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OPTiMAL: A new machine learning approach for GDGT-based palaeothermometry

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Abstract

In the modern oceans, the relative abundances of Glycerol dialkyl glycerol tetraether (GDGTs) compounds produced by marine archaeal communities show a significant dependence on the local sea surface temperature at the site of formation. When preserved in ancient marine sediments, the measured abundances of these fossil lipid biomarkers thus have the potential to provide a geological record of long-term variability in planetary surface temperatures. Several empirical calibrations have been made between observed GDGT relative abundances in late Holocene core top sediments and modern upper ocean temperatures. These calibrations form the basis of the widely used TEX_{86} palaeothermometer. There are, however, two outstanding problems with this approach, first the appropriate assignment of uncertainty to estimates of ancient sea surface temperatures based on the relationship of the ancient GDGT assemblage to the modern calibration data set; and second, the problem of making temperature estimates beyond the range of the modern empirical calibrations (>30 ºC). Here we apply modern machine-learning tools, including Gaussian Process Emulators and forward modelling, to develop a new mathematical approach we call OPTiMAL (**O**ptimised **P**alaeothermometry from **T**etraethers v**i**a **MA**chine **L**earning) to improve temperature estimation and the representation of uncertainty based on the relationship between ancient GDGT assemblage data and the structure of the modern calibration data set. We reduce the root mean square uncertainty on temperature predictions (validated using the modern data set) from ~± 6 ºC using TEX_{86} based estimators to ± 3.6 ºC using Gaussian Process estimators for temperatures below 30 ºC. We also provide a new but simple quantitative measure of the distance between an ancient GDGT assemblage and

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the nearest neighbour within the modern calibration dataset, as a test for significant non-analogue behaviour. Finally, we advocate against the use of temperature estimates beyond the range of the modern empirical calibration dataset, given the absence – to date - of a robust predictive biological model or extensive and reproducible mesocosm experimental data in this elevated temperature range.

1. Introduction

Glycerol dialkyl glycerol tetraethers (GDGTs) are membrane lipids consisting of isoprenoid carbon skeletons ether-bound to glycerol (Schouten et al., 2013). In marine systems they are primarily produced by ammonia oxidising marine Thamarchaeota (Schouten et al., 2013), although some bacterial production may also be important, especially in sub-freezing ecosystems (Siliakus et al., 2017). In modern marine core top sediments, the relative abundance of GDGT compounds with more ring structures increases with the mean annual sea surface temperature (SST) of the overlying waters (Schouten et al., 2002). This trend is most likely driven by the need for increased cell membrane stability and rigidity at higher temperatures (Sinninghe Damsté et al., 2002). On this basis, the TEX_{86} (tetraether index of tetraethers containing 86 carbon atoms) ratio was derived to provide an index to represent the extent of cyclisation (Eq. 1; where GDGT-x represents the fractional abundance of GDGT-x by LCMS peak area, and cren' is the peak area of the regioisomer of crenarchaeol) (Schouten et al., 2002) and was shown to be positively correlated with mean annual SSTs:

$$TEX_{86} = (\text{GDGT-2} + \text{GDGT-3} + \text{cren'})/ (\text{GDGT-1}+ \text{GDGT-2} + \text{GDGT-3} + \text{cren'}) \quad \text{(Eq. 1)}$$

Early applications of TEX_{86} to reconstruct ancient SSTs were promising, especially in providing temperature estimates in environments where standard carbonate-based proxies are hampered by poor preservation (Schouten et al., 2003; Herfort et al., 2006; Schouten et al., 2007; Huguet et al., 2006; Sluijs et al., 2006; Brinkhuis et al., 2006; Pearson et al., 2007; Slujis et al., 2009). The TEX_{86} approach also extended beyond the range of the widely used alkenone-based $U^{k'}_{37}$ thermometer, in both temperature space, where $U^{k'}_{37}$ saturates at ~28ºC (Brassell, 2014; Zhaung et al., 2017), and back into the early Cenozoic (Bijl et al., 2009; Hollis et al., 2009; Bijl et al., 2013; Inglis et al., 2015) and Mesozoic (Schouten et al., 2002; Jenkyns et al., 2012; O'Brien et al., 2017) where haptophyte-derived alkenones are typically absent from marine sediments (Brassell, 2014). Initially, TEX_{86} was converted to SSTs using an equation derived by Schouten et al. (2002) (Eq. 2):

$$\text{SST ºC} = 66.7 * TEX_{86} – 18.7 \quad \text{(Eq. 2)}$$

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However as the number and range of applications of TEX_{86} palaeothermometry grew, concerns arose about proxy behaviour at both the high (Liu et al., 2009) and low (Kim et al., 2008) temperature ends of the modern calibration. In response to these criticisms, a new expanded modern core top dataset (Kim et al., 2010) was used to generate two new forms of the GDGT proxy – TEX_{86}^{L} (Eq. 3), an exponential function that does not include the crenarchaeol regio-isomer and was recommended for use across the entire temperature range of the new core top data (-3 to 30 ºC, particularly when SSTs are lower than 15 ºC), and TEX_{86}^{H} (Eq. 4), also exponential, and recommended for use when SSTs exceeded 15 ºC (Kim et al. 2010). TEX_{86}^{L} also excludes GDGT abundance data from the high-temperature regimes of the Red Sea, with the rationale that high-salinity conditions are responsible for somewhat anomalous GDGT compositions in this region (Kim et al. 2010).

$$TEX_{86}^{L} = log\left(\frac{[GDGT2]}{[GDGT1]+[GDGT2]+[GDGT3]}\right) \qquad \text{Eq. 3}$$

$$TEX_{86}^{H} = log\left(\frac{[GDGT2]+[GDGT3]+[Cren']}{[GDGT1]+[GDGT2]+[GDGT3]+[Cren']}\right) \text{ Eq. 4}$$

Despite the recommendations of Kim et al. (2010), both TEX_{86}^{H} and TEX_{86}^{L} were widely used and tested across a range of temperatures and palaeoenvironments, including comparisons against other palaeotemperature proxy systems (Hertzberg et al., 2016; Zhang et al., 2014; Seki et al., 2014; Douglas et al., 2014; Linnert et al., 2014; Tyler; Hollis et al. 2012; Dunkley Jones et al. 2013; Lunt 2012). The rationale was that both TEX_{86}^{L} and TEX_{86}^{H} were calibrated across a full temperature range, with the exception of the inclusion or exclusion of Red Sea core-top data. The difference in model fit between the two proxy formulations to the calibration dataset was also minor (Kim et al. 2010). In certain environments, however, TEX_{86}^{L} was subject to significant variability in derived temperatures that were not apparent in TEX_{86}^{H} (Taylor et al. 2013). This was mostly due to changing GDGT2 to GDGT3 ratios, which strongly influence TEX_{86}^{L}, and may be related to the GDGT productivity environment and deep-water lipid production, (Taylor et al., 2013). As a result, TEX_{86}^{L} is no longer regarded as an appropriate tool for palaeotemperature reconstructions, except in limited Polar conditions (Kim et al., 2010; Tierney, 2012).

Three fundamental issues have always troubled the TEX_{86} proxy. The first is a concern about undetected non-analogue palaeo-GDGT assemblages, for which the modern calibration data set is inadequate to provide a robust temperature estimation. Although various screening protocols, with independent indices

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and thresholds, have been proposed to test for an excessive influence of terrestrial lipids (BIT index; Hopmans et al. 2004), within sediment methanogenesis (Methane Index, 'MI'; Zhang et al., 2011) and non-thermal effects such as nutrient levels and archaeal community structure to impact the weighted average of cyclopentane moieties (Ring Index, 'RI;' Zhang et al., 2016), these do not provide a fundamental measure of the proximity between GDGT abundance distributions in the modern, and ancient GDGT abundance distributions recorded in sediment samples. The fundamental question remains – are measured ancient assemblages of GDGT compounds anything like the modern assemblages, from which palaeotemperatures are being estimated? Understanding this question is not helped by the use of indices – TEX_{86} itself, or BIT and MI – that collapse the dimensionality of GDGT abundance relationships onto a single axis of variation.

Second, from the earliest applications of the TEX_{86} proxy to deep-time warm climate states (Schouten et al., 2003) it was recognized that reconstructed temperatures beyond the range of the modern calibration (>30 ºC), were highly sensitive to model choice within the modern calibration range. Thus, Schouten et al. (2003) restricted their calibration data for deep-time temperature estimates to core-top data in the modern with mean annual SSTs over 20 ºC. However, this problem of model choice, and its impact on temperature estimation beyond the modern calibration range, persists (Hollis et al. in review), with current arguments focused on whether there is an exponential (e.g. Cramwinckel et al., 2018) or linear (Tierney & Tingley, 2015) dependency of TEX_{86} on SSTs, and the effect of these models on temperature estimates over 30 ºC.

Culture and mesocosm studies are sometimes cited in support of extrapolations beyond the modern calibration range when reconstructing ancient SSTs (Kim et al., 2010, Hollis et al., in review). However, close examination of these culture studies reveals a significant variation in the patterns of archaeal GDGT production in response to increasing growth temperature (e.g., Elling et al., 2015). At present, there are a limited number of pure Thaumarchaeotal strains that can be cultured in the laboratory (Qin et al., 2014, 2015). Of the existing studies on these cultures, several focus on non-thermal environmental or physiological variables, such as oxygen availability (Qin et al., 2015), that may also influence TEX_{86}. Early mesocosm studies indicated that a TEX_{86} to temperature relationship was maintained up to ~35-40 ºC, but with differing linear slopes from modern core top calibrations (Schouten et al., 2007; Wuchter et al., 2004). The production of the crenarchaeol regional isomer (cren') in these elevated temperature mesocosms is typically lower than that found in sediments (Pearson & Ingalls, 2013; Schouten et al., 2007), indicating that the GDGT production environment in the mesocosms was in some fundamental way not analogous to the time-averaged GDGT assemblages recovered from core-top samples. A more recent study of three pure archaeal cultures (Elling et al. 2015) found that TEX_{86} ratios for two of the three cultures showed positive relationships with growth temperature (but with different slopes and intercepts), while the third, an isolate

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from the surface waters of the South Atlantic, showed no relationship between TEX_{86} and growth temperature. The available evidence is that there is not a uniform response in GDGT-production to growth temperature across distinct strains of archaea in culture (Elling et al., 2015). More fundamentally, in natural systems, it is likely that aggregated GDGT abundance variations in response to growth temperatures result from changing compositions of archaeal populations as well as the physiological response of individual strains to growth temperature (Elling et al. 2015). For instance, a multiproxy study of Mediterranean Pliocene-Pleistocene sapropels indicates that specific distributions of archaeal lipids might be reflective of temporal changes in thaumarchaeael communities rather than temperature alone (Polik et al., 2018). Indeed, the potential influence of community switching on GDGT composition can be seen in mesocosm studies, with different species preferentially thriving at different growth temperatures (e.g., Schouten et al., 2007). To use the responses of single, selected archaeal strains in culture to validate a particular model of community-level responses to growth temperature is clearly problematic even in the modern system (Elling et al., 2015). For deep time applications it is even more difficult, where there is no independent constraint on the archaeal strains dominating production or their evolution through time (Elling et al. 2015). What is notable, however, is that the Ring Index (RI) - calculated using all commonly measured GDGTs (Zhang et al., 2016) – has a more robust relationship with culture temperature between archaeal strains than TEX_{86}, indicating a potential loss of information within the TEX_{86} index (Elling et al. 2015).

Finally, traditional uses of the TEX_{86} proxy poorly represent the true uncertainty of palaeotemperature estimates, as they include no assessment of non-analogue behavior relative to the modern core-top data. Instead, uncertainty is typically based on the residuals on the modern calibration, with no reference to the relationship between GDGT distributions of an ancient sample and the modern calibration data. An improved Bayesian uncertainty model "BAYSPAR" is now in widespread use for SST estimation, which uses sub-sampling approaches to improve temperature estimation and model uncertainty (Tierney and Tingley, 2015). The Bayesian approach, however, still does not appropriately model uncertainty based on the structure of fossil GDGT abundances relative to modern data, and is insensitive to detecting wildly non-analogue behaviour in ancient GDGT distributions, as it still functions on one-dimensional TEX_{86} index values.

All empirical calibrations of GDGT-based proxies assume that mean annual SST is the master control on GDGT assemblages both today and in the past. Mean annual SST, however, is strongly correlated with many other environmental variables (e.g., seasonality, pH, mixed layer depth, and productivity). In the modern calibration dataset, mean annual SST shows the strongest correlation with TEX_{86} index (Schouten et al., 2002), but this does not preclude an important (but undetectable) influence of these other

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environmental variables. The use of empirical GDGT calibrations to infer ancient sea surface temperatures thus implicitly assumes that the relationships between mean annual SST and all other GDGT-influencing variables are invariant through time. This assumption is inescapable until, and unless, a more complete biological mechanistic model of GDGT production emerges.

Here, we return to the primary modern core-top GDGT assemblage data (Tierney and Tingley, 2015), and systematically explore the relationships between the modern GDGT distributions and surface ocean temperatures using powerful mathematical tools. These tools can investigate correlations without prior assumptions on the best form of relationship or *a priori* selection of GDGT compounds to be used. This analysis is then extended through the exploration of the relationships between the modern core top GDGT distributions and two compilations of ancient GDGT datasets, one from the Eocene (Inglis et al. 2015) and one from the Cretaceous (O'Brien et al. 2017). We explore simple metrics to answer the fundamental question – are modern core-top GDGT distributions good analogues for ancient distributions? We propose the first robust methodology to answer this question, and so screen for significantly non-analogue palaeo-assemblages. From this, we go on to derive a new machine learning approach 'OPTiMAL' (**O**ptimised **P**alaeothermometry from **T**etraethers v**i**a **MA**chine **L**earning) for reconstructing SSTs from GDGT datasets, which outperforms previous GDGT palaeothermometers and includes robust error estimates that, for the first time, accounts for model uncertainty.

2. Models for GDGT-based Temperature Reconstruction

Our new analyses use the modern core-top data compilation, and satellite-derived estimates of SSTs, of Tierney and Tingley (2015) as well as compilations of Eocene (Inglis et al. 2015) and Cretaceous (O'Brien et al. 2017) GDGT assemblages. Within these fossil assemblages, only data points with full characterisation of individual GDGT relative abundances were used. We also note that, in the first instance, all available fossil assemblage data were interrogated, although later comparisons between BAYSPAR and our new temperature predictor excludes fossil data that was regarded as unreliable based on standard pre-screening indices, as noted within the original compilations (Inglis et al. 2015; O'Brien et al. 2017). All data used in this study are tabulated in the supplementary information.

In order to enable meaningful comparison between new and existing temperature predictors, we use the following consistent procedure for evaluating all predictors throughout this paper. We divide the modern core-top data set of 854 data points into 85 validation data points (chosen randomly) and 769 calibration points. We calibrate the predictor on the calibration points, and then judge its performance on the validation

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points using the square root of the average of the square of the difference between the prediction at each validation point, and the true (i.e. measured) temperature value:

$$\delta T = \sqrt{\frac{1}{N_v - 1}\sum_{k=1}^{N_v}(\hat{T}(x_k) - T(x_k))^2} \qquad \text{(Eq. 5)}$$

where the sum is taken over each of N_v = 85 validation points, T is the known measured temperature (which we refer to as the true temperature) and $\hat{T}$ is the predicted temperature. For conciseness, we refer to δT as the predictor standard error. It is useful to compare the accuracy of the predictor to the standard deviation of all temperatures in the data set σT, which corresponds to using the mean temperature as the predictor in Equation 1; for the modern data set, σT= 10.0 ºC. The so-called coefficient of determination R^2, given by

$$R^2 \equiv 1 - \left(\frac{\delta T}{\sigma T}\right)^2 \qquad \text{(Eq. 6)}$$

provides a measure of the fraction of the fluctuation in the temperature explained by the predictor. To facilitate performance comparisons between different methods of predicting temperature, we use the same subset of validation points for all analyses. To avoid sensitivity to the choice of validation points, we repeat the calibration-validation procedure for 10 random choices from the validation dataset.

2.1 Nearest neighbours

We begin with an agnostic approach to using some combination of the six observables - GDGT-0, GDGT-1, GDGT-2, GDGT-3, crenarchaeol and the crenarchaeol regio-isomer (cren'), which we will jointly refer to as GDGTs - to predict sea surface temperatures. Whatever functional form the predictor might take, it can only provide accurate temperature predictions if nearby points in the six-dimensional observable space - i.e. the distribution of all of the six commonly reported GDGTs - can be translated to nearby points in temperature space. Conversely, if nearby points in the observable space correspond to vastly different temperatures, then no predictor, regardless of which combination of GDGTs are used, will be able to provide a useful temperature estimate. In other words, the structuring of GDGT distributions within multi-

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dimensional space, must have some correspondence to the temperatures of formation (or rather the mean annual SSTs used for standard calibrations).

We therefore consider the prediction offered by the temperature at the nearest point in the GDGT parameter space. Of course, nearness depends on the choice of the distance metric. For example, it may be that sea surface temperatures are very sensitive to one observable, so even a small change in that observable corresponds to a significant distance, and rather insensitive to another, meaning that even with a large difference in the nominal value of that observable the distance is insignificant. In the first instance, we use a very simple Euclidian distance estimate $D_{x,y}$ where the distance along each observable is normalised by the total spread in that observable across the entire data set. This normalisation ensures that a dimensionless distance estimate can be produced even when observables have very different dynamical ranges, or even different units. Thus, the normalised distance D between parameter data points x and y is

$$D_{x,y}^2 \equiv \sum_{i=0}^{6} \frac{GDGT_i(x) - (GDGT_i(y))^2}{var(GDGT_i)}$$

(Eq. 7)

We show the distribution of nearest distances of points in the modern data set, excluding the sample itself, in (Fig. 1).

The nearest-sample temperature predictor is $\hat{T}_{\mathrm{nearest}}$ (x) = $T(y)$ where y is the nearest point to x over the calibration data set, i.e., one that minimises $D_{x,y}$. Fig. 2 shows the scatter in the predicted temperature when using the temperature of the nearest data point to make the prediction. Overall, the failure of the nearest-neighbour predictor to provide accurate temperature estimates even when the normalised distance to the nearest point is small, $D_{x,y} \leq 0.5$, casts doubt on the possibility of designing an accurate predictor for temperature based on GDGT observations. This is most likely due to additional environmental controls on GDGT abundance distributions in natural systems, in particular the water depth (Zhang and Liu, 2018), nutrient availability (Hurley et al., 2018; Polik et al., 2018; Park et al., 2018), seasonality, growth rate (Elling et al., 2014) and ecosystem composition (Polik et al., 2018), that obscure a predominant relationship to mean annual SSTs.

On the other hand, the standard error for the nearest-neighbour temperature predictor is $\delta T_{\mathrm{nearest}}$ = 4.5 ºC. This is less than half of the standard deviation σT in the temperature values across the modern data set. Thus, the temperatures corresponding to nearby points in GDGT observable space also cluster in temperature space. Consequently, there is hope that we can make some useful, if imperfect, temperature

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predictions. The value of $\delta T_{\text{nearest}}$ will also serve as a useful benchmark in this design: while we may hope to do better by, say, suitably averaging over multiple nearby calibration points rather than adopting the temperature at one nearest point as a predictor, any method that performs worse than the nearest-neighbour predictor is clearly suboptimal.

2.2 TEX_{86} and Bayesian applications

The TEX_{86} index reduces the six-dimensional observable GDGT space to a single number. While this has the advantage of convenience for manipulation and the derivation of simple analytic formulae for predictors, as illustrated below, this approach has one critical disadvantage: it wastes significant information embedded in the hard-earned GDGT distribution data. Fig. 3 illustrates both the advantage and disadvantage of TEX_{86}. On the one hand, there is a clear correlation between TEX_{86} and temperature (top panel of Fig. 3), with a correlation coefficient of 0.81 corresponding to an overwhelming statistical significance of 10^{-198}. On the other hand, very similar TEX_{86} values can correspond to very different temperatures. We can apply the nearest-neighbour temperature prediction approach to the TEX_{86} value alone rather than the full GDGT parameter space; this predictor yields a large standard error of $\delta T_{\text{nearestTEX86}}$ = 8.0 ºC (bottom panel of Fig. 3). While smaller than σT, this is significantly larger than $\delta T_{\text{nearest}}$ (Fig. 2), consistent with the loss of information in TEX_{86}. We therefore do not expect other predictors based on TEX_{86} to perform as well as those based on the full available data set.

Indeed, this is what we find when we consider predictors of the form $\hat{T}_{1/\text{TEX}} = a + b/\text{TEX}_{86}$ and $\hat{T}_{\text{TEXH}} = c + d \log_{\text{TEX86}}$ (Liu et al., 2009; Kim et al., 2010), i.e., the established relationships between GDGT distributions and SST. We fit the free parameters *a, b, c,* and *d* by minimising the sum of squares of the residuals over the calibration data sets. We find that $\delta T_{1/\text{TEX}}$ = 6.1 ºC (note that this is slightly better than using the fixed values of *a* and *b* from (Kim et al., 2010), which yield $\delta T_{1/\text{TEX}}$ = 6.2 ºC). We note that the corresponding R^2 value associated with these TEX_{86} based predictors is 0.64, which is lower than the R^2 values in Kim et al. (2010). We attribute this to the fact that we are using a larger dataset based on Tierney and Tingley (2015), including data from the Red Sea (Kim et al. 2010).

Tierney and Tingley (2014) proposed a more sophisticated approach to obtaining the transfer function from TEX_{86} to temperature, continuing to use simple linear regression, but with the addition of Gaussian processes to model spatial variability in the temperature-TEX_{86} relationship and working with a forward model which is subsequently inverted to produce temperature predictions. This forward model 'BAYSPAR' is capable of generating an infinite number of calibration curves relating TEX_{86} to sea surface

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temperatures (Tierney and Tingley, 2014). In order to derive a calibration for a specific dataset, the user edits a range of parameters which vary depending on whether the dataset in question is from the relatively recent past or deep time (Tierney and Tingley, 2014). For deep time applications, the authors propose a modern analogue-type approach, in which they search the modern data for 20º x 20º grid boxes containing `nearby' TEX_{86} measurements and subsequently apply linear regression models calibrated on the analogous samples for making predictions.

However, along with the simpler TEX_{86}-based models described above, this approach still suffers from the arbitrary reduction of a six-dimensional data set to a single number. Therefore, it is not surprising that even the simplest nearest-neighbour predictor (such as the one described above) that makes use of the full six-dimensional dataset outperforms single-dimensional forward modelling approaches. Additionally, uncertainty estimates do not account for the fact that TEX_{86} is, fundamentally, an empirical proxy, and so its validity outside the range of the modern calibration is not guaranteed. This is a fundamental issue for attempts to reconstruct surface temperatures during Greenhouse climate states, when tropical and sub-tropical SSTs were likely hotter than those observed in the modern oceans.

2.3 Machine learning Approaches – Random Forests

There are a number of options to improve on nearest-neighbour predictions using machine learning techniques such as artificial neural networks and random forests. These flexible, non-parametric models would ideally be based on the underlying processes driving the GDGT response to temperature, but since these processes remain unconstrained at present, we choose to deploy models which can reasonably reflect predictive uncertainty and will be sufficiently adaptable in future (as new information regarding controls on GDGTs emerge). These machine learning approaches are all based on the idea of training a predictor by fitting a set of coefficients in a sufficiently complex multi-layer model in order to minimise residuals on the calibration data set. As an example of the power of this approach, we train a random forest of decision trees with 100 learning cycles using a least-squares boosting to fit the regression ensemble. Figure 4 shows the prediction accuracy for this random forest implementation. This machine learning predictor yields δT = 4.1 ºC degrees, outperforming the naive nearest-neighbour predictor by effectively applying a suitable weighted average over multiple near neighbours. This corresponds to a very respectable $R^2 = 0.83$, meaning that 83% of the variation in the observed temperature is successfully explained by our GDGT-based model.

2.4 Gaussian Process Regression

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One downside of the random forest predictor is the difficulty of accurately estimating the uncertainty on the prediction (Mentch and Hooker, 2016), although this is possible with, e.g., a bootstrapping approach (Coulston et al., 2016). Fortunately, Gaussian process (GP) regression provides a robust alternative. For full details on GP regression refer to Williams and Rasmussen (20060 and Rasmussen and Nickisch (2010). Loosely, the objective here is to search among a large space of smoothly varying functions of GDGT compositions for those functions which adequately describe temperature variability. This, essentially, is a way of combining information from all calibration data points, not just the nearest neighbours, assigning different weights to different calibration points depending on their utility in predicting the temperature at the input of interest. The trained Gaussian process learns the best choice of weights to fit the data. Typically, the GP will give greater weight to closer points, but, as we discuss below, it will learn the appropriate distance metric on the multi-dimensional GDGT input space.

The weighting coefficients learned by the GP emulator represent a covariance matrix on the GDGT parameter space. We can use this as a distance metric to provide meaningfully normalised distances between points, removing the arbitrariness from the nearest neighbour distance ($D_{x,y}$) definition used earlier. If the temperature is insensitive to a particular GDGT input coordinate (i.e., the value of that input has a minimal effect on the temperature) then points within GDGT space that have large differences in absolute input values in that coordinate are still near. We find that Cren has very limited predictive power, and so points with large Cren differences are close in term of the normalised distance. Conversely, if the temperature is sensitive to small changes in a particular GDGT variant, then points with relatively nearby absolute input values in that coordinate are still distant. We find that most GDGT parameters other than Cren are comparably useful in predicting temperature, with GDGT-0 and GDGT-3 marginally the most informative.

We use a Gaussian process model with a squared exponential kernel with automatic relevance determination (ARD) to allow for a separate length scale for each GDGT predictor. We fit the GP parameters with an optimiser based on quasi-Newton approximation to the Hessian. Prediction accuracy is shown in Figure 5, and we find that δT = 3.72 ºC, which is a substantial improvement over the existing indices, at least on the modern data. As mentioned, the GP framework provides a natural quantification of predictive uncertainty, which includes uncertainty about the learned function. This is in contrast to, for example, the TEX_{86} proxy, whereby the uncertainty associated with the selection of the particular functional form used for predictions is ignored. While Tierney & Tingley (2014) also use Gaussian processes to model uncertainty, they model spatial variability in the TEX_{86}-temperature relationship with a Gaussian process

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prior. While this is a valuable approach to understand regional effects in the TEX_{86}-temperature relationship, it does not deal with the `non-analogue' situations we are concerned with in this paper.

2.5 Data Structure

The random forest (Section 2.3) and GPR approaches (Section 2.4) are agnostic about any underlying bio-physical model that might impart the observed temperature-dependence on GDGT relative abundances produced by archaea. They are essentially optimized interpolation tools for mapping correlations between temperature and GDGT abundances within the range of the modern calibration data set; they can make no sensible inference about the behavior of this relationship outside of the range of this training data. To move from interpolation within, to extrapolation beyond, the modern calibration requires an understanding of, and model for, the temperature-dependence of GDGT production. To explore these relationships and the extent to which the ancient and modern data reside in a coherent relationship within GDGT space, we employed two forms of dimensionality reduction to enable visualisation of the data in two or three dimensions. The fundamental point is that if temperature is the dominant control, all of the data should lie approximately on a one-dimensional curve in GDGT space, and the arclength along this curve should correspond to temperature; we will revisit this point below.

We first employed a version of principal component analysis (PCA) tailored to compositional data (Aitcheson, 1982, 1983; Aitcheston and Greenacre, 2002; Filzmoser et al., 2009a; Filzmoser et al., 2009b; Filzmoser et al., 2012). Taking into account the compositional nature of the data is important because the sum-to-one constraint induces correlations between variables which are not accounted for by classical PCA. Furthermore, apparently nonlinear structure in Euclidean space often corresponds to linearity in the simplex (i.e. the restricted space in which all elements sum to one) (Egozcue et al., 2003). Figure 6 shows the modern, Eocene and Cretaceous data projected onto the first two principal components. Aside from the obvious outlying cluster of Cretaceous data, characterised by GDGT-3 fractions above 0.6, the bulk of the data occupy a two-dimensional point cloud with a small amount of curvature. The large majority of the Cretaceous data has more positive PC1 values relative to the modern data.

We also explored the data using diffusion maps (Coifman et al., 2005; Haghverdi et al., 2015), a nonlinear dimensionality reduction tool designed to extract the dominant modes of variability in the data. Such diffusion maps have been successfully used to infer latent variables that can explain patterns of gene expression. In the case of biological organisms, this latent variable is commonly developmental age (called pseudo-time) (Haghverdi et al., 2016). In our case, the assumption would be that this latent variable

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corresponds to temperature. Inspection of the eigenvalues of the diffusion map transition matrix suggests that four diffusion components are adequate to represent the data; we plot the second, third and fourth of these components in Figure 7 for the modern and ancient data. The separate clusters marked `A' are the outlying Cretaceous points with high GDGT-3 values. The bulk of the modern data lies on the branch marked `B', while the bulk of the Cretaceous data lies on the branch marked `C'. Notably, the majority of the modern points lying on branch C are from the Red Sea, which suggests that the Red Sea data is essential for understanding ancient climates (particularly Cretaceous climates).

The relationship between the first diffusion component and TEX_{86} for all data is shown in Figure 8. There is a clear correlation, despite the presence of some outlying Cretaceous points, some of which are not shown because they lie so far outside the majority data range within this projection. This suggests that TEX_{86} is, in one sense, a natural one-dimensional representation of the data. We also plot the first diffusion component for the modern data as a function of temperature (Figure 9). We see a similar pattern emerging to that displayed by TEX_{86} - there is little sensitivity to temperature below 15 ºC, and between ~20 and 25 ºC. An interesting avenue for future research might be to explore the temperature-GDGT system from a dynamical systems perspective, i.e. use simple mechanistic mathematical models to explore the temperature-dependence of steady-state GDGT distributions. It may be that such models suggest that only a few steady-states exist, and that temperature is a bifurcation parameter, i.e. it controls the switch between the steady states. Note also the downward slope in the residual pattern in Figure 4 between 0 and 15-17 degrees celsius, and again at higher temperatures. This pattern is consistent with predictions that are biased towards the centre of each `cluster', i.e. a system which is not very sensitive to temperature, but can distinguish between high and low temperatures reasonably well. This observation also links to recent culture studies (Elling et al., 2015) and Pliocene-Pleistocene sapropel data (Polik et al., 2018), which support the existence of discrete populations with unique GDGT-temperature relationships and that temporal changes in population over time can drive changes in TEX_{86}.

2.6 Forward Modelling

Based on the analysis of the combined modern and ancient data structure outlined above, there appears to be some consistency to underlying trends in the overall variance of GDGT relative abundances. These trends provide some hope that models of this variance, and its relationship to sea surface temperature, within the modern dataset could be developed to predict ancient SSTs. TEX_{86} and BAYSPAR are such models, but they are limited by, first, the reduction of six-dimensional GDGT space to a one-dimensional index; and second, by an *ad hoc* model choice – linear, exponential – that does not account for uncertainty in

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model fit to the modern calibration data, and the resultant uncertainty in the estimation of ancient SSTs relating to model choice. To overcome these issues, we develop a forward model based on a multi-output Gaussian Process (Alvarez et al., 2012), which models GDGT compositions as functions of temperature, accounting for correlations between GDGT measurements. This model is then inverted to obtain temperatures which are compatible with a measured GDGT composition. In simple terms, we posit that a measured GDGT composition is generated by some unknown function of temperature and corrupted by noise, which may be due to measurement error or some unmodelled particularity of the environment in which the sample was generated. We proceed by defining a large (in this case infinite) set of functions of temperature to explore and compare them to the available data, throwing away those functions which do not adequately fit the data. This means, of course, that the behaviour of the functions we accept is allowed to vary more widely outside the range of the modern data than within it. With no mechanistic underpinning, choosing only one function (such as the inverse of TEX_{86}) based on how well it fits the modern data grossly underestimates our uncertainty about temperature where no modern analogue is available.

The forward modelling approach is similar to that of Haslett et al. (2006), who argue that it is preferable to model measured compositions as functions of climate, before probabilistically inverting the model to infer plausible climates given a composition. The cost of modelling the data in this more natural way is the loss of degrees of freedom -- we are now attempting to fit a one-dimensional line through a multidimensional point cloud rather than fit a multidimensional surface to the GDGT data, which means that the predictive power of the model suffers, at least on the modern data. The existing BAYSPAR calibration also specifies the model in the forward direction, but ignores model uncertainty. As with all GP models, the choice of kernel has a substantial impact on predictions (and their associated uncertainty) outside the range of the modern data, where predictions revert to the prior implied by the kernel. Given that we have no mechanistic model for the data generating process, we recommend the use of kernels which do not impose strong prior assumptions on the form of the GDGT-temperature relationship (e.g. kernels with a linear component) and thus reasonably represent model uncertainty outside the range of the modern data. We choose a zero-mean Matern 3/2 kernel for the applications below. Note, however, that since we are working in ilr-transformed coordinates, this corresponds to a prior assumption of uniform compositions at all temperatures, i.e. all components are equally abundant.

The residuals for the forward model are shown in Figure 10. The clear pattern in the residuals does not necessarily indicate model misspecification, since no explicit noise model is specified for temperatures. Predictive distributions are to be interpreted in the Bayesian sense, in that they represent a 'degree of belief' in temperatures given the model and the modern data. The residual pattern is similar to that of the random

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forest (Figure 4) with two clear downward slopes, suggesting again that the data are clustered into temperatures above and below 16-17 degrees celsius, and that predictions tend towards temperatures at the centres of these clusters.

An advantage of the forward modelling approach is that the inversion can incorporate substantive prior information about temperatures for individual data points. In particular, other proxy systems can be used to elicit prior distributions over temperatures to constrain GDGT-based predictions, particularly when attempting to reconstruct ancient climates with no modern analogue in GDGT-space. We emphasise that outside the range of the modern data, the utility of the models is almost solely due to the prior information included in the reconstruction. At present, the only priors being used in the forward model prescribe a reasonable upper limit and lower limit on temperatures (see Supplementary Information). The only way to improve these reconstructions will be for future iterations to incorporate prior information from other proxies. It is worth noting that the predictive uncertainty, while reasonably well-described by the standard deviation in cases where ancient data lie quite close to the modern data in GDGT space, can be highly multimodal (Fig. 11). This is the case when estimates are significantly outside of the modern calibration dataset, such as low latitude data in the Cretaceous, or where there is considerable scatter in the modern calibration data, for example in the low temperature range (<5 ºC).

3. Non-analogue behavior and Extrapolation

In principle, the predictors described above can be applied directly to ancient data, such as data from the Eocene or Cretaceous (Inglis et al., 2015; O'Brien et al., 2017). In practice, one should be careful with using models outside their domain of applicability. The machine learning tools described above, which are ultimately based on the analysis of nearby calibration data in GDGT space, are fundamentally designed for *interpolation*. To the extent that ancient data occupy a very different region in GDGT space, *extrapolation* is required, which the models do not adequately account for. The divergence between modern calibration data and ancient data is evident from Fig. 12, which shows histograms of minimum normalised distances between 'high quality' Eocene/Cretaceous data points (those that passed the screening tests applied by O'Brien et al., 2017 and Inglis et al., 2015) and the nearest point in the full modern data set. We strongly recommend the use of the nearest neighbor distance metric ($D_{nearest}$) as a screening method to determine whether the modern core top GDGT assemblage data is an appropriate basis for ancient SST estimation on a case-by-case basis. Note that this distance measure is weighted by the scale length of the relevant parameter as estimated by the Gaussian process emulator in order to quantify the relative position of ancient GDGT assemblages to the modern core-top data. By using the GP-estimated covariance as the distance

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metric, we account for the sensitivity of different GDGT components to temperature. Our inference is that samples with $D_{nearest}$ >0.5, *regardless of the calibration model or approach applied*, are unlikely to generate temperature estimates that are much better than informed guesswork. In these instances, in both our GPR and Fwd models, the constraints provided by the modern calibration data set are so weak that estimates of temperature have large uncertainty bands that are dictated by model priors; i.e. are unconstrained by the calibration data (e.g., Figure 13 and Figure 14). This uncertainty is not apparent from estimates generated by BAYSPAR or TEX_{86}^{H} models, although the underlying and fundamental lack of constraints are the same. While 93% of validation data points in the modern data have $D_{nearest}$ <0.5, this is the case for only 33% of Eocene samples and 3% for Cretaceous samples.

Where ancient GDGT distributions lie far from the modern calibration data set ($D_{nearest}$ >0.5), we argue that there is no suitable set of modern analogue GDGT distributions from which to infer growth temperatures for this ancient GDGT distribution. Both the GPR and Fwd models revert to imposed priors once the distance from the modern calibration dataset increases. We propose that this is more rigorous and justified model behavior than extrapolation of TEX_{86} or BAYSPAR predictors to non-analogue samples far from the modern calibration data. As a result, the predictive models can only be applied to a subset of the Eocene and Cretaceous data. We also note that there are two broad, non-mutually-exclusive categories of samples that lie far from the modern calibration dataset ($D_{nearest}$ >0.5), the first are samples that seem to lie 'beyond' the temperature-GDGT calibration relationship, likely with (unconstrained) GDGT formation temperatures higher than the modern core-top calibrations; the second are samples with anomalous GDGT distributions lying on the margins of, or far away from the main GDGT clustering in 6-dimensional space (see outliers in Fig. 8).

Given the (current) limit on natural mean annual surface ocean temperatures of ~30 ºC, extending the GDGT-temperature calibration might be possible through, 1) integration of full GDGT abundance distributions produced in high temperature culture, mesocosm or artificially warmed sea surface conditions into the models; followed by, 2) validation through robust inter-comparisons of any new GDGT palaeothermometer for high temperatures conditions with other temperature proxies from past warm climate states. As discussed in the introduction, the first approach is limited by the ability of culture or mesocosm experiments to accurately represent the true diversity and growth environments and dynamics of natural microbial populations. Such studies clearly indicate a more complex, community-scale control on changing GDGT relative abundances to growth temperatures (e.g., Elling et al., 2015). Community-scale temperature dependency can be modelled relatively well with analyses of natural production preserved in core-top sediments, especially with more sophisticated model fitting, including the GPR and Fwd model

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presented here. Above ~30ºC, however, the behavior of even single strains of archaea are not well-constrained by culture experiments, and the natural community-level responses above this temperature are, so far, completely unknown. Significantly more culture and mesocosm data at these high temperatures, spanning a range of microbial diversity and growth conditions, could provide some of these constraints in future. Until such data exist, we see no robust justification for any particular extrapolation of modern core-top calibration data sets into the unknown above 30 ºC, although the coherent patterns apparent across GDGT space, between modern, Eocene and Cretaceous data (Figures 7), does provide some grounds for hope that the extension of GDGT palaeothermometry beyond 30ºC might be possible in future.

4. OPTiMAL and $D_{nearest}$: A more robust method for GDGT-based paleothermometry

A more robust framework for GDGT-based palaeothermometry, could be achieved with a flexible predictive model that uses the full range of six GDGT relative abundances, and has transparent and robust estimates of the prediction uncertainty. In this context, the Gaussian Process Regression model (GPR; Section 2.4) outperforms the Forward model (Fwd; Section 2.6) within the modern calibration dataset and we recommend standard use of the GPR model, henceforth called OPTiMAL, over the Fwd model. Model code for the calculation of $D_{nearest}$ values and OPTiMAL SST estimates (Matlab script) and the Fwd Model SST estimates (R script) are archived in the GITHUB repository, https://github.com/carbonatefan/OPTiMAL.

To investigate the behaviour of the new OPTiMAL model, we compare temperature predictions including uncertaintities for the Eocene and Cretaceous datasets, made by OPTiMAL and the BAYSPAR methodology of Tierney and Tingley (2014) (Figures 13 and 14). The OPTiMAL model systematically estimates slightly cooler temperatures than BAYSPAR, with the biggest offsets below ~15 ºC (Figure 13). Fossil GDGT assemblages that fail the $D_{nearest}$ test are shown in grey, which clearly illustrate the regression to the mean in the OPTiMAL model, whereas BAYSPAR continues to make SST predictions up to and exceeding 40 ºC for these "non-analogue" samples. A comparison of error estimation between OPTiMAL and BAYSPAR is shown in Figure 14. For most of the predictive range below the $D_{nearest}$ cut-off of 0.5, OPTiMAL has smaller errors than BAYSPAR, especially in the lower temperature range. As $D_{nearest}$ increases, i.e. as the fossil GDGT assemblage moves further from the constraints of the modern calibration dataset, the error on OPTiMAL increases, until it reaches the standard deviation of the modern calibration dataset (i.e., is completely unconstrained). In other words, OPTiMAL generates maximum likelihood SSTs with robust confidence intervals, which appropriately reflect the relative position of an ancient sample used for SST estimation and the structure of the modern calibration data set. Where there are strong constraints

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from near analogues in the modern data, uncertainties will be small, where there are weak constraints, uncertainty increases. In contrast, BAYSPAR, because it is fundamentally based on a *parametric* linear model and therefore does not account for model uncertainty, assigns similar uncertainty intervals as to the rest of the data, despite there being no way of reasonably testing whether the linear model is an appropriate description of the data far from the modern dataset.

5. Conclusions

Although the fundamental issue of non-analogue behaviour is a key problem for GDGT-temperature estimation, it has an undue impact on the community's general confidence in this method. In part, this is because these issues have not been clearly stated and circumscribed - rather they have been allowed to erode confidence in the entire GDGT-based methodology through the inappropriate use of GDGT-based palaeothermometry far outside the modern constraints on the behavior of this system. The use of GDGT abundances to estimate temperatures in clearly non-analogue conditions is, at present, difficult to justify on the basis of the available calibration constraints or a good understanding of underlying biophysical models. We hope that this study prompts further investigations that will improve these constraints for the use of GDGTs in deep-time paleoclimate studies, where they clearly have substantial potential as temperature proxies. Temperature estimates based on fossil GDGT assemblages that are within range of, or similar to, modern GDGT calibration data, do, however, rest on a strong, underlying temperature-dependence observed in the empirical data The failure to have an effective means of separating the "good from the bad", either leads to false confidence and inappropriate inferences in non-analogue conditions, or a false pessimism when the community's trust in the overall method is eroded by the clear influence of methodological choice on SST estimates outside of the modern calibration range.

In this study, we apply modern machine-learning tools, including Gaussian Process Emulators and forward modelling, to improve temperature estimation and the representation of uncertainty in GDGT-based SST reconstructions. Using our new nearest neighbour test, we demonstrate that >60% of Eocene, and >90% of Cretaceous, fossil GDGT distribution patterns differ so significantly from modern that it is inappropriate to interpret them using modern empirical calibrations of any formulation. For data that does show sufficient similarity to modern, we present OPTiMAL, a new multi-dimensional Gaussian Process Regression tool which uses all six GDGTs (GDGT-0, -1, -2, -3, Cren and Cren') to generate an SST estimate with associated uncertainty. The key advantages of the OPTiMAL approach are: 1) that these uncertainty estimates are intrinsically linked to the strength of the relationship between the fossil GDGT distributions and the modern calibration data set, and 2) by considering all GDGT compounds in a multi-dimensional regression model it avoids the dimensionality reduction and loss of information that takes place when calibrating single parameters (TEX_{86}) to temperature. The methods presented above make very few assumptions about the data. We argue that such methods are appropriate with the current absence of any reasonable mechanistic model for the data generating process, in that they reflect model uncertainty in a natural way.

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Figure Captions:

Figure 1. A histogram of the normalised distance to the nearest neighbour in GDGT space ($D_{x,yt}$) for all samples in the modern calibration dataset of Tierney and Tingley (2015).

Figure 2. The error of the nearest-neighbour temperature ($D_{x,y}$) predictor, for modern core-top data, as a function of the distance to the nearest calibration sample.

Figure 3. Top: The temperature of the modern data set as a function of the TEX_{86} value, showing a clear correlation between the two, but also significant scatter. Bottom: the error of the predictor based on the nearest TEX_{86} calibration point.

Figure 4. The error of a random forest predictor as a function of the true temperature.

Figure 5. The error of the GPR (Gaussian Process regression) predictor as a function of the true temperature.

Figure 6. Modern and ancient data projected onto the first two compositional principal components. Black: Modern; Blue: Eocene (Inglis et al., 2015); Red: Cretaceous (O'Brien et al., 2017).

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Figure 7. Diffusion map projection of the modern and ancient data. Black: Modern; Blue: Eocene (Inglis et al., 2015); Red: Cretaceous (O'Brien et al., 2017). separate clusters marked `A' are the outlying Cretaceous points with high GDGT-3 values. Branch 'B' is dominated by modern data points; branch 'C' by Cretaceous data.

Figure 8. The first diffusion component as a function of TEX_{86} . Some outlying points have been excluded from the plot for the purposes of visualisation. Black: Modern; Blue: Eocene (Inglis et al., 2015); Red: Cretaceous (O'Brien et al., 2017).

Figure 9. The first diffusion component as a function of temperature (modern data only).

Figure 10. Temperature residuals for the forward model.

Figure 11. The posterior distributions over temperature from the forward model for selected examples of high and low temperature, Eocene and Cretaceous, data points. The Gaussian error envelope from the GPR model is shown for comparison.

Figure 12. A histogram of normalised distances to the nearest sample in the modern data set for Eocene and Cretaceous data, excluding samples that had been screened out in previous compilations using BIT, MI and RI following the approach of (Inglis et al., 2015; O'Brien et al., 2017).

Figure 13. Comparison of temperature estimates for the BAYSPAR and the OPTiMAL GPR model, greyed out data fails the $D_{nearest}$ test (>0.5), and the colour scaling reflects $D_{nearest}$ values for those datapoints that pass

Figure 14. Inter-comparison of temperature estimates (top) and errors (bottom) for the Eocene and Cretaceous data calculated using BAYSPAR and OPTiMAL. Greyed out data fails the $D_{nearest}$ test (>0.5), and the colour scaling reflects $D_{nearest}$ values for those datapoints that pass. The black dashed line shows the $D_{nearest}$ threshold (>0.5).

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Climate of the Past
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Figure 1

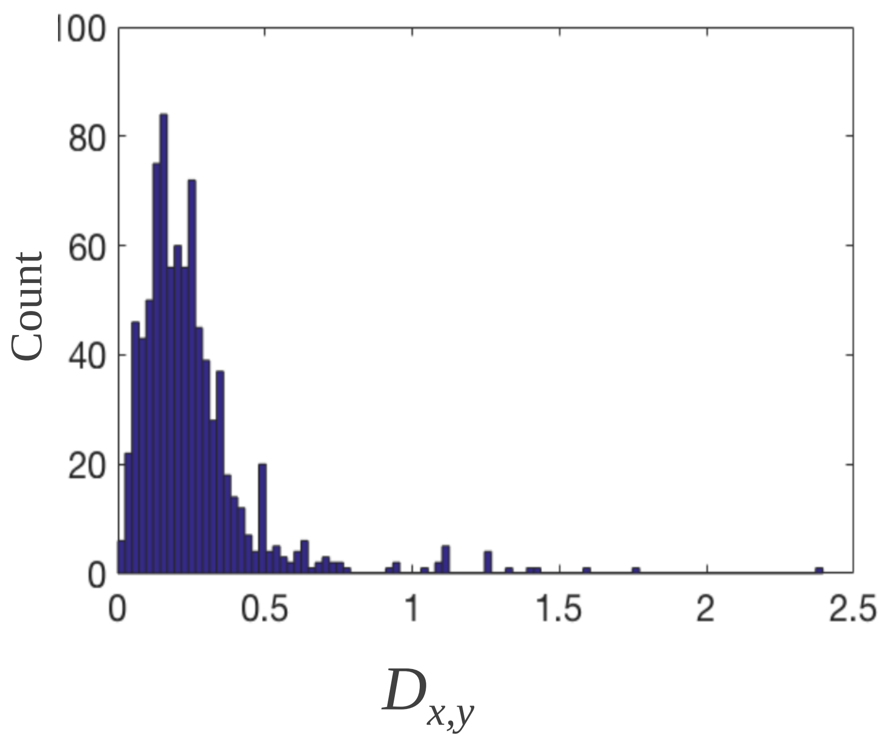

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Figure 2

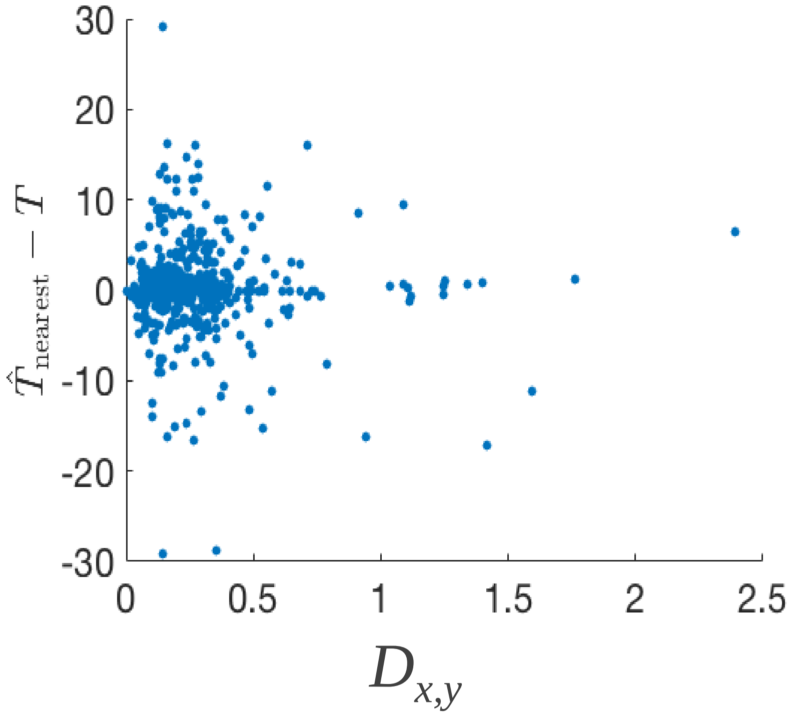

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Figure 3

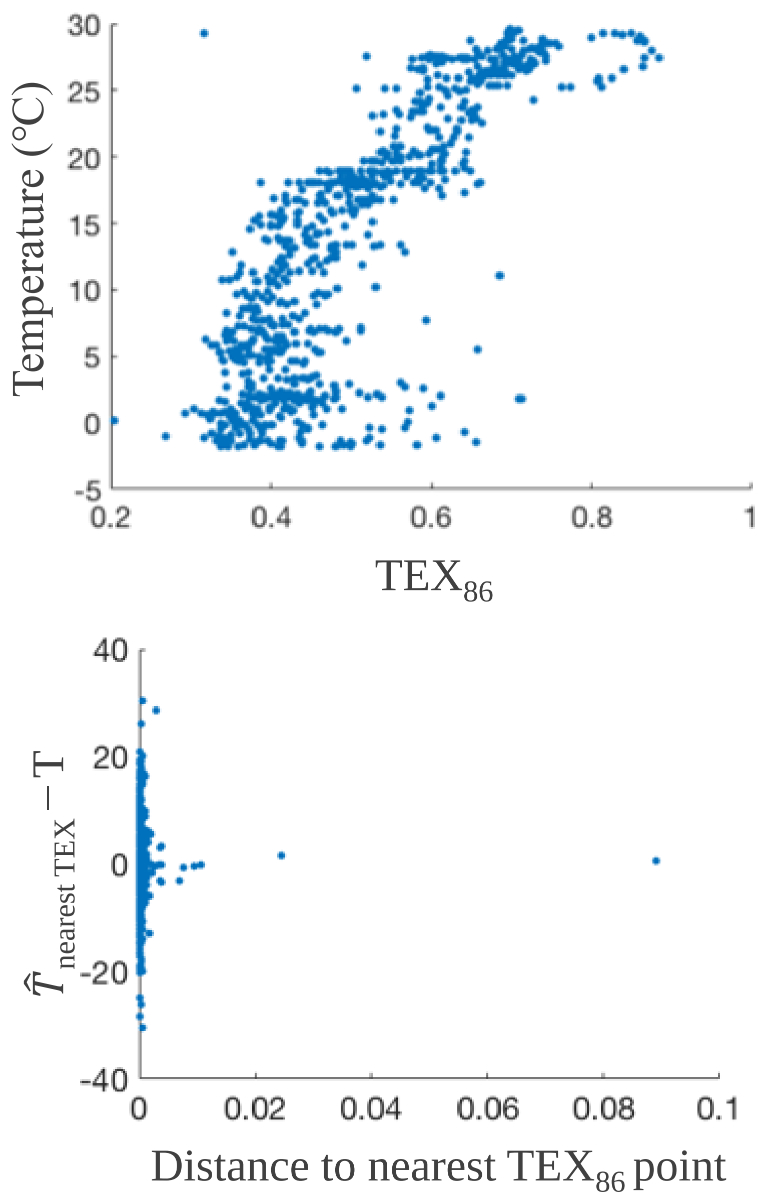

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Figure 4

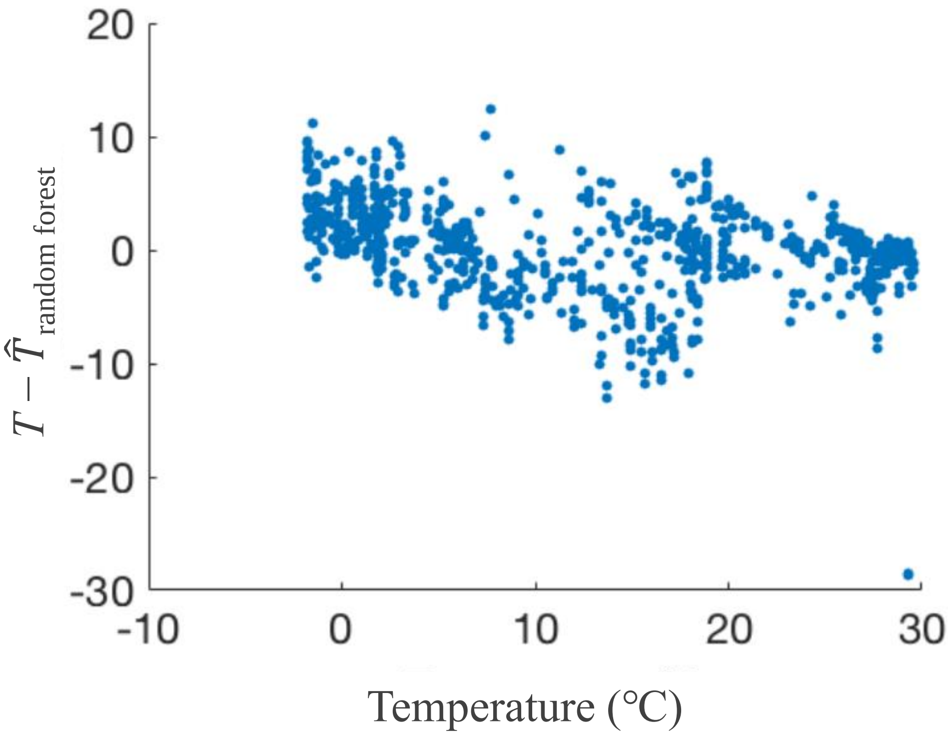

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Figure 5

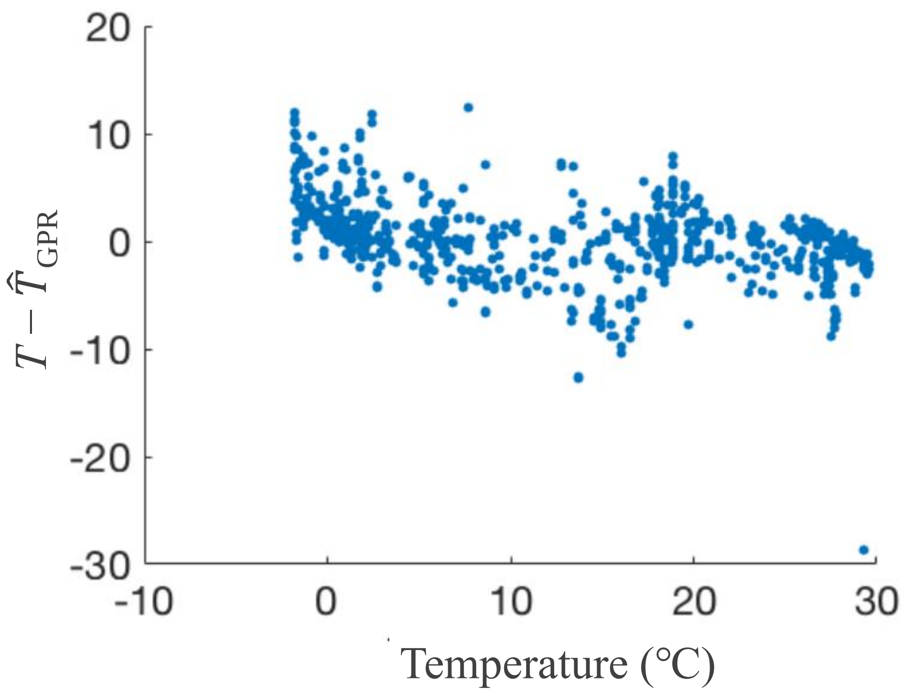

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Figure 6

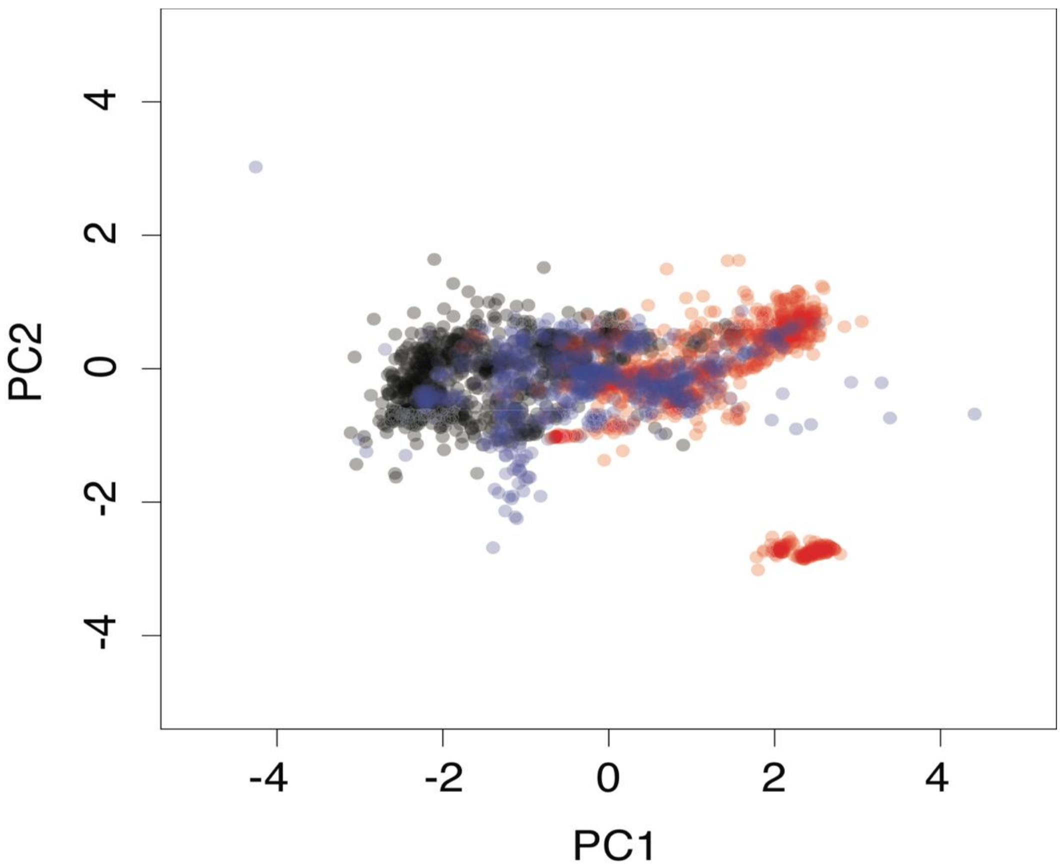

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Figure 7

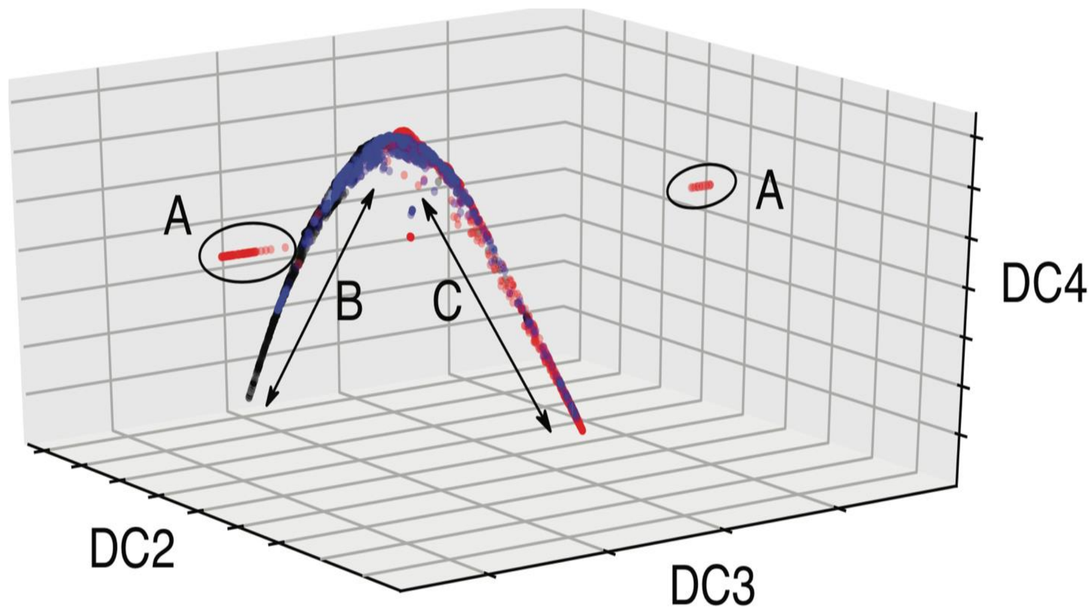

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Figure 8

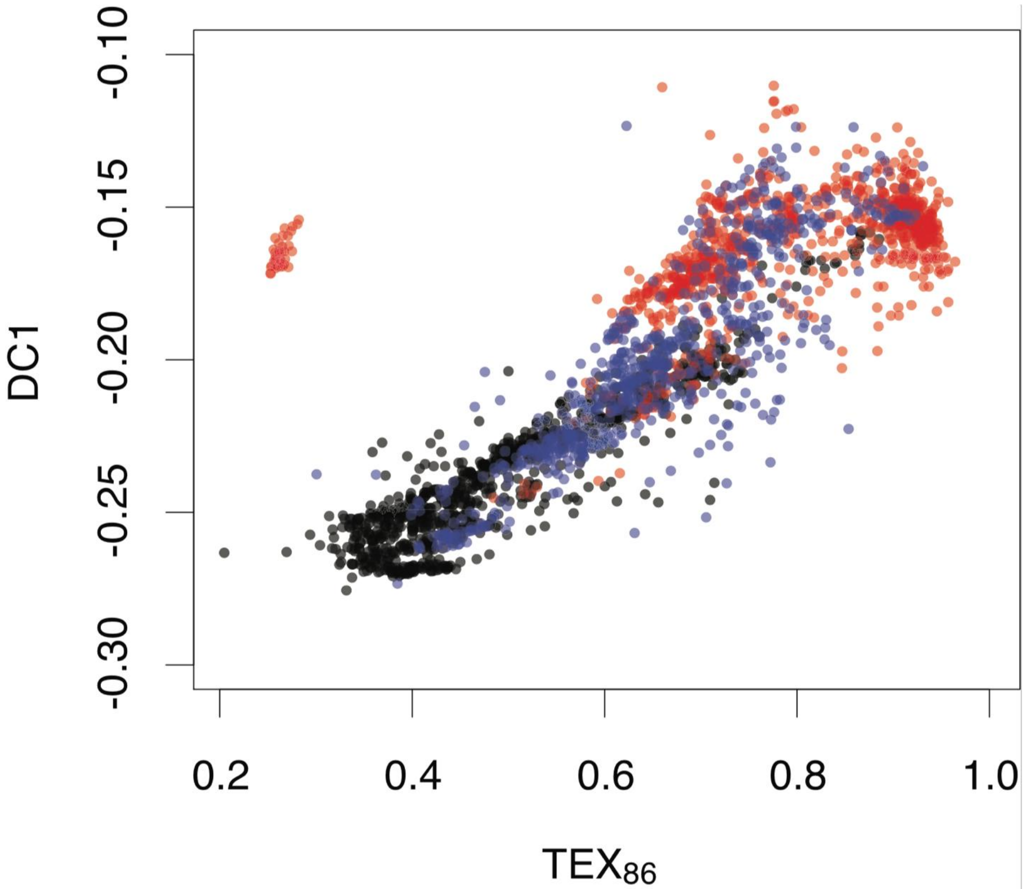

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Figure 9

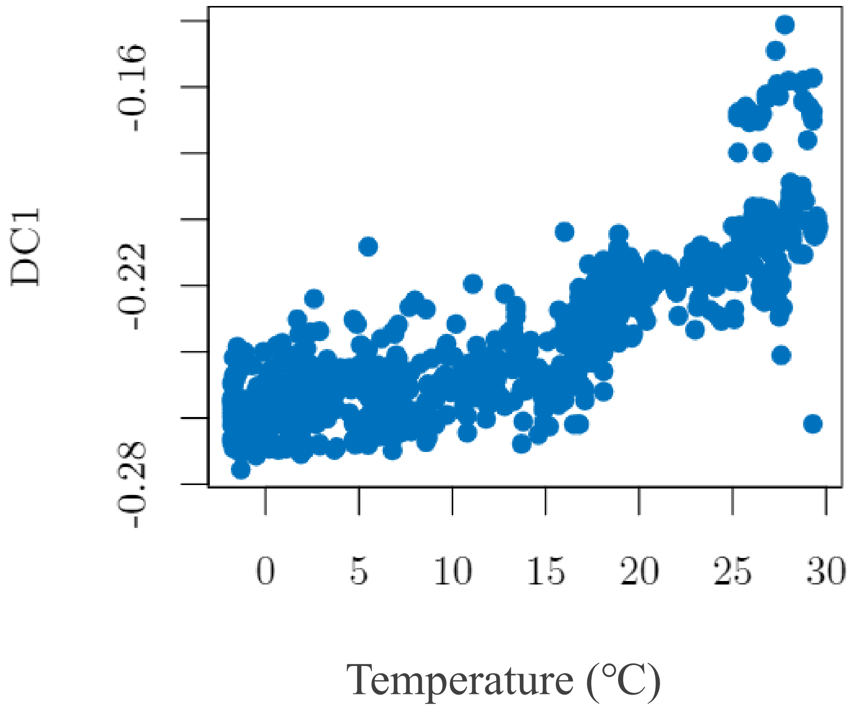

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Figure 10

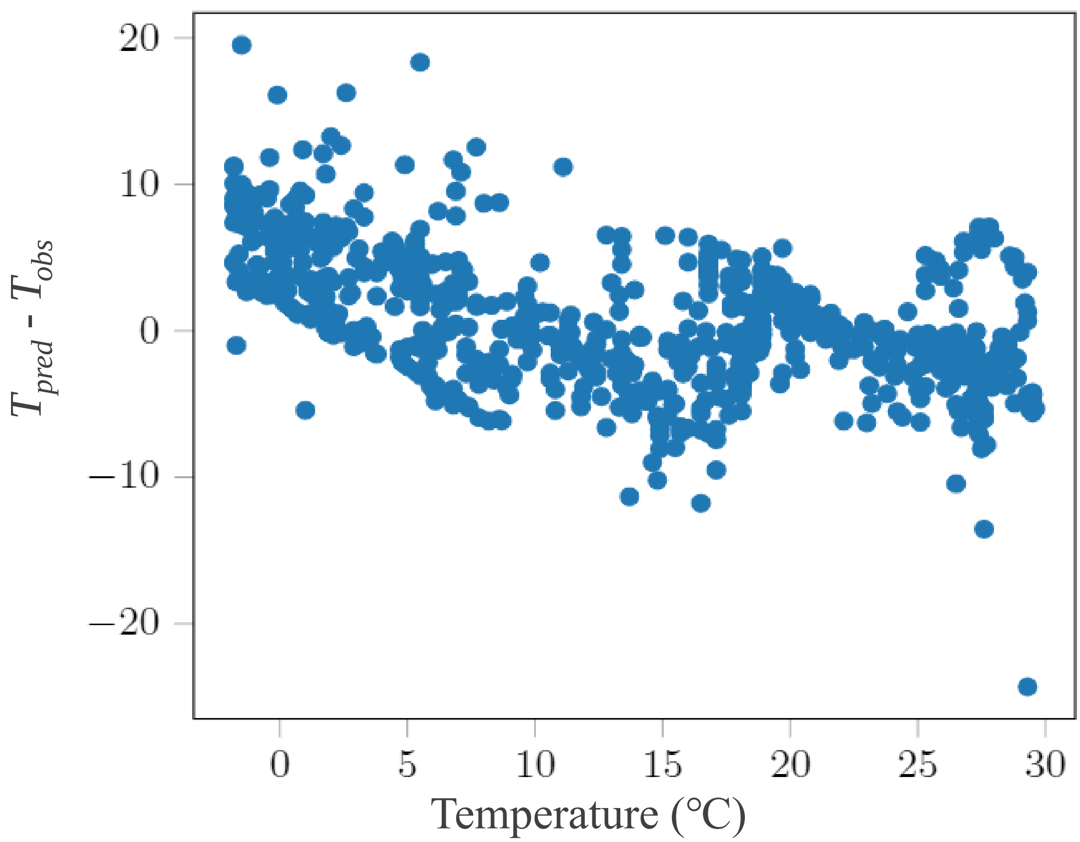

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Figure 11

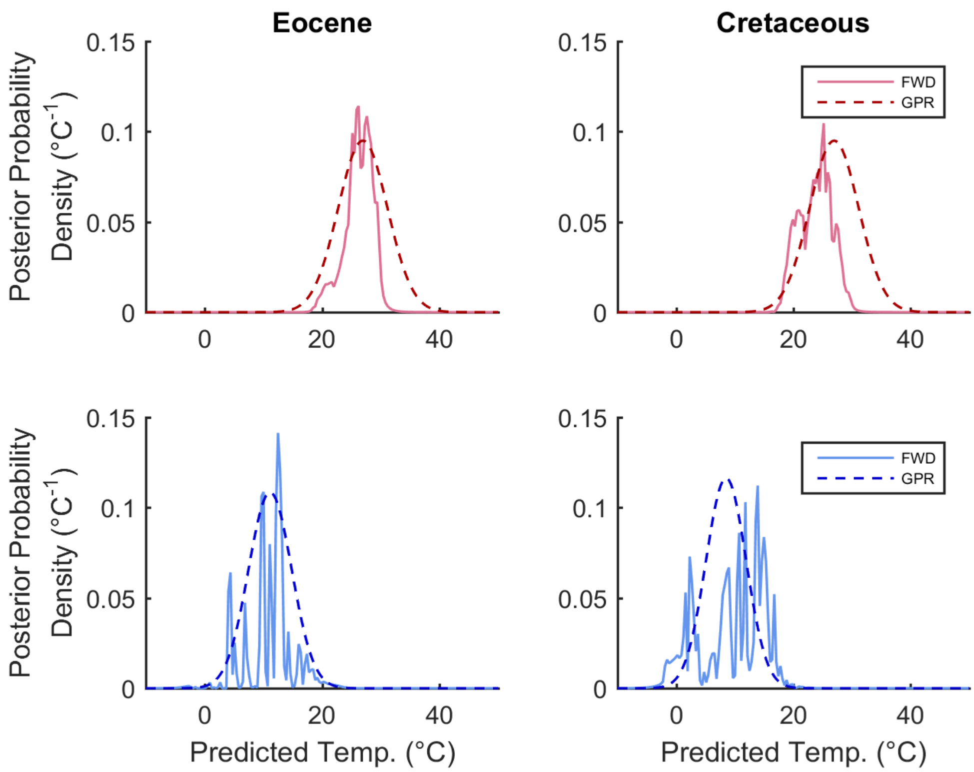

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Figure 12

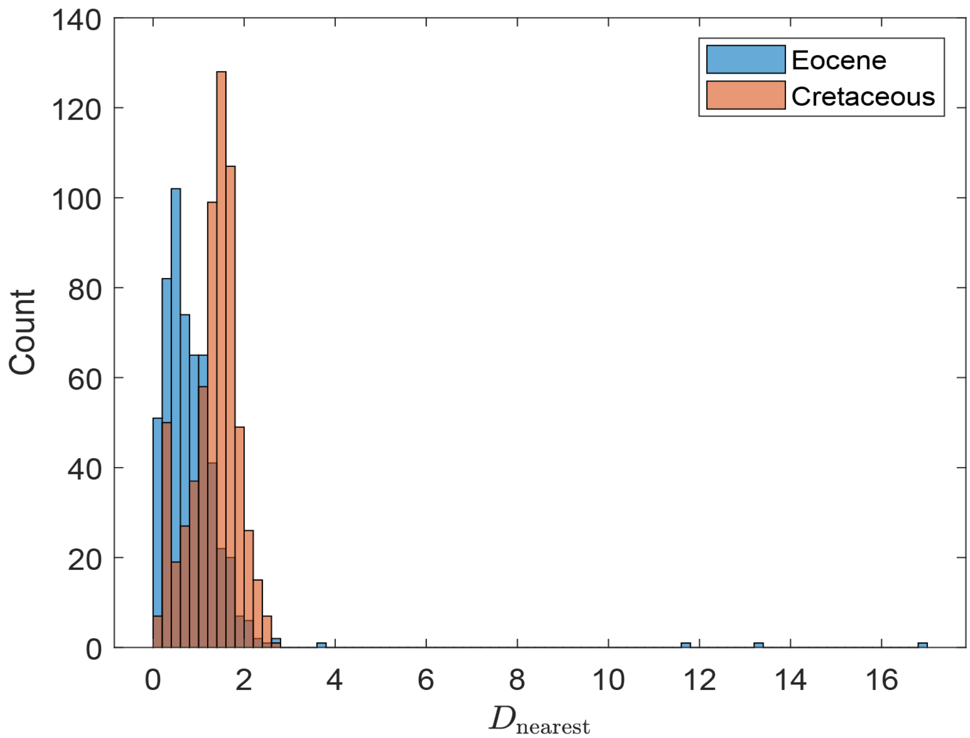

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Figure 13

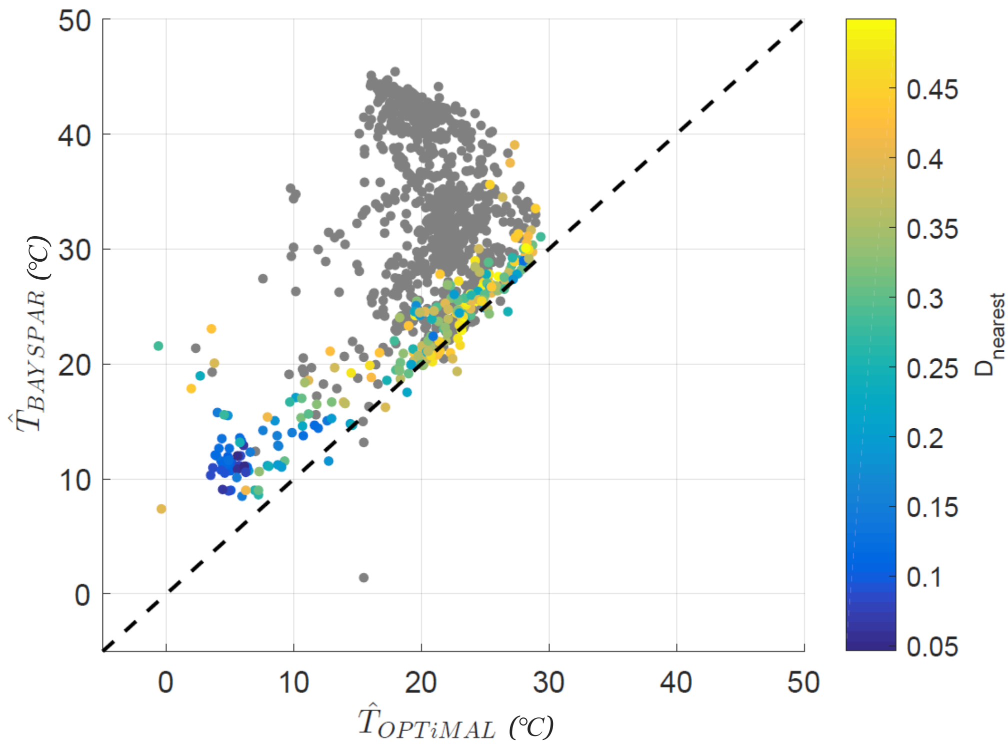

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Figure 14