Mechanistic Insights Into Molecular Proxies Through Comparison of Subannually Resolved Sedimentary Records With Instrumental Water Column Data in the Santa Barbara Basin, Southern California

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Abstract

Lipid biomarkers archived in marine sediments include widely applied proxies to reconstruct sea surface temperature (SST). Two prominent groups of SST sensitive biomarkers are long-chain alkenones from haptophyte algae and glycerol dibiphytanyl glycerol tetraethers (GDGTs) from planktonic Thaumarchaeota. The corresponding proxies, UKT37 and TEX86, respectively, are strongly correlated with mean annual SST. However, culture experiments suggest that other factors such as nutrients could also influence the proxy signals. We created monthly resolved records of molecular SST proxies via mass spectrometry imaging at 200-μm resolution in varved sediments from Santa Barbara Basin deposited between 1984 and 2009. Direct comparison to coeval water column data determined at seasonal resolution allows new mechanistic insights into environmental parameters influencing proxy signal formation. The UKT37 responds sensitively to SST variations, while also being influenced by seasonal variations in nutrient concentrations. Surface water nitrate concentrations above or below ~2 μmol/L are associated with UKT37 values that overestimate or underestimate actual SST, respectively. Distributions of the two major GDGTs, expressed as the Crenarchaeol-Caldarchaeol-Tetraether index (CCaT), are highly similar to those of the minor cycloalkylated compounds GDGT-1 to GDGT-3, presented as the corresponding ring index. The CCaT is correlated with subsurface chemical properties, which are controlled by interannual variations in upwelling intensity linked to dynamics of the California Current System. This relationship is attributed to the impact of nutrients on thaumarchaeal growth rates and GDGT cyclization. The coupling of CCaT to SST was weak but enhanced for temperatures averaged across the upper 100 m of the water column.

1. Introduction

Lipid biomarkers are valuable tools for extracting paleoenvironmental information from sedimentary archives. Originating from lipid membranes of microorganisms that once inhabited the water column, they provide information on environmental properties such as temperature within their biological producers’ habitats. A prominent example is long-chain alkenones from marine haptophytes (Brassell et al., 1986); the degree of unsaturation of these compounds is dependent on the ambient temperature encountered in the algal habitat (Pralh et al., 1988), and the signal is faithfully recorded in marine sediments (Müller et al., 1998). Long-chain alkenones are consequently used to reconstruct sea surface temperatures (SST) using the UKT37 proxy (e.g., Castañeda et al., 2010; Kennedy & Brassell, 1992; Naafs et al., 2010). Another group of SST proxies is based on the relative distribution of the isoprenoidal glycerol dibiphytanyl glycerol tetraethers (GDGTs) from marine Thaumarchaeota (Schouten et al., 2002). This group includes the widely applied TEX86 (Schouten et al., 2002) and the Crenarchaeol-Caldarchaeol-Tetraether index (CCaT, Wörmer et al., 2014), a proxy based on the SST-sensitive ratio of the two major GDGTs, caldarchaeol (GDGT-0) and crenarchaeol (GDGT-5) (Schouten et al., 2002). GDGTs are ubiquitous in marine sediments and can be found in ancient sediments back to the mid-Cretaceous (Kuypers et al., 2001). Marine Thaumarchaeota increase cyclization in their GDGT membrane lipids to adapt to higher growth temperature (Wuchter et al., 2004). Evidence exists that factors other than temperature may additionally influence the signals recorded by the aforementioned SST proxies. This is evidenced, for example, in mismatches of reconstructed TEX86 SSTs...
with \textit{in situ} temperatures in suspended particulate matter (e.g., Basse et al., 2014; Hurley et al., 2018; Mollenhauer et al., 2015; Zhu et al., 2016). For example, ecological factors (Conte et al., 1998) and physiological responses to nutrients (Conte et al., 1998; Epstein et al., 1998; Prahl et al., 2003) and light stress (Conte et al., 1998; Prahl et al., 2003) have been suggested to also influence alkenone content and composition. Likewise, the sole dependency of GDGT cyclization on temperature has been challenged by culture experiments, which showed that the degree of cyclization is influenced by growth stage (Cobban et al., 2020; Elling et al., 2014), oxygen concentration (Cobban et al., 2020; Qin et al., 2015), taxonomic affiliation of the GDGT-producing Thaumarchaeon (Elling et al., 2015), and nutrient availability (Cobban et al., 2020; Evans et al., 2018; Hurley et al., 2016). In addition to the potential impact of thaumarchaeal ecology (Elling et al., 2015), the ecology of planktonic archaea in general may influence the GDGT signal exported to sediments. This is due to the possible contribution of GDGTs from a second archaeal clade, the Marine Group II Euryarchaeota (MG II), of which no cultured representatives exist to date. The evidence regarding a contribution of this planktonic archaeal group to the sedimentary GDGT record is controversial (Besseling et al., 2020; Lincoln et al., 2014; Ma et al., 2020; Zeng et al., 2019) so that an unambiguous assignment of the sedimentary GDGT signal to a predominant thaumarchaeal or mixed thaum- and euryarchaeal source is currently not possible without access to pure cultures of MG II representatives.

Exploring the proxy signal formation in marine sediments is further hampered by the minimum sample amount required for biomarker extraction. Depending on the sedimentation rate, the associated centimeter-sized samples lead to an averaging of the archived signal to several years up to centuries. Even in high sedimentation rate settings, this averaging results, for example, in an underrepresentation of strong El Niño events (Herbert et al., 1998; Kennedy & Brasell, 1992). Additionally, it cannot be determined whether a proxy signal in the sediment is seasonally biased or mirrors the yearly cycle. Recently, we introduced an extraction-free, mass spectrometry imaging (MSI)-based approach that increases the resolution of molecular proxy records to the $\mu$m-scale (Alfken et al., 2019; Wörmer et al., 2014, 2019). Applied to high-resolution sedimentary records, this approach has the potential to overcome the limitations of the conventional extraction-based proxy analysis and provide new insights into the fine-scale distribution of lipid biomarkers and related proxies.

Varved sediments of the Santa Barbara Basin (SBB), located offshore of Southern California, provide a unique record for high-resolution climate reconstruction (reviewed in Schimmelmann et al., 2016; Schimmelman & Lange, 1996). The suboxic conditions in the bottom waters in combination with a seasonally alternating high sedimentation rate favor the preservation of laminated sediments (Emery & Hülsemann, 1961; Soutar & Crill, 1977; Thunell et al., 1995). Oceanographic conditions in the SBB are strongly influenced by the California Current System (CCS) including the equatorward California Current, the poleward offshore California Undercurrent, extending north off Point Conception, and the inshore southern California Countercurrent (Figure 1a; Hendershott & Winant, 1996; Hickey, 1979). The seasonal upwelling intensity along the California Margin is influenced by interannual and decadal-scale variability related to El Niño-Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO, Mantua & Hare, 2002), and North Pacific Gyre Oscillation (NPGO, di Lorenzo et al., 2008). Upwelling intensity decreases during the positive (warm) PDO phases and El Niño events, whereas an increase in upwelling intensity and primary productivity between 38°N and 30°N is associated with the NPGO (di Lorenzo et al., 2008). Kennedy and Brassell (1992) showed that long-chain alkenones from haptophyte algae extracted from SBB sediment could be used to reveal annual oscillations in SST and warming associated with 20th century El Niño events. This study has remained one of the most highly resolved biomarker records. With respect to the utility of archaeal GDGTs, Huguet et al. (2007) found that TEX$_{86}$ based temperatures reconstructed from sediments and particulate organic matter from the SBB were substantially lower than actual SST in surface waters. They attributed this observation to the subsurface habitat of the proxy-signal producing Thaumarchaeota. Indeed, highest abundances of archaeal rRNA in the SBB have been detected in subsurface depth intervals (Massana et al., 1997) coinciding with the nitrite maximum (Murray et al., 1999). By applying MSI to varved sediment sections from SBB box core SPR0901-05BC (N34°16′56.496″, W120°2′20.436″, 888 m water depth, Figure 1a) we created $\Delta^{13}$C and CCAT records with approximately monthly resolution. These records were directly compared to a 25-year record from AD 1984–2009 of seasonally measured
instrumental water column data from the California Cooperative Oceanic Fisheries Investigation (CalCOFI, 2018) station 81.8 46.9 (Figure 1a). The comparison of these high-resolution proxy and instrumental data sets allowed us to (i) investigate small-scale differences between these two molecular proxy types; (ii) identify alternative oceanographic factors that shape the sedimentary proxy records; and (iii) evaluate the sensitivity of these molecular proxies to large-scale oceanic and atmospheric oscillations such as ENSO, PDO, or NPGO.

2. Methods

2.1. Sediment Samples and Instrumental Data

Santa Barbara box core SPR0901-05BC (N34°16′56.496″, W120°2′20.436″, 588 m water depth, Figure 1) was collected from the center of SBB. At the time of its subsampling, the 30-cm slab from the box core was about 40 cm in length and spanned AD 1900–2009. An X-ray photograph of the slab was taken to visualize the varves by their density differences. The age model of 05BC was implemented by identification of specific marker layers and additional varve counting, allowing for an accuracy of ±1 year for the data presented in this study (Schimmelmann & Lange, 1996) (supporting information Figure S1). To implement correlations between instrumental water column data and our MSI-based proxy results, the age model has been further refined using the minima of the water temperature profile from 0 to 30 m water depth as tie points.
to the corresponding minima in the $\delta^{13}C_P$ profile. The reference points have been defined within the accuracy of the age model ($\pm 1$ year) and are listed in Table S1.

The sediment slab was subsampled twice using double L-channels (LL-channel) to create two overlying intact sediment sections from the same position. One LL-channel was used for MSI and further subsampled into ~5-cm sections, frozen at ~80°C, freeze-dried, and prepared for μm-scale molecular imaging according to Alfken et al. (2019). This study focuses on the upper ~7.5 cm of the sediment slab corresponding to AD 1984–2009. This time period can be directly compared to seasonally measured instrumental water column characteristics such as temperature, nutrients, oxygen, and salinity from California Cooperative Oceanic Fisheries Investigation station 81.8 46.9 at the center of SBB (N34°16'29.64", W120°1'30", Figure 1a) (CalCOFI, 2018). Instrumental data cover the entire water column (Figure S3) with dominant spacing of 10 m for the upper 50 m of the water column, followed by a 25-m spacing until 150 m water depth, 50-m spacing down to 300 m, and data at 400 and 500 m water depth. Additional data exist for various depths irregularly distributed between the main intervals and down to 580 m. Only the years 1984 to 1985, and the first sampling in 1986 do not include data below 550 m water depth, and have the deepest data taken between 400 and 500 m water depth. To account for irregular data coverage and smaller sampling intervals in the surface water, values representative of defined water parcels were calculated by the sum of all integrals between available measurement depths, divided by the size of the water parcel. For comparison to molecular proxy records, ENSO is represented by the Niño 3.4 region (5°N–5°S, 120°–170°W), and the PDO data set used in this study was obtained from the Joint Institute for the Study of Atmosphere and Oceans (JISAO). Both time series are available from the U.S. National Oceanic and Atmospheric Administration (NOAA; https://www.esrl.noaa.gov/psd/gcos_wgsp/Timeseries/). The index for the NPGO (di Lorenzo et al., 2008) can be downloaded (http://www.o3d.org/npgo/).

2.2. Mass Spectrometry Imaging of Molecular Proxies

Mass Spectrometry Imaging (MSI) was performed with a 7T solarX XR FT-ICR-MS coupled to a MALDI source equipped with a Smartbeam II laser (Bruker Daltonik, Bremen, Germany). Following the protocol of Alfken et al. (2019), the sample was prepared by stabilizing the intact, freeze-dried 5-cm sediment pieces in a gelatin-based mixture (5% gelatin, 2% sodium carboxymethyl cellulose; Sigma Aldrich Chemie GmbH, Munich, Germany) and subsequently slicing sequential 60-μm thick sections with a cryomicrotome (Microm HM 505 E Cryostat, GMI, Ramsey, Minnesota, USA). The 60-μm slices were adhered onto indium tin oxide (ITO)-coated glass slides, and high-resolution data were produced by rastering with the laser across the sample in a defined rectangular area at a 200-μm resolution spot distance. Mass spectra for isoprenoidal GDGTs and alkenones were generated on individual slices with a 95% data reduction during acquisition in the fmsControl software program (Bruker Daltonik). To improve sensitivity, spectra were acquired in continuous accumulation of selected ions (CASI) mode with an isolation window of $m/z = 1,320 \pm 40$ for GDGTs and 550 ± 30 for alkenones. External mass calibration was performed in electrospray ionization mode with sodium trifluoroacetate (NaTFA), followed by internal lock mass calibration of single MSI spectra on the Na⁺ aduct of GDGT-5MS ($m/z 1,314.22636$) and the Na⁺ aduct of pheophorbide ($m/z 557.25231$). The term GDGT-5MS accounts for the $m/z$ value of all GDGTs with five double bond equivalents detected by FT-ICR-MS. For the ~7.5 cm (25 years) section analyzed in this work, about 14,000 single spectra were generated with a large laser focus at a raster width of 200 μm. Laser power, number of shots, and frequency were optimized for best signal intensities with final settings of 40%, 500 shots and 1,000 Hz, respectively, for GDGTs and 35%, 700 shots and 1,000 Hz, respectively, for alkenones.

The CCaT calculation followed the equation by Wörmer et al. (2014) with the modified nomenclature of GDGT-5MS for the reasons described above.

$$\text{CCaT} = \frac{\text{GDGT} - 5\text{MS}}{\text{GDGT} - 0 + \text{GDGT} - 5\text{MS}}$$ (1)

In order to capture compositional changes among the minor GDGTs with one, two, and three cyclopentane rings (GDGT-1, GDGT-2, and GDGT-3), we calculated the ring index, $R_{\text{GDGT-1-3}}$ (Equation 2) and the TEX$^{13}$S ratio (Equation S1; Kim et al., 2010). As quantities of GDGT-3 were minor, successful spectra were defined as spectra which include GDGT-2 and GDGT-1.
The alkenone-based $U_{37}^{K}$ index is based on the equation by Prahl and Wakeham (1987) with the SST transformation according to Prahl et al. (1988).

$$U_{37}^{K} = \frac{C_{37:2}}{C_{37:2} + C_{37:3}}$$

(3)

$$U_{37}^{K} = 0.034T + 0.039$$

(4)

Raw data produced by MSI of the first ~5 cm correspond to the proxy maps shown as proof of concept in Alfken et al. (2019) and Wörmer et al. (2019) for the implementation of new sample preparation protocols described in those method-oriented publications. Data processing has been advanced in the present study and resulted in slightly different downcore profiles. Before averaging spectra along each horizon to create a downcore profile at 200-μm resolution, the mapped areas were corrected for tilted laminae. The tilt correction was done by visual identification of single laminae in the X-ray photograph and selection of a minimum of four tie points per lamina. The inverse spatial 2-D transformation to horizontal laminae was done using tforminv in MATLAB 2016a (The MathWorks, Natick, USA). A detailed description can be found in Text S1.

2.3. Conventional Sediment Extraction and Lipid Extract Analysis

To compare our MSI-based proxy results to the traditional extraction-based approach, 12 sediments samples were taken from the second, subjacent LL-channel and extracted following the modified Bligh and Dyer protocol (Sturt et al., 2004; Wörmer et al., 2015). The freeze-dried and homogenized sediment samples were extracted by ultrasonication using a solvent mixture of methanol (MeOH), dichloromethane (DCM) and aqueous buffer (2:1:0.8 by volume). The first two steps were performed using a phosphate buffer (8.7 g/L KH$_2$PO$_4$, pH 7.4), followed by two extraction steps with a trichloroacetic buffer (50 g/L, pH 2). After each step, supernatants were transferred to a separation funnel and subsequently separated into the organic and aqueous phase by addition of DCM and deionized MilliQ water. The organic phase was collected, and the water phase washed three more times with DCM, transferring the organic phase after each step. The pooled organic phase was washed three times with deionized MilliQ water. The total lipid extract (TLE) was evaporated under a stream of nitrogen and stored at $-20^\circ$C.

Isoprenoidal GDGTs and alkenones were analyzed according to Becker et al. (2015) using a Dionex Ultimate 3000RS UHPLC system coupled to a maXis Ultra-High Resolution quadrupole time-of-flight tandem mass spectrometer (qToF-MS; Bruker Daltonik, Bremen, Germany) equipped with an APCI-II ion source operating in positive mode (HPLC/APCI-MS). Chromatographic separation was achieved with two coupled Acquity BEH Amide columns (2.1 x 150 mm; 1.7 μm; Waters, Eschborn, Germany). Target compounds were identified based on exact m/z and characteristic retention times.

Given the chromatographic separation of the isomer of crenarchaeol (here referred to as GDGT-5′), the TEX$_{86}$ of the extracted sediment samples was calculated according to Schouten et al. (2002).

$$\text{TEX}_{86} = \frac{\text{GDGT-2 + GDGT-3 + GDGT-5'}}{\text{GDGT-1 + GDGT-2 + GDGT-3 + GDGT-5'}}$$

(5)

2.4. Statistical Analysis

To implement correlations between instrumental water column data and our MSI-based proxy results, all data, MSI and instrumental, were linearly interpolated to the same resolution of 0.25 years. As the only exception, phosphate reveals a data gap in May 1988, which, in the course of linear interpolation, results in two data gaps for this parameter in this year. Since normality is not present throughout the...
instrumental data, the correlations between proxy and instrumental data are based on the nonparametric Spearman’s rank correlations ($r_s$). Comparisons within the generated proxy data, as well as between surface water temperature and UK$^{37}$-based SST, are indicated by linear correlations and the associated coefficient of determination ($r^2$).

3. Results and Discussion

Two molecular proxy systems sensitive to marine SST are amenable to MSI: the alkenone-based UK$^{37}$ and the GDGT-based CCaT. The conventionally used TEX$^{86}$ cannot be determined because the crenarchaeol isomer used in its calculation has the same exact mass as crenarchaeol and is therefore not separable (cf. Wörmer et al., 2014). Due to the more widespread archaeal sources of GDGT-0 relative to its cycloalkylated analogues, the CCaT may be biased by post depositional production of this compound. In order to assess such contributions from sedimentary archaea, we compared the CCaT with ratios capturing distributional changes of the minor GDGTs, that is, compounds included in the TEX$^{86}$. These ratios are the RI$_{GDGT1-3}$ (Figure 3a; Figure S5b) and the TEX$^{86}_{58}$ (Figure S5c). Apart from the fact that the TEX$^{86}_{58}$ is only applicable for cold waters (<15°C; Kim et al., 2010), the CCaT provides superior analytical data and thus enables a higher temporal resolution as it is based on the two major compounds, GDGT-0 and GDGT-5.

3.1. Conventional and Laser-Based Determination of Molecular Proxies

Overall, the MSI-based results show a strong consistency with the traditional extraction-based results (Figure 2). The UK$^{37}$ and CCaT records reveal similar trends with matching absolute values in both techniques. This comparison also shows that MSI as well as the extraction-based CCaT data closely match the widely used TEX$^{86}$ proxy data (Figure 2b), with consistent converted temperatures from 9.5 to 14.9°C and 10.5 to 13.6°C, respectively. CCaT-based temperatures were calculated according to Wörmer et al. (2014) (Equation S3) and TEX$^{86}$-based temperatures are based on the calibration by Kim et al. (2008) (Equation S4). Dotted rectangles indicate the corresponding depth range averaged for one sample used for extraction and horizontal lines display the corresponding mean value of the MSI data.

Figure 2. Comparison of MSI-based and conventional extraction-based data of UK$^{37}$ (a) and CCaT (b). The CCaT was additionally compared to the TEX$^{86}$ (blue circles in (b)). The extraction-based values of CCaT and TEX$^{86}$ show a linear correlation ($r^2 = 0.492$, Figure S6). The corresponding temperatures of CCaT and TEX$^{86}$ range from 9.5 to 14.9°C and 10.5 to 13.6°C, respectively. CCaT-based temperatures were calculated according to Wörmer et al. (2014) (Equation S3) and TEX$^{86}$-based temperatures are based on the calibration by Kim et al. (2008) (Equation S4). Dotted rectangles indicate the corresponding depth range averaged for one sample used for extraction and horizontal lines display the corresponding mean value of the MSI data.
to the averaging of signals inherent to conventional analysis (see below) rather than to poor analytical accuracy. In fact, we have previously demonstrated with homogenized sediment samples that MSI analysis captures the CCaT ratio determined by extraction and LC–MS analysis with an accuracy of 0.012 CCaT units (standard error of regression; Wörmer et al., 2014). Corresponding data for the UK037 are not yet available, but we have no reason to assume that the analytical quality would be lower than for the CCaT.

When comparing the MSI data with conventionally determined data, one needs to consider that variations in productivity and fluxes of the molecules included in the discussed proxy ratios will impact these two data sets differently. By averaging several millimeters of sediment into one sample the proxy ratio is biased by the period of highest flux into the sediment. MSI analysis of varved SBB sediments, on the other hand, is only averaging the signals in the ~200 μm thick layers, corresponding to an average period of sedimentation of less than a month, and is therefore only minimally impacted by intra-annual variation in fluxes of proxy molecules. Due to the high likelihood of temporal variations of proxy signal fluxes, we do not expect the average of a series of MSI observations to coincide with the extraction-based value of a corresponding large-volume sample. Consequently, the observed deviations between these parameters illustrated in Figure 2 cannot be unambiguously attributed to either the analytical uncertainty of both techniques or a flux-related bias inherent to the conventional technique. The overall consistency of both UK037 and CCaT values from both techniques supports the notion that the cyclic variations of MSI profiles are indeed recording natural variations of these parameters.

Figure 3. Records of molecular SST proxies in comparison to instrumental measurements. Monthly resolved CCaT and quarterly resolved RI_{GDGT-1-3} records (a) and UK037 record with derived SST (b) compared to seasonally measured water temperature integrated for 0 to 30 m water depth from the California Cooperative Oceanic Fisheries Investigation (CalCOFI, 2018) station 81.8 46.9 (c) from AD 1984 to 2009. Thin lines in (a) and (b) show the standard error of averaged values along individual layers. To enable robust comparison between CCaT and RI_{GDGT-1-3} ($r^2 = 0.37$, Figure S5b), the RI_{GDGT-1-3} was reduced to a quarterly resolution (i.e., 0.25 year) to collect a sufficient number of successful spectra. Horizontal gray lines in (b) and (c) show the 25-year means of the temperature for the UK037 SST and the instrumental temperature, that is, 14.4 and 14.1°C, respectively.
The compound GDGT-0 was originally excluded from the TEX$_{86}$ and related SST proxies due to concerns related to its diverse archaeal sources such as in situ production from methanogenic archaea (Schouten et al., 2002), although similar arguments could be made for the minor cycloalkylated compounds GDGT-1 to GDGT-3, which can be contributed to methane-oxidizing archaea (Liu et al., 2011; Zhang et al., 2011). In the case of the SBB sediments, the good correlation of the CCaT with both the Rl$_{GDGT-3}$ (Figure 3a; Figure S5b, $r^2 = 0.37$) and the TEX$_{86}$ (Figure S5c, $r^2 = 0.47$), as well as the close correspondence of the extraction-based CCaT and TEX$_{86}$ (Figure 2c; Figure S6, $r^2 = 0.492$) suggests that in the studied interval both compound groups, the major and minor GDGTs, are largely derived from the same biological source, that is, planktonic archaea.

### 3.2. Different Responses of Alkenone-Versus Tetraether-Based Proxies to Seasonal SST Variation

The approximately monthly-resolved CCaT and $U_{37}^K$ records exhibit distinct patterns (Figures 3a and 3b), suggesting that these two proxies respond to different processes. Only the $U_{37}^K$ (Figure 3b) resembles the seasonal temperature profile derived from instrumental measurements and integrated for 0 to 30 m water depth (Figure 3c; cf. section 2 and Text S4 for calculation of spatial averages), thus showing an annual cyclicity for most parts of the record. As haptophyte production in SBB is mainly limited to the upper 30 m (Herbert et al., 1998), we used the measurements from this depth interval as reference. Converted into SST (Prahl et al., 1988), the reconstructed $U_{37}^K$ temperatures vary between 12.5 and 16.3°C — a narrower range compared to the instrumental data (10.4–20.0°C). The lower amplitude of our $U_{37}^K$ record could indicate a varying depth of haptophyte production. The chlorophyll a maximum can be found at an average water depth of 14.4 m but varies between 0 and 49 m. Assuming the alkenone export depth oscillates similarly, the corresponding temperature range at the chlorophyll a maximum would be 11.0 to 18.4°C, closer to the proxy record. Besides a variation in habitat depth, dissolved nutrient concentrations have been shown to influence the alkenone unsaturation index (Conte et al., 1998; Epstein et al., 1998; Prahl et al., 2003). Since nutrient concentrations in the haptophyte depth habitat vary with the seasonal upwelling, that is, higher nutrient concentrations during periods of upwelling and thus colder SST, the difference in instrumental water temperature and calculated SST may also reflect a physiological response to nutrient availability in SBB surface water. As this effect has been previously noted in culture studies (Conte et al., 1998; Epstein et al., 1998; Prahl et al., 2003), but not yet in the sedimentary record, we systematically investigated the impact of nutrients on the $U_{37}^K$ in the course of this study.

The comparison of the $U_{37}^K$ with the CCaT and the Rl$_{GDGT-3}$ (Figure 3) indicates that the $U_{37}^K$ records the yearly cycle and broadly captures the SST range of the top 30 m of the water column, while the archaeal lipid-based indices show patterns that mostly lack annual cyclicity and instead exhibit dominant multiannual cycles (Figures 3a and 3b).

### 3.3. Planktonic Archaeal Lipids Integrate Characteristics of the Entire Water Column

The main habitat of marine Thaumarchaeota and the corresponding export zone of isoprenoidal GDGTs are located close to the concentration maximum of nitrite, that is, the initial product of thaumarchaeal ammonium oxidation (Hurley et al., 2018; Massana et al., 1997; Murray et al., 1999). The poor relationship between variations of GDGT-based SST estimates and surface water temperature is thus not unexpected and has been described previously for the SBB (Huguet et al., 2007). Assuming that a vertically alternating planktonic archaeal habitat depth contributes to the signal recorded in the sediment, as suggested by Huguet et al. (2007), we examined relationships with the temperature of the depth interval extending from the nitrite maximum 50 m downward. Between 1984 and 2009, the nitrite maximum in the SBB varied between the surface and 73 m water depth. Even though CCaT-based SST estimates of 9.8 to 16.9°C are more similar to the water temperature at this depth range (9.4 to 16.1°C) than to surface waters, the CCaT profile and the water temperature at the depth range of the nitrite maximum are not correlated ($r_{s} = 0.088$, $p > 0.05$; Figure S4).

In order to identify drivers of the molecular proxy signal exported to the sediment, we examined CCaT and $U_{37}^K$ profiles for the time period AD 1984–2009 in relation to coeval seasonally measured temperature, salinity, oxygen, and nutrients in the water column at CalCOFI station 81.8 46.9. This period was chosen because it features the most complete data set with respect to temporal coverage and number of variables determined within the time span covered by our sediment core. To facilitate correlation analysis, various
water column characteristics were integrated for different depth intervals, and the age model was further refined by fixing the minima in the U$^{137}_{\text{C}}$ profile to the corresponding minima in the temperature profile averaged from 0 to 30 m water depth. Tie points were set within the range of the precision of the age model (±1 year) and are presented in the Table S1. The returned CCaT and U$^{137}_{\text{C}}$ records, as well as the instrumental data, were linearly interpolated with a quarterly (0.25 year) spacing. As the sampling depth of the bottom water is variable in the CalCOFI data set, the lower boundary of the water parcels including the deepest sampling points is referred to as BW (bottom water).

The combination of seasonal upwelling and its low-frequency interannual variability due to large-scale fluctuations in the California Current System (CCS) is visualized with the salinity, phosphate, and oxygen profiles of SBB waters integrated from 50 m to BW from AD 1984–2009 (Figure 4a). During years of intense upwelling, relatively nutrient-rich, saline, oxygen-depleted water reaches the surface. Years with reduced upwelling, such as the 1997/1998 El Niño have the opposite pattern (Figure 4a). Notably, the CCaT mirrors this pattern, with low values during periods of intense upwelling and vice versa (Figure 4). Since CCaT has a weaker correlation with temperature relative to the chemical parameters influenced by upwelling intensity, the CCaT pattern is probably not simply driven by the lower temperature of upwelled waters (Figure 5).

Systematic examination of the molecular proxies in relation to the upwelling-related properties salinity, oxygen, temperature, and nutrient concentrations across 14 distinct depth intervals of the water column (further details in Text S4) revealed that correlations of the CCaT profile with salinity and oxygen concentrations were strongest when integrated for the depth interval from 50 m to BW (Figures 4, 5, and Table S2). The CalCOFI data profiles (Figure S3) show that this depth interval reflects the water column below the photic zone. For the same depth interval, moderate negative correlations exist with phosphate and silicate, the two nutrients accumulating in the BW (Table S2). Even though planktonic archaeal biomarkers are used as SST proxies, only a weak correlation between surface water temperature (0–50 m) and CCaT was found ($r_s = 0.260$, $p < 0.05$, Figure 5). By including a larger water parcel, that is, the upper 100 m, the Spearman’s rank correlation coefficients slightly increase ($r_s = 0.265$, $p < 0.05$ for CCaT). Interestingly, in surface waters, the CCaT is most strongly correlated with nitrate and nitrite (Figure 5). This is consistent with the key role of Thaumarchaeota in nitrification and the previously demonstrated link between GDGT cyclization and nitrifying activity (Hurley et al., 2016).

Our correlation analysis of the CCaT to water column properties for various depth intervals (Figure 5) reveals the tendency of increasing correlative relationships with increasing thickness of the averaged
depth interval. The stronger correlations with increasing contribution of subsurface water are suggestive of two conceivable scenarios, whose relative importance cannot be determined on the basis of the available data: (i) Thaumarchaeota are known to inhabit the entire water column (Karner et al., 2001). However, subsurface depths beneath the photic zone are commonly viewed as hotspots for the export of thaumarchaeal lipids (Hurley et al., 2018; Massana et al., 1997; Murray et al., 1999) although there is evidence of export from deeper layers as well (Taylor et al., 2013). The basin topography of the SBB, with low-oxygen conditions below sill depth, may enhance upward export of thaumarchaeal lipids from deeper waters. (ii) Seasonal monitoring of the whole water column may more efficiently capture the changes driving proxy variability than data from a vertically constrained water mass, thus resulting in more significant correlations with the continuously exported signal.

3.4. Nutrients Influence Planktonic Archaeal and Haptophyte-Derived SST Proxies

Culture experiments reveal no systematic change in GDGT cyclization with salinity (Elling et al., 2015; Wuchter et al., 2004). However, it has been shown that oxygen limitation resulted in higher GDGT cyclization (Cobban et al., 2020; Qin et al., 2015). In this study we observe the opposite effect, decreasing cyclization with lower oxygen concentration. We therefore conclude that the inverse correlation of CCaT with salinity and the positive correlation with oxygen (Figures 4 and 5) are based on indirect relationships and that the GDGT signal exported to and preserved in the sediments is instead influenced by the supply of nutrients associated with the upwelled oxygen-depleted waters of elevated salinity.

The negative correlation of the CCaT with nutrients (Figures 4 and 5) is consistent with observations by Hurley et al. (2016) and Evans et al. (2018) who showed a dependency of GDGT cyclization on ammonia oxidation rate and ammonia supply, respectively. Ammonium concentrations are only available in the CalCOFI data set from 2008 onward, precluding an evaluation of its relationship with the CCaT, which is presumably largely based on lipids from thaumarchaeal ammonium oxidizers. While ammonium delivery from deeper to shallower waters to the surface via upwelling is not the major supply route, we expect strong coupling of the ammonium supply with upwelling intensity due to the stimulation of primary production and
remineralization of organic matter, which results in ammonium release. The positive correlation with the temperature of the upper 100‐m water depth shows that an unambiguous attribution to one driving factor is impossible as both temperature and nutrients are directly influenced by upwelling. Consequently, in the SBB, CCaT primarily records water column properties associated with varying upwelling intensity of subsurface waters (Figures 4 and 5).

In contrast to the CCaT, the $^{137}$Cs is strongly correlated with SST (Figures 3, 5, and Table S2). Besides temperature, strong to moderate negative correlations of $^{137}$Cs also exist with nutrient concentrations in surface water (Figure 5). The correlations with nutrients could either indicate an indirect effect, since the upwelling‐induced supply of nutrients in the surface water tracks the seasonal temperature signal, or a direct effect of nutrients on the $^{137}$Cs signal. A potential direct effect would be consistent with observations from batch cultures of *Emiliania huxleyi*, which revealed a systematic decline in $^{137}$Cs values of up to 0.11 units (~3°C) with a decrease in nitrate (Prahl et al., 2003).

In order to clarify the potential impact of nutrients, we investigated the influence of nitrate concentrations on the residuals of $^{137}$Cs SST and measured SST in the haptophyte habitat depth (0–30 m; Figure 6). Indeed, we observed a clear relationship between nitrate concentrations and SST residuals. The majority (27 out of 33 values) of $^{137}$Cs‐derived SST estimates with nitrate concentrations <2.1 μmol/L is lower than actual SST, while the majority of $^{137}$Cs SST values (54 out of 65) with nitrate ≥2.1 μmol/L exceeds actual SST (Figure 4). Analogous relationships are observed for phosphate and a threshold value of 0.47 μmol/L (supporting Figure S7) as well as for the annual averages based on the non‐refined age model for the $^{137}$Cs, with a nitrate threshold of <3.1 μmol/L explaining 8 out of 9 years with proxy‐based temperatures colder than actual SSTs, while 16 out of 17 years with nitrate concentrations ≥3.1 μmol/L reveal warmer temperatures (Figure S8). This impact of seasonally variable nutrient concentrations on sedimentary $^{137}$Cs is consistent with observations in cultures and sediment traps by Prahl et al. (2003). This nitrate effect can additionally account for (i) the lower amplitude of our $^{137}$Cs SST record compared to actual SST, especially during years of strongly reduced upwelling such as the 1997/1998 El Niño, and (ii) the lower slope of the $^{137}$Cs versus SST

![Figure 6. Relationship of surface water nitrate concentrations with $^{137}$Cs reconstructed SST.](image)
relationship observed in our study (Figure 6a) relative to that observed in global data sets (Müller et al., 1998). These results, enabled through unprecedented temporal resolution in sedimentary biomarker measurements, provide mechanistic insights into UK037 signal formation in the SBB. Presumably, such effects of nutrient availability have not been observed in previous studies using conventional protocols for biomarker analysis because typical sample volumes integrate periods of decades to centuries and thus provide information on long-term average conditions. In this context, we note that the 25-year average SST record reconstructed via the UK037 is essentially equal to the corresponding instrumentally-determined SST (14.4°C vs. 14.1°C, respectively; Figure 3). Nevertheless, our results imply that the influence of nutrients on the sedimentary UK037 signal should be carefully considered in paleoenvironmental applications, especially when there is evidence that the studied systems oscillated between oligotrophic and eutrophic conditions.

3.5. Planktonic Archaeal Lipids Respond to Oceanographic Variations in the North Pacific

The SBB is influenced by the large-scale fluctuations of the CCS (Field et al., 2006). The intensity of upwelling strength of subsurface nutrient-rich waters in the CCS is modulated by basin-scale climate indices, that is, ENSO, PDO, and NPGO. Upwelling intensity is weaker (stronger) during the positive (negative) PDO phase (Chavez et al., 2003; Chhak & Di Lorenzo, 2007; Mantua et al., 1997) and during El Niño (La Niña) events (Bograd & Lynn, 2001; Bonino et al., 2019; Chavez et al., 2002; Jacox et al., 2015; Lynn et al., 1995). The NPGO correlates with fluctuations in nutrients, salinity, and chlorophyll a as a result of interannual and decadal variations in wind-driven upwelling (di Lorenzo et al., 2008).

Examination of the relationship between the CCaT record and the three indices that capture the variation of PDO, ENSO, and NPGO reveals the similarity of the proxy record to these oscillations (Figure 7). The inverse relationship between CCaT and NPGO (Figure 7c) is supported by significant correlation between NPGO and salinity in the Southern California Current between 30°N and 38°N (di Lorenzo et al., 2008).

Figure 7. Imprint of (sub)decadal oceanographic variability in the North Pacific on the CCaT record. ENSO presented as Niño 3.4 (a), PDO (b) and reversed NPGO (c) compared to age-refined monthly resolved CCaT from AD 1984–2009.
Additionally, the apparent resemblance of CCaT to both ENSO and PDO variability (Figures 7a and 7b) supports our suggestion of the CCaT being sensitive to low-frequency variations in the upwelling intensity. The correlations between CCaT and local water column characteristics together with the ability of CCaT to capture the main features of NE Pacific Ocean-climate indices demonstrate the potential of the CCaT proxy to reconstruct past upwelling variability associated to large-scale climatic oscillation in the CCS and the Pacific climate.

4. Conclusions

Our study shows that the high spatial resolution obtained by MSI enables investigation of the sub-annual differences of archaeal versus haptophyte lipids, both thought to be sensitive to SST variations. In SBB sediments, the monthly-resolved U^{13}C records the annual cycle of SST variation, but its amplitude is dampened by a nutrient-effect, which so far has been only shown in culture experiments and was indicated in suspended particulate matter (Prah1 et al., 2003). Planktonic archaeal lipid distributions lack a strong correlation with SST. However, in varved sediments from the SBB, the high-resolution CCaT records variations in water column characteristics associated with low-frequency upwelling variability linked to Pacific climate variability on interannual to decadal timescales.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data from this work are available at PANGAEA, Data Publisher for Earth & Environmental Science (https://doi.org/10.1594/PANGAEA.914380).

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