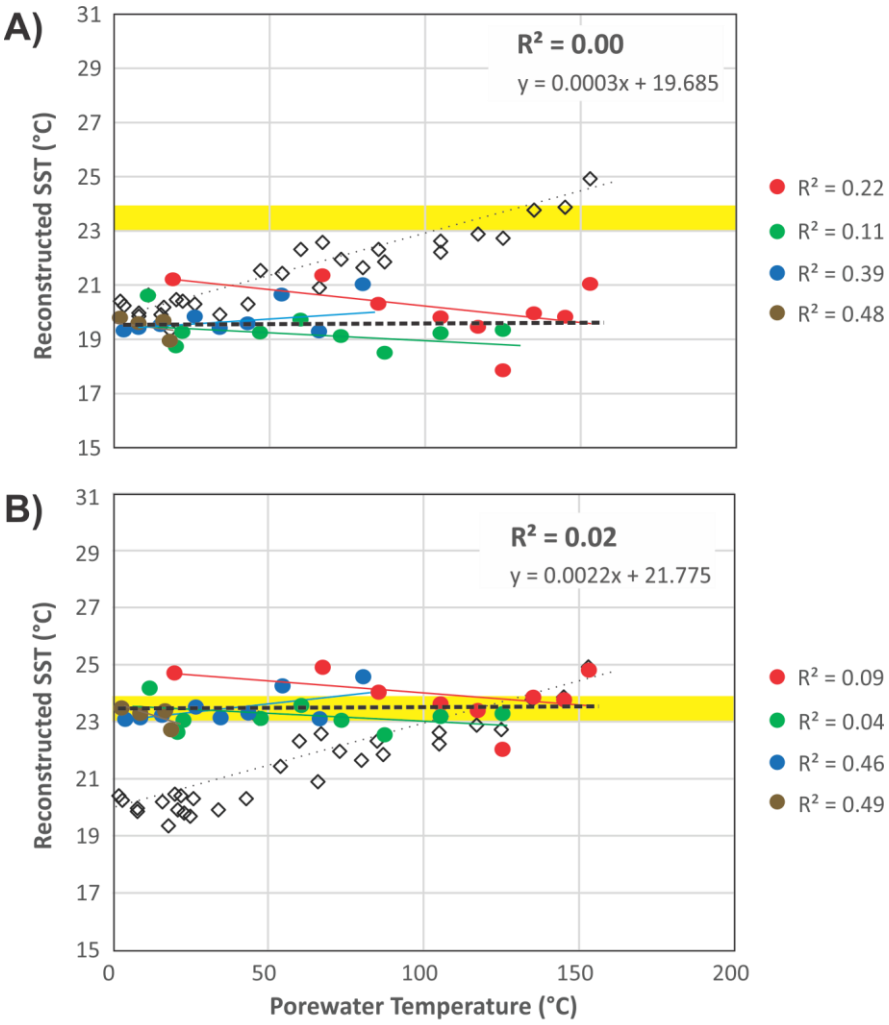

FIGURE 6. Reconstructed combined $_{SS}TEX_{86}$ and SSTs $_{WC}TEX_{86}$from Eq. 4 (A) with and (B) without φ, *K*, and θ scaling parameters compared to measured porewater temperatures. Red, green, blue, and brown circles indicate recorded values from cores 1, 2, 3, and 4, respectively. $_{M}TEX_{86}$ values are plotted for reference (open black diamonds). Yellow field is the 23–24 °C range observed for the 21-year (1982–2004) satellite-derived MASST data (Herrera-Cervantes et al., 2007).

606 **Table 2.** Reconstructed sea surface temperatures.
607

Sample	Depth (cmbsf)	Porewater Temp. (°C)	*t* Time (yrs.)	$_{M}TEX_{86}$ (Measured *i*GDGT TEX_{86})	TEX_{86}^{H} Reconstructed SST (°C)	TEX_{86} 1G- & 2G-GDGT IPLs (μg g^{-1})	Cumulative 1G- & 2G-GDGTs Loading with Depth (μg g^{-1})	$_{Sed}TEX_{86}$ (i.e. 1G- & 2G-GDGT $_{IPL}TEX_{86}$)	$c(d_{0\text{-}n})$ Cumulative Weighted IPL Loading (Eq. 5)
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	0.49	0.00
Core 2 (2-4cm)	3	22	20	0.54	20.4	1.80	4.33	0.57	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	0.73	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
ore 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	0.56	0.03
Core 3 (2-4cm)	3	8	20	0.53	19.9	1.79	3.51	0.51	0.01
Core 3 (4-6cm)	5	15	30	0.53	19.9	1.45	5.30	0.57	0.01
Core 3 (6-8cm)	7	26	40	0.54	20.3	1.77	6.74	0.55	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	0.71	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	0.73	0.04
Core3 (18-21cm)	20	80	90	0.57	21.6	2.10	19.61	0.65	0.02
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	0.44	0.01
Core 4 (4-6cm)	5	16	30	0.54	20.2	2.15	4.18	0.49	0.02

Core 4 (6-8cm)	7	18	40	0.52	19.3	1.76	6.34	0.47	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**				
Cumulative Avg.					**19.68**				
Cumulative Std. Dev.					**0.79**				

* Marks inherited values from the above sediment horizon.

Table 2. Reconstructed sea surface temperatures (continued).

Sample	Eq. 4 excluding φ+θ+*K*			Eq. 4 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. 6) (where s^2 = 0.20; Table S4)	$_{SS+WC}TEX_{86}$	$_{SS+WC}TEX_{86}^{H}$ Reconstructed SST (°C) (after Kim et al., 2010)
Core 1 (0-2cm)	0.56	-0.25	21.2	1.12	0.63	24.7
Core 1 (2-4cm)	0.56	-0.25	21.4	1.12	0.63	24.9
Core 1 (4-6cm)	0.54	-0.27	20.3	1.13	0.62	24.2
Core 1 (6-8cm)	0.53	-0.27	19.8	1.13	0.61	23.9
Core 1 (8-10cm)	0.52	-0.28	19.5	1.14	0.61	23.7
Core 1 (10-12cm)	0.50	-0.30	17.9	1.15	0.58	22.6
Core 1 (12-15cm)	0.53	-0.27	20.0	1.13	0.62	24.2
Core 1 (15-18cm)	0.53	-0.27	19.8	1.13	0.61	24.1
Core 1 (18-21cm)	0.55	-0.26	21.0	1.13	0.63	25.0
Avg.	**0.54**	**-0.27**	**20.10**	**1.13**	**0.61**	**24.14**
Std. Dev.	**0.02**	**0.02**	**1.08**	**0.01**	**0.02**	**0.75**
Core 2 (0-2cm)	0.55	-0.26	20.6	1.13	0.62	24.2
Core 2 (2-4cm)	0.52	-0.28	19.2	1.14	0.60	23.3
Core 2 (4-6cm)	0.51	-0.29	18.7	1.14	0.59	22.9
Core 2 (6-8cm)	0.52	-0.28	19.3	1.14	0.60	23.4
Core 2 (8-10cm)	0.53	-0.28	19.7	1.14	0.61	23.8
Core 2 (10-12cm)	0.52	-0.28	19.1	1.14	0.60	23.4
Core 2 (12-15cm)	0.51	-0.29	18.5	1.14	0.59	23.0
Core 2 (15-18cm)	0.52	-0.28	19.2	1.14	0.60	23.5
Core 2 (18-21cm)	0.52	-0.28	19.3	1.14	0.60	23.6
Avg.	**0.52**	**-0.28**	**19.32**	**1.14**	**0.60**	**23.47**
Std. Dev.	**0.01**	**0.01**	**0.60**	**0.00**	**0.01**	**0.40**
Core 3 (0-2cm)	0.52	-0.28	19.4	1.14	0.60	23.3
Core 3 (2-4cm)	0.52	-0.28	19.4	1.14	0.60	23.3
Core 3 (4-6cm)	0.53	-0.28	19.5	1.14	0.60	23.4
Core 3 (6-8cm)	0.53	-0.27	19.9	1.13	0.60	23.6
Core 3 (8-10cm)	0.52	-0.28	19.4	1.14	0.60	23.3
Core 3 (10-12cm)	0.53	-0.28	19.6	1.14	0.60	23.5
Core 3 (12-15cm)	0.55	-0.26	20.7	1.13	0.62	24.3
Core 3 (15-18cm)	0.52	-0.28	19.3	1.14	0.60	23.4
Core3 (18-21cm)	0.55	-0.26	21.0	1.13	0.62	24.6
Avg.	**0.53**	**-0.27**	**19.79**	**1.14**	**0.60**	**23.64**
Std. Dev.	**0.01**	**0.01**	**0.62**	**0.00**	**0.01**	**0.49**
Core 4 (0-2cm)	0.53	-0.27	19.8	1.13	0.60	23.6
Core 4 (2-4cm)	0.53	-0.28	19.7	1.14	0.60	23.4

Core 4 (4-6cm)	0.53	-0.28	19.8	1.14	0.60	23.5
Core 4 (6-8cm)	0.52	-0.29	19.0	1.14	0.59	22.9
Core 4 (8-10cm)	-	-	-	-	-	-
Core 4 (10-12cm)	-	-	-	-	-	-
Core 4 (12-15cm)	-	-	-	-	-	-
Avg.	**0.53**	**-0.28**	**19.51**	**1.07**	**0.60**	**23.38**
Std. Dev.	**0.01**	**0.01**	**0.38**	**0.00**	**0.01**	**0.31**
Cumulative Avg.			**19.68**			**23.66**
Cumulative Std. Dev.			**0.79**			**0.59**

4. Conclusions

In this study, we demonstrate a pronounce overprint of *c*GDGTs sourced from the ocean floor sedimentary archaeal community at the Cathedral Hill vent site in Guaymas Basin. The overprint is marked by lipids with more cyclized ring moieties marking an adaptive response by archaea to rigidify the cellular membranes against localized heat stress. This in turn has resulted in the commonly used TEX_{86} paleoclimate proxy to partially record advecting porewaters temperatures. As the vast majority of *c*GDGTs in these sediments is sourced from the overlying water column, the impact on the TEX_{86} ratio is further the product of rapid lipid turnover rates and diagenetic and catagenetic alteration processes potentially unique to the hydrothermal system. Together, these factors 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. To untangle the impact of these coupled drivers on the TEX_{86} proxy, we further present a method to correct the overprints by both the water column and subsurface archaeal community 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 modern 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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