



Invited review

Evaluating global temperature calibrations for lacustrine branched GDGTs: Seasonal variability, paleoclimate implications, and future directions

Boyang Zhao^{a,*}, James M. Russell^a, Victor C. Tsai^a, Ansis Blaus^b, Meredith C. Parish^a, Jie Liang^c, Alexander Wilk^a, Xiaojing Du^a, Mark B. Bush^b

^a Department of Earth, Environmental, and Planetary Sciences, Brown University, Providence, RI, 02912, USA

^b Institute for Global Ecology, Florida Institute of Technology, Melbourne, FL, 32901, USA

^c Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, 100101, China

ARTICLE INFO

Article history:

Received 4 March 2023

Received in revised form

4 May 2023

Accepted 6 May 2023

Available online 18 May 2023

Handling Editor: P Rioual

Keywords:

Branched GDGT

Temperature calibration

Seasonality

Lake sediments

Tropics

Mid- and high latitude region

Reconstruction

ABSTRACT

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) preserved in lake sediments are increasingly used to investigate past terrestrial temperatures. brGDGTs are ubiquitous in sedimentary environments, well-preserved, and the number of methyl groups in different brGDGTs is generally controlled by temperature. Current brGDGT calibrations largely rely on empirical correlations between the relative abundances of different brGDGTs in surface sediments and either mean annual or warm season air temperatures. These approaches may introduce complications in global temperature calibrations due to differences in the seasonality of temperature and variations in brGDGT production with latitude that are difficult to constrain. Here, we report new brGDGTs data from lake surface sediments obtained throughout the tropics including South America ($n = 57$), East Africa ($n = 21$), and Southeast Asia ($n = 13$), and revisit globally distributed brGDGT data. We find a uniform response of brGDGTs to mean annual air temperature across the tropics despite differences in the environmental and geological conditions in different regions highlighting the dominant influence of temperature on brGDGT distributions. brGDGTs in mid- and high latitude sediment show a qualitatively similar but quantitatively different response to those in the tropics. We show that temperature seasonality can partially explain the latitudinal differences, implying the need for latitudinally-dependent brGDGT calibrations and/or improved observations and models to constrain seasonal effects on brGDGTs. Combining our new data with previously published brGDGT data, we develop and apply improved temperature calibrations.

© 2023 Elsevier Ltd. All rights reserved.

1. Introduction

Paleoclimate reconstructions provide essential information to understand Earth's climate. These records allow us to evaluate climate model simulations under boundary conditions that differ from today and to develop novel theories on the causes of regional to global climate variations. Quantitative temperature reconstructions are particularly important given ongoing and future anthropogenic warming. To this end, many studies have reconstructed temperatures using a variety of proxies preserved in natural archives, such as alkenones and foraminiferal magnesium/

calcium in marine sediments (Lear et al., 2000; Volkman et al., 1980), fossil pollen and chironomids in lacustrine sediments (Fréchette et al., 2008; Medeiros et al., 2022), and geochemical approaches such as clumped isotopes (Eiler, 2011). Whereas proxies for sea surface temperature (SST) are well-developed and can produce reconstructions with high accuracy and precision (e.g., Herbert et al., 2010), an equivalent proxy for terrestrial temperature, independent of vegetation change, has been lacking.

Lipid biomarkers have produced important insights (Castañeda and Schouten, 2011; Inglis et al., 2022). In particular, branched glycerol dialkyl glycerol tetraethers (brGDGTs), a suite of bacterial membrane lipids, have emerged as a potentially valuable and widely applicable paleothermometer. brGDGTs consist of straight alkyl core chains with varying structures, including four to six methyl groups, and zero to two cyclopentyl moieties (De Jonge

* Corresponding author.

E-mail address: boyang_zhao@brown.edu (B. Zhao).

et al., 2014a; Sinninghe Damsté et al., 2000; Weijers et al., 2007). When the ambient environment changes, microbes can alter the compositions of their lipid membranes, including modifications in the degree of methylation of the lipids, to maintain appropriate membrane fluidity and permeability (Ernst et al., 2016; Sinensky, 1974; Zhang and Rock, 2008). brGDGTs are ubiquitous in many terrestrial archives, including soils, peats, loess, lacustrine sediments, and even fossil bones (Blaga et al., 2009, 2010; Buckles et al., 2014; Donders et al., 2009; Naafs et al., 2017b; Peterse et al., 2012; Wang et al., 2020; Weijers et al., 2006, 2007; Zhao et al., 2020). Variations in their structural chemistry are theoretically controlled by temperature, and many studies have shown that their relative abundances can be empirically calibrated to reconstruct past temperatures (De Jonge et al., 2014a; Dearing Crampton-Flood et al., 2020; Martínez-Sosa et al., 2021; Naafs et al., 2017b; Peterse et al., 2012; Raberg et al., 2021, 2022; Russell et al., 2018; Zhao et al., 2021b).

The first brGDGT calibration was reported by Weijers et al. (2007), who analyzed 130 globally distributed soil samples and found that changes in the degree of methylation and cyclization of the brGDGTs were dependent to mean annual air temperature (MAAT) and soil pH. Specifically, CBT (cyclization of branched tetraethers) was correlated with soil pH, and MBT (methylation of branched tetraethers) was related to both MAAT and soil pH. Thus, measurements of MBT paired with CBT might be used to determine past temperatures in sedimentary successions (Weijers et al., 2007). Further calibration of soil-derived brGDGTs as well as studies of brGDGT distributions in lake sediment, peats, and other environments refined the MBT-CBT proxy and broadened its use to a variety of sedimentary environments (Blaga et al., 2010; Loomis et al., 2012; Peterse et al., 2009, 2012; Tierney et al., 2010; Tierney and Russell, 2009; Weijers et al., 2011). De Jonge et al. (2014a) used an improved high performance liquid chromatography (HPLC) method to separate and analyze 5- and 6-methyl brGDGT isomers (Hopmans et al., 2016), and found that MBT^{SME}, which measures the degree of methylation of 5-methyl branched tetraethers, substantially improved soil brGDGT calibrations (De Jonge et al., 2014a; Dearing Crampton-Flood et al., 2020; Naafs et al., 2017a).

Many studies have successfully applied brGDGTs to estimate temperature in lakes, peats, and marine sediments (e.g., Dearing Crampton-Flood et al., 2021; Garelick et al., 2022; B. Zhao et al., 2022). Among these, brGDGTs in lake sediments have received the most intensive effort and study. Lacustrine brGDGT calibrations are particularly important as lakes are widely distributed in the environment, their sediments accumulate rapidly and often continuously, and the brGDGTs in well-dated sediment cores can be used to reconstruct past temperatures assuming the fossil brGDGTs record ambient temperatures at the time they were deposited. Initially, lacustrine brGDGTs were thought to derive from terrestrial input (Hopmans et al., 2004); however, further studies showed that brGDGTs in lakes derive primarily from *in situ* production (Bechtel et al., 2010; Colcord et al., 2015; Loomis et al., 2014b; Miller et al., 2018; Sinninghe Damsté et al., 2009; Tierney et al., 2010, 2012; Tierney and Russell, 2009; van Bree et al., 2020; Wang et al., 2012, 2023; Weber et al., 2015, 2018; Zhao et al., 2021b). For example, stable carbon isotopes of lacustrine brGDGTs are notably more depleted than those in the catchment soils (Weber et al., 2015), and the distribution of lacustrine sedimentary brGDGTs are often considerably different from surrounding soils (Tierney and Russell, 2009). Following the work of De Jonge et al. (2014a), Russell et al. (2018) analyzed brGDGTs in eastern African lake surface sediments and produced the first lacustrine brGDGT calibration to MAAT (Russell et al., 2018). This work showed that, on average, the lacustrine brGDGT calibration is $> 7^{\circ}\text{C}$ 'warmer' than the soil

brGDGT calibration (Russell et al., 2018). This finding was in agreement with previous work that did not separate brGDGT isomers (Loomis et al., 2011; Tierney et al., 2010), demonstrating a different temperature-brGDGT relationship in soils and lakes (De Jonge et al., 2014a; Russell et al., 2018). Since then, numerous studies developed lacustrine brGDGT calibrations that could be applied *in situ*, regionally or, potentially, globally (Dang et al., 2018; Feng et al., 2019; Liang et al., 2022; Martínez-Sosa et al., 2021; Raberg et al., 2021; Wang et al., 2021; Zhao et al., 2021b).

There are a variety of approaches to calibrate brGDGT to temperatures. Experimental data showed that brGDGTs in temperature-controlled microcosms produced a range of values consistent with field-based empirical calibrations (Martínez-Sosa et al., 2020). *In situ* calibrations are based on comparisons between brGDGTs produced in a target lake and corresponding continuous temperature observations (Zhao et al., 2021b) over seasons to years. Although their use in reconstructing temperature from broadly distributed lakes is uncertain, and long-term observations are difficult to obtain in most lakes, *in situ* studies can help validate the use of lacustrine brGDGTs to reconstruct past temperatures (B. Zhao et al., 2022). Given the limitations of experimental and *in situ* studies, most brGDGT calibrations use a space-for-time substitution in which brGDGT abundances in surface sediments from numerous lakes are compared with local temperatures. Due to a lack of observational lake temperature monitoring, these studies calibrate brGDGTs to air temperature (Livingstone et al., 1999). Whereas some of these calibrations have been done regionally (Russell et al., 2018), Martínez-Sosa et al. (2021) provided a global brGDGT Bayesian calibration including sites from low-, mid-, and high-latitude regions. Similarly, Raberg et al. (2021) analyzed brGDGT samples from 43 lakes in Arctic Canada and Iceland and combined them with data from previous studies, and produced several brGDGT-temperature calibrations that could form the basis for temperature reconstructions in Arctic and near-Arctic environments.

The development and application of global lacustrine brGDGT calibrations remain difficult, however, due to several assumptions and potential biases. Among these, Martínez-Sosa et al. (2021) and Raberg et al. (2021) emphasized that lacustrine brGDGTs in mid- and high latitude regions could have seasonal biases, presumably owing to lower rates of brGDGT production during cold seasons. They therefore calibrated brGDGTs to the mean temperature during the Months Above Freezing (MAF, defined as the average value of monthly temperatures that are above 0°C) instead of MAAT. MAF and MAAT in the tropics are equal because the tropics do not experience significant seasonal temperature cycles (Martínez-Sosa et al., 2021; Raberg et al., 2021), allowing integration of samples from tropical and higher latitude calibrations into global ones. Whereas monitoring studies have shown that although brGDGT production is suppressed in mid- and high-latitude lakes in winter, supporting calibration of brGDGTs to MAF, brGDGTs are produced in winter in lake water columns (e.g., Loomis et al., 2014b). The assumption that winter brGDGT fluxes can be ignored in calibrations to MAF is therefore sensitive to the relative summer and winter production, and could bias temperature estimates in regions with little seasonality and/or if seasonal brGDGT fluxes and temperature seasonality change through time.

Moreover, in existing global calibrations, the currently available sites for brGDGT calibration in the tropics are almost entirely from Africa (Russell et al., 2018), with only four sites from tropical South America (relative to 73 from Africa) (Martínez-Sosa et al., 2021; Russell et al., 2018). Although recent research points to brGDGT production by Acidobacteria (Chen et al., 2022; Halamka et al., 2023; Sinninghe Damsté et al., 2011, 2018), the organisms responsible for brGDGT production in lakes remain unknown (van Bree

et al., 2020; Weber et al., 2018). Studies in soils suggest important controls of microbial community composition on brGDGTs (De Jonge et al., 2019), and water chemistry could impact brGDGTs in lacustrine environments (Wang et al., 2021). These observations suggest that brGDGT-based temperature calibrations might be improved through more broadly distributed tropical sampling.

Here, we examine brGDGTs in lake surface sediments from pan-tropical sites, including South America ($n = 57$), East Africa ($n = 21$), and Southeast Asia ($n = 13$). We reevaluate the current global calibrations, investigate the impact of seasonality on brGDGT calibrations, and establish improved lacustrine brGDGT calibrations for lakes across the globe.

2. Materials and methods

2.1. Sample collection, lipid extraction, and brGDGT analysis

Surface sediments (within the top 5 cm) were obtained from 91 tropical lakes (Fig. 1). All sediment samples were freeze-dried and then homogenized. To acquire the total lipid extract (TLE), a Dionex accelerated solvent extractor (ASE 350) was used with a solution of dichloromethane (DCM) and methanol (MeOH) (9:1, v/v). All TLEs were separated into apolar and polar fractions with column chromatography using alumina oxide as the stationary phase, and hexane/DCM (9:1, v/v) and DCM/MeOH (1:1, v/v) as mobile phases. The polar fractions containing the brGDGTs were dried under gentle N_2 flow and dissolved in hexane/isopropanol (99:1, v/v). Subsequently, the polar fractions were filtered through 0.45 μm PTFE syringe filters, and analyzed on an Agilent/Hewlett Packard 1100 series high-performance liquid chromatograph-mass spectrometer (HPLC-MS) at Brown University using the method presented in Hopmans et al. (2016) to differentiate the 5- and 6-methyl brGDGT isomers. Mass scanning was conducted in selected ion monitoring mode for mass/charge ratios of 1302, 1300, 1298, 1296, 1292, 1050, 1048, 1046, 1036, 1034, 1032, 1022, 1020, and 1018.

2.2. Statistical analyses

We combine the 91 new tropical lacustrine samples with brGDGT data from previous studies (Baxter et al., 2019; Cao et al., 2020; Dang et al., 2018; Li et al., 2017; Liang et al., 2022; Martínez-Sosa et al., 2021; Ning et al., 2019; Qian et al., 2019; Raberg et al., 2021; Russell et al., 2018; Wang et al., 2021; Weber et al., 2018; Zhao et al., 2021b) to generate a new global dataset containing 552 sites with 187 tropical sites in total.

We used redundancy analyses (RDA) to evaluate the relationship between fractional abundances of brGDGTs and explanatory environmental parameters, including MAAT, MAF, water depth, and lake surface area. We performed RDA for brGDGTs from tropical and mid-to high latitude lakes separately, due to the different brGDGT patterns that we will discuss below.

To assess the relationship between brGDGT methylation and temperatures, we used the previously established MBT'_{5ME} index (De Jonge et al., 2014a) which has been widely used to investigate past temperatures (e.g., Miller et al., 2018).

$$MBT'_{5ME} = (Ia + Ib + Ic)/(Ia + Ib + Ic + IIa + IIb + IIc + IIIa) \quad (1)$$

Higher abundances of more methylated brGDGTs (e.g., IIa, IIIa) decrease MBT'_{5ME} in environments with a lower temperature, whereas higher abundances of less methylated brGDGTs (e.g., Ia) increase the MBT'_{5ME} in warmer climatic conditions.

The MBT'_{6ME} index (Eq. (2)) was defined in Dang et al. (2016), wherein 6-methyl brGDGTs substitute for the corresponding 5-methyl brGDGTs in MBT'_{5ME} .

$$MBT'_{6ME} = (Ia + Ib + Ic)/(Ia + Ib + Ic + IIa' + IIb' + IIc' + IIIa') \quad (2)$$

MBT'_{6ME} was found to correlate with temperature in some alkaline lakes (Dang et al., 2018; Liang et al., 2022), although it has not been widely applied worldwide.

The isomer ratio (IR_{6ME} , Eq. (3)) is an index commonly used to evaluate the relative abundances of 5- and 6-methyl brGDGTs (De Jonge et al., 2014b; Yang et al., 2015). The strong correlation

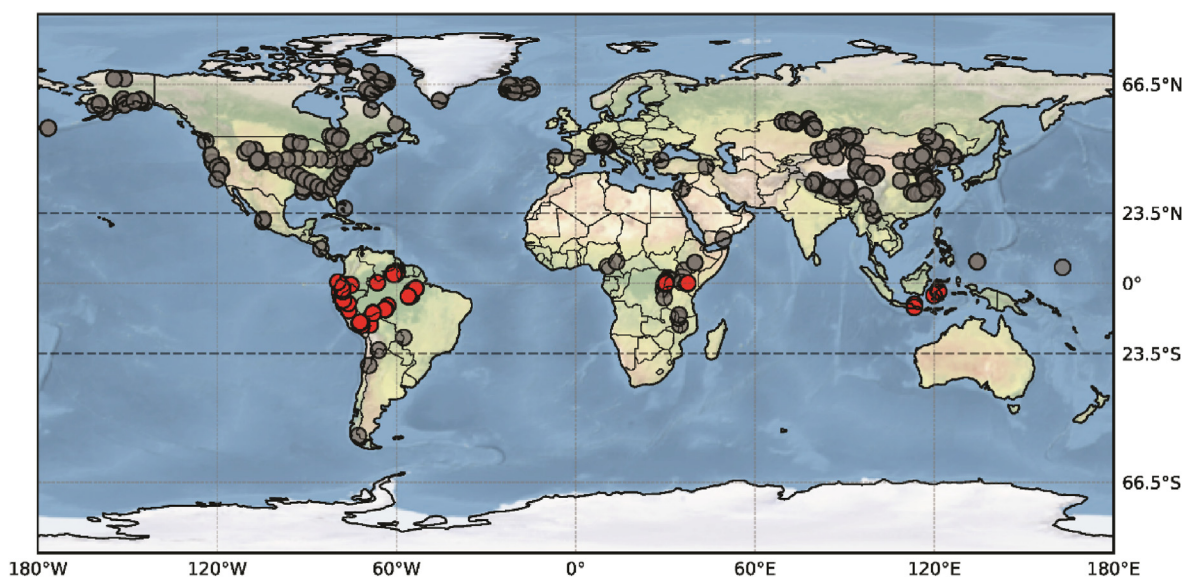


Fig. 1. Global map with all locations of brGDGTs discussed in the text. The red circles represent the samples from our study. Grey circles represent the samples from previous studies (Baxter et al., 2019; Cao et al., 2020; Dang et al., 2018; Li et al., 2017; Liang et al., 2022; Martínez-Sosa et al., 2021; Ning et al., 2019; Qian et al., 2019; Raberg et al., 2021; Russell et al., 2018; Wang et al., 2021; Weber et al., 2018; Zhao et al., 2021b). brGDGTs from the lakes located between both the thick dashed lines ($<23.5^\circ N$ and $>23.5^\circ S$) are used to calculate the pan-tropical calibrations.

between IR_{6ME} and pH was found first in soils (De Jonge et al., 2014a). Recent studies show that IR_{6ME} is potentially controlled by pH or salinity in lake environment (Raberg et al., 2022; Wang et al., 2021).

$$\text{IR}_{6\text{ME}} = (\text{IIa}' + \text{IIb}' + \text{IIc}' + \text{IIla}' + \text{IIlb}' + \text{IIlc}')/(\text{IIa} + \text{IIa}' + \text{IIb} + \text{IIb}' + \text{IIc} + \text{IIc}') \quad (3)$$

We explored the use of several existing lacustrine calibrations to estimate temperatures from brGDGT distributions in our samples. The first one is based on the relationship between MBT'_{5ME} from a suite of East African lakes and MAAT (Russell et al., 2018):

$$\text{MAAT} = -1.21 + 32.42 \times \text{MBT}'_{5\text{ME}} \quad (4)$$

Raberg et al. (2021) developed new calibrations of brGDGTs to MAF (instead of MAAT) using both “Meth set” and “Full set” brGDGTs. By grouping brGDGTs with the same number of cyclopentane rings and the same methylation positions, the “Meth set” was designed to solely reflect the degree of methylation (Raberg et al., 2021). The fractional abundances were calculated within the “Meth set” and then correlated quadratically against MAF (Raberg et al., 2021). The Meth set calibration is:

$$\begin{aligned} \text{MAF} = & 92.9 (\pm 15.98) + 63.84 (\pm 15.58) \times \text{flb}^2_{\text{Meth}} - 130.51 \\ & (\pm 30.73) \times \text{flb}_{\text{Meth}} - 28.77 (\pm 5.44) \times \text{flIa}^2_{\text{Meth}} - 72.28 \\ & (\pm 17.38) \times \text{flIb}^2_{\text{Meth}} - 5.88 (\pm 1.36) \times \text{flIc}^2_{\text{Meth}} + 20.89 \\ & (\pm 7.69) \times \text{flIa}^2_{\text{Meth}} - 40.54 \\ & (\pm 5.89) \times \text{flIa}_{\text{Meth}} - 80.47 (\pm 19.19) \times \text{flIb}_{\text{Meth}} \end{aligned} \quad (5)$$

The “Full set” calculation used all 15 isomers without grouping brGDGTs by isomer, cyclization, or methylation (Raberg et al., 2021). Similar quadratic regression was performed and the Full set calibration is:

$$\begin{aligned} \text{MAF} = & -8.06 (\pm 1.56) + 37.52 (\pm 2.35) \times \text{fla}_{\text{Full}} - 266.83 \\ & (\pm 98.61) \times \text{flb}^2_{\text{Full}} + 133.42 (\pm 19.51) \times \text{flb}_{\text{Full}} + 100.85 \\ & (\pm 9.27) \times \text{flIa}^2_{\text{Full}} + 58.15 (\pm 10.09) \times \text{flIa}^2_{\text{Full}} + 12.79 \\ & (\pm 2.89) \times \text{flIa}_{\text{Full}}. \end{aligned} \quad (6)$$

We also tested the global Bayesian calibration for lacustrine brGDGTs (BayMBT) using the MATLAB function developed by Martínez-Sosa et al. (2021).

In this study, we use linear regression model to explore the relationship between temperature and MBT'_{5ME}. Such regression of temperature on MBT'_{5ME} may be affected by ‘regression dilution’, where errors in the independent variable may bias the slope towards zero (Deearing Crampton-Flood et al., 2020; Naafs et al., 2017a). Applying Deming regression may help alleviate this bias (Naafs et al., 2017a); however, this approach requires knowledge of (or assumptions for) the uncertainties in both temperature and MBT'_{5ME}. Temperature uncertainties are not well constrained in the temperature dataset we use for this study (Fick and Hijmans, 2017). The analytical errors of MBT'_{5ME} are hard to estimate since the brGDGT data we use here are generated by different labs across the globe. Although assessment of the effects of regression dilution would be ideal, our approach should give unbiased predictions of temperature if we assume the errors of the independent variable are the same as the ones in the predictive model (Carroll et al., 2006).

2.3. Environmental data

Temperatures in previous calibrations were derived from a variety of sources including observations, local models, and gridded climate data products. To avoid potential biases from mixed data sources, air temperatures at all lakes analyzed in this study are

obtained from the Worldclim dataset (version 2.1) (Fick and Hijmans, 2017). The Worldclim dataset provides monthly average temperatures from 1970 to 2000 CE with a horizontal resolution of 30 s (~1 km) (Fick and Hijmans, 2017). Air temperature data were obtained not only for the 91 new lakes analyzed for this study but also for all previously published studies (Cao et al., 2020; Dang et al., 2018; Li et al., 2017; Liang et al., 2022; Martínez-Sosa et al., 2021; Ning et al., 2019; Qian et al., 2019; Raberg et al., 2021; Russell et al., 2018; Wang et al., 2021; Weber et al., 2018; Zhao et al., 2021b). We note that the Worldclim data have been successfully used in some previous studies, for example in Raberg et al. (2021), Wang et al. (2021), and Liang et al. (2022). We obtained MAAT (the average of the temperatures for a total of 12 months) as well as MAF (the average of the monthly temperatures that are above zero). For the tropical lakes, the Worldclim temperature data show a significant correlation to the observed MAAT in the previous studies (Loomis et al., 2014a; Russell et al., 2018) with a small RMSE of 1.04 °C (Fig. S1), validating the usage of the Worldclim temperature data in our study.

Lake water depths, and surface area for all lakes are acquired from the original references (Dang et al., 2018; Liang et al., 2022; Loomis et al., 2014a; Martínez-Sosa et al., 2021; Raberg et al., 2021; Wang et al., 2021; Weber et al., 2018; Zhao et al., 2021b) and the references therein.

2.4. Nonlinear modeling of lacustrine brGDGTs

To investigate the potential impacts of seasonality on brGDGT-based temperature calibrations, we used the nonlinear modeling framework previously applied to soil brGDGTs by J. Zhao et al. (2022). This framework assumes that brGDGTs in soils accumulate over a relatively long time span, that the rate of their production has a nonlinear relationship with temperature, and that environmental factors such as soil moisture and pH could contribute to the brGDGT distribution changes as well. This model explicitly incorporates the influences of temperature seasonality, seasonal growth, and/or preservation on changes in the MBT'_{5ME} index (Zhao et al., 2022). This model is consistent with lab experiments and shows promise in reducing the uncertainty in soil-based brGDGT calibrations and applications (Zhao et al., 2022).

Our goal in using this model is to test the effects of temperature seasonality on brGDGTs in lake sediments. We therefore simplified the model by removing the effects of moisture and pH:

$$\ln \left(\frac{1}{\text{MBT}'_{5\text{ME}}} - 1 \right) = m_0 + m_1 (\Delta T) + m_2 (\Delta T)^2 + m_3 (\Delta T)^3 + m_s T_s^2 \quad (7)$$

where m_0 , m_1 , m_2 , m_3 , and m_s are unknown parameters to be fitted to data and ΔT and T_s describe different aspects of temperature that explain MBT'_{5ME}. Unlike MAF, which removes all months with a temperature below 0 °C, we use a modified MAAT (MAAT_{modified}) that assigns a value of 0 °C to all months with a temperature below 0 °C. This assumes that brGDGT production in lake water columns continues near freezing in months with average air temperatures below freezing. ΔT is MAAT_{modified} - T_0 and T_0 was adopted as 10 °C according to J. Zhao et al. (2022). Temperature seasonality is modeled as a seasonal sinusoid which has an amplitude of T_s . It should be noted that T_s is near zero in both tropical and polar regions because temperature seasonality is naturally weak in the tropics and the seasonal temperature amplitude is reduced by using 0 °C for winter months in the Arctic. Thus, T_s is largest in mid-latitude regions.

Table 1
Parameter values for the nonlinear lacustrine brGDGT model parameter.

T_0 ($^{\circ}\text{C}$)	m_0	m_1 ($^{\circ}\text{C}^{-1}$)	m_2 ($^{\circ}\text{C}^{-2}$)	m_3 ($^{\circ}\text{C}^{-3}$)	m_5 ($^{\circ}\text{C}^{-2}$)
10	3.88×10^{-1}	-7.96×10^{-2}	1.86×10^{-3}	-4.33×10^{-4}	-3.08×10^{-3}

The model was trained with brGDGTs in global lake surface sediments ($n = 552$) including our new and previously published data and paired modified MAAT (Table 1). To assess the influences of nonlinear temperature effects and seasonality, we calculated a linear regression between $\text{MBT}'_{5\text{ME}}$ and $\text{MAAT}_{\text{modified}}$, as well as a nonlinear model without temperature seasonality (T_5).

3. Results

3.1. brGDGT distributions

brGDGTs were found in all 91 lake surface sediment samples we analyzed. In all samples, brGDGT-Ia dominates the distribution with a mean fractional abundance of 0.59 (Fig. 2a). brGDGTs-IIa, IIa', Ib, IIIa, IIIa', IIb, IIb', and Ic are found in most of the samples with mean fractional abundances of 0.12, 0.08, 0.07, 0.05, 0.03, 0.02, 0.02, and 0.02, respectively. Other brGDGT compounds (brGDGT-IIc, IIc', IIIb, IIIb', IIc, and IIc') were present in measurable quantities only in some samples and their fractional abundance is lower than 0.01. The relative abundances of tetramethyl, pentamethyl, and hexamethyl brGDGTs vary in our samples following a pattern that is similar to the global lacustrine brGDGT distributions (Fig. 2b).

Since more than 50% of the 187 tropical lake sediment samples do not contain one or more of brGDGT-IIIb, IIIb', IIc, IIc', IIc, and IIc', these compounds were removed from the data. We then calculate the fractional abundances ($f(x)$) of the remaining nine brGDGTs (which constitute 99.3% of the brGDGTs), i.e., the fractional abundance of brGDGT-Ia is written as $f(\text{Ia})$ prior to statistical analysis (RDA and regression). $\text{MBT}'_{5\text{ME}}$ and the fractional abundances of brGDGT Ia and Ib, have strong positive scores on the first axis of the Principal Component analysis (PC1), which explained 84.47% of the variance in the brGDGT data (Fig. 3a). brGDGT IIa and IIIa exhibit strong negative scores on PC1. Meanwhile, MAAT has the strongest positive score of the environmental variables on PC1. Limnological

parameters (depth and surface area) show more variance on the second axis of the Principal Component analysis (PC2) (Fig. 3a). In mid- and high latitude lakes (Fig. 3b), fractional abundances are calculated based on all 15 brGDGTs. $\text{MBT}'_{5\text{ME}}$ and brGDGT Ib, Ic, IIa', IIb, and IIIa have strong positive scores on PC1 while brGDGT IIIa shows a distinct negative score on PC1. Both MAAT and MAF have positive scores on PC1, and MAF has a stronger positive score. Limnological parameters, including depth and surface area, are more connected to PC2. Thus, the RDA of tropical and mid-to high latitude lakes show generally similar patterns and suggest a strong influence of temperature on brGDGT distributions.

3.2. Models and calibrations for brGDGTs

Application of the global calibrations (Martínez-Sosa et al., 2021; Raberg et al., 2021) to the tropical lake dataset shows that although the predicted temperatures track trends in observed temperatures (Fig. 4a, c, and e), the models generally overestimate temperatures (Fig. 4b, d, and f), particularly in the coldest tropical lakes (Fig. 4). Observed temperatures are generally lower than the brGDGT-inferred temperatures based on the Bayesian, Meth set, and Full set calibrations (Martínez-Sosa et al., 2021; Raberg et al., 2021) applied to our tropical lake sediment samples. This bias is most apparent in the Full set calibration, which overestimates temperatures at both cold and warm lakes, but is also present in the application of the BayMBT and the Meth set calibrations (Fig. 4b, d). The warm bias reaches a maximum of 9.7 $^{\circ}\text{C}$ when the Bayesian calibration was applied to the surface sediments from Lake Progreso in South America (Fig. 4b). The Meth Set calibration has the smallest bias.

Application of the non-linear model also reveals differences in the response of $\text{MBT}'_{5\text{ME}}$ to temperature. The nonlinear and linear models are generally similar, with RMSEs (root mean square error) of 0.111 and 0.116, respectively (Fig. 5b). The "full model", which

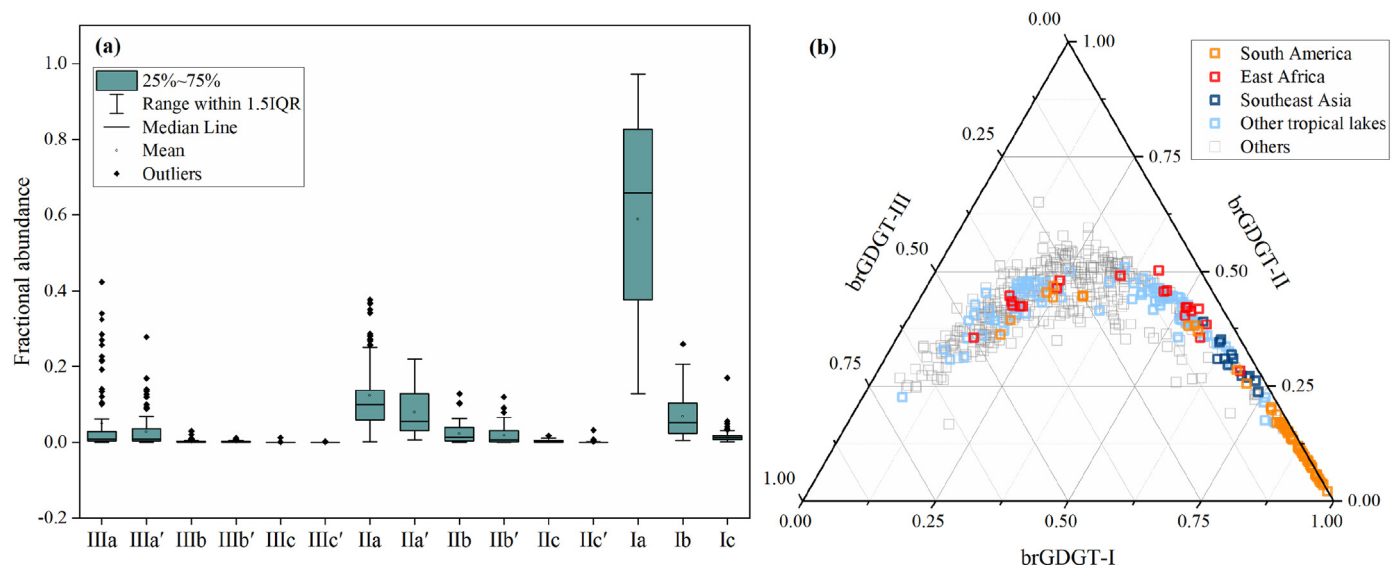


Fig. 2. (a) Fractional abundances of our new brGDGT dataset. (b) Ternary plot showing the comparison between our new data and the brGDGTs in surface sediment from global lakes.

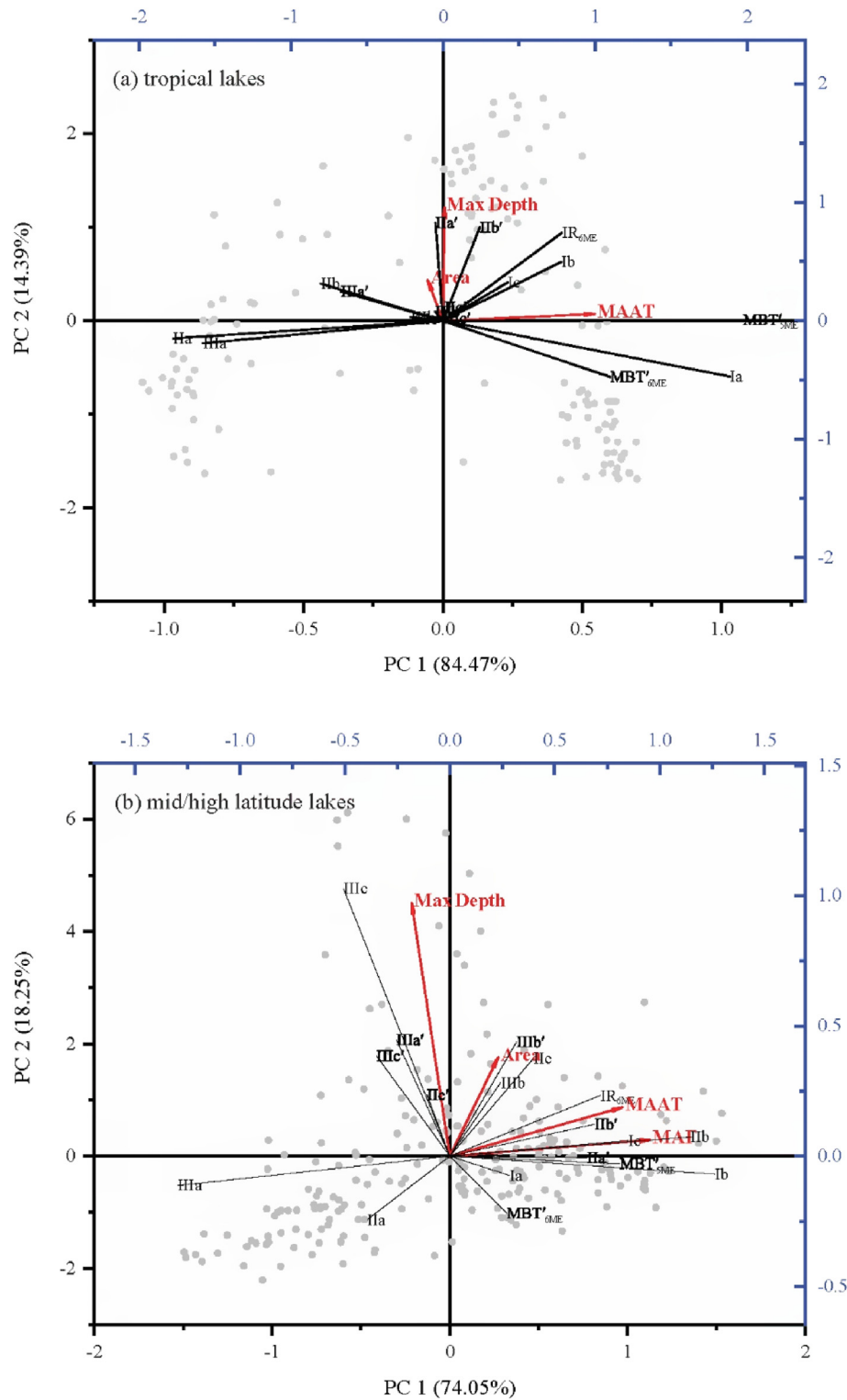


Fig. 3. Redundancy analysis (RDA) results for tropical lakes (a) and mid-to high latitude lakes (b). The grey dots indicate axis scores of surface sediments. The black vectors represent axis scores of brGDGTs. The red vectors represent axis scores of environmental data, including lake max depth (Max Depth), lake surface area (Area), MAAT, and MAF.

incorporates both non-linear and seasonal effects, better captures variations in MBT_{5ME} than the linear and non-linear models. Analysis of residuals indicates that temperature bias increases as a function of seasonality (T_3 , Fig. 5c). Parameters for the full model are given in Table 1.

4. Discussion

4.1. Lacustrine brGDGTs from different regions have varying responses to temperatures

The application of global brGDGTs calibrations to predict

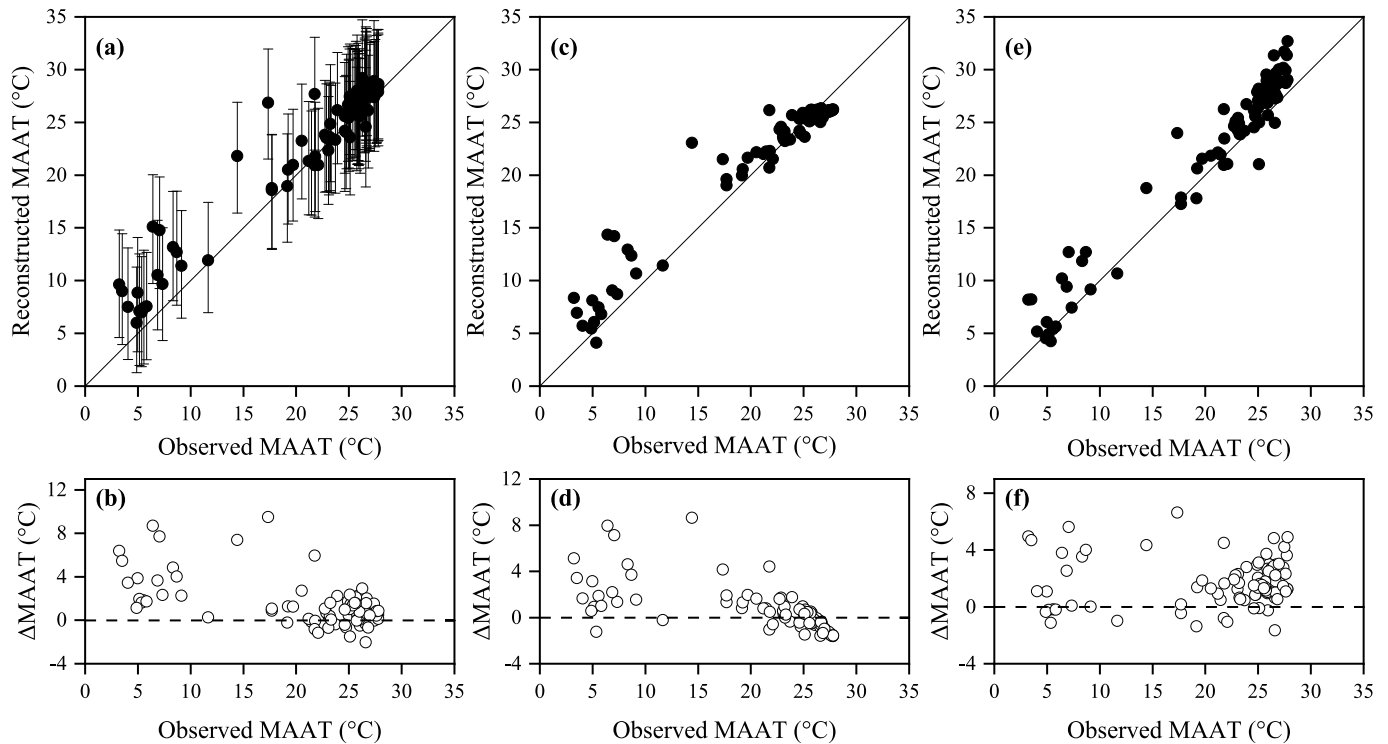


Fig. 4. Observed MAAT of our new tropical lakes compared to brGDGT inferred MAAT reconstructions with BayMBT (a), Meth set (c), and Full set (e) calibrations (Martínez-Sosa et al., 2021; Raberg et al., 2021). The corresponding offsets between reconstruction and observations are shown in (b), (d), and (f).

temperatures (Martínez-Sosa et al., 2021; Raberg et al., 2021) in our new tropical lake dataset revealed a notable warm bias. The bias is especially notable for high-elevation cold lakes, although the Full set calibration seems to over-predict the temperatures for the entire dataset (Fig. 4b, d, and f). The estimated temperatures did generally track the observed temperatures, indicating that the calibrations qualitatively captured the gradients in temperature between sites (Fig. 4). These global calibrations generally used MAF instead of MAAT. The use of MAF as a calibration target assumes that lacustrine brGDGTs are mainly produced in summer and thus reflect summer temperatures, whereas cold season production and temperatures (air temperature below 0 °C) suppress brGDGT production enough to make the contributions negligible. This assumption was likely justified in many soils, where frozen conditions would limit bacterial activity. Data to test this assumption in lakes is limited, but studies of Lower King Pond, and Basin Pond in Northeast USA, and Lake Igaliu in southern Greenland (Loomis et al., 2014b; Zhao, 2021; Zhao et al., 2021a) analyzed monthly brGDGT fluxes in the settling particulate matter in lake water columns and observed brGDGT fluxes to the sediment in winter under the ice when air temperatures averaged less than 0 °C. This suggests that winter brGDGTs should not be completely ignored in calibrations.

Based on these studies, MAF calibrations could ignore a potentially important flux of “cold brGDGTs” to the sediments. Omitting the winter brGDGT fluxes and associated temperatures would thus result in the calibration of the integrated annual flux of brGDGTs to temperatures warmer than the brGDGT producers experienced. This bias, in turn, could result in an overestimation of MAAT in sites in the tropics, where MAF is equivalent to MAAT, explaining the patterns we observe in our tropical samples. Related to this MAF bias, in global lacustrine brGDGT calibrations (Martínez-Sosa et al., 2021; Raberg et al., 2021), the warmest sites are mostly from East Africa (Russell et al., 2018), whereas cold sites are a combination of

the high elevation tropical lakes, also mostly in East Africa, and lakes located at high latitudes (e.g., Raberg et al., 2021). This geographic sampling bias could explain the trends in the residuals of the global calibrations in our study samples (Fig. 4b, d). The bias for the low elevation tropical sites is relatively small (Fig. 4b, d), as samples from the warm sites in the global calibrations are primarily derived from tropical sites (mainly Africa) and are not ‘mixed’ with mid- and high latitude sites in which brGDGTs carry strong seasonality effects.

To further investigate the ‘warm bias’ in our tropical brGDGT data, we examined the brGDGT distributions and the corresponding temperatures from tropical lakes that have a MAAT (equivalent to MAF) lower than 10 °C and in Arctic lakes north of 60° N (Table 2, Fig. 6). The brGDGTs from the Arctic and the high elevation tropics represent the majority of the cold sites in previously published global calibrations of brGDGTs to MAF (Martínez-Sosa et al., 2021; Raberg et al., 2021). The slope of MAAT against MBT_{5ME} becomes nearly vertical, suggesting MBT_{5ME} may be ineffective for MAAT reconstruction in the Arctic (Fig. 6a), where the MBT_{5ME} generally shows better correlations with MAF (Fig. 6b). Nevertheless, although the cold sites do not have identical ranges of MAAT or MAF, the relative abundances of group I, II, and III brGDGTs are generally similar (Fig. 6c and d), suggesting a similar mechanism for the response(s) of the relevant bacteria to changing temperatures (Raberg et al., 2022).

Using MAF instead of MAAT clearly improves the calibration of brGDGTs in high latitude lakes (e.g., Raberg et al., 2021). Microorganismally-based paleothermometers, like brGDGTs, almost certainly have a warm season bias in high latitude regions because of enhanced microbial activity when the temperature and biological productivity are higher (Duguay et al., 2003; Hamilton et al., 2001; Shanahan et al., 2013; Zhao et al., 2021b). Using MAF helps to correct this seasonal bias and reconcile poor correlations between brGDGTs and MAAT in these settings. However, the means

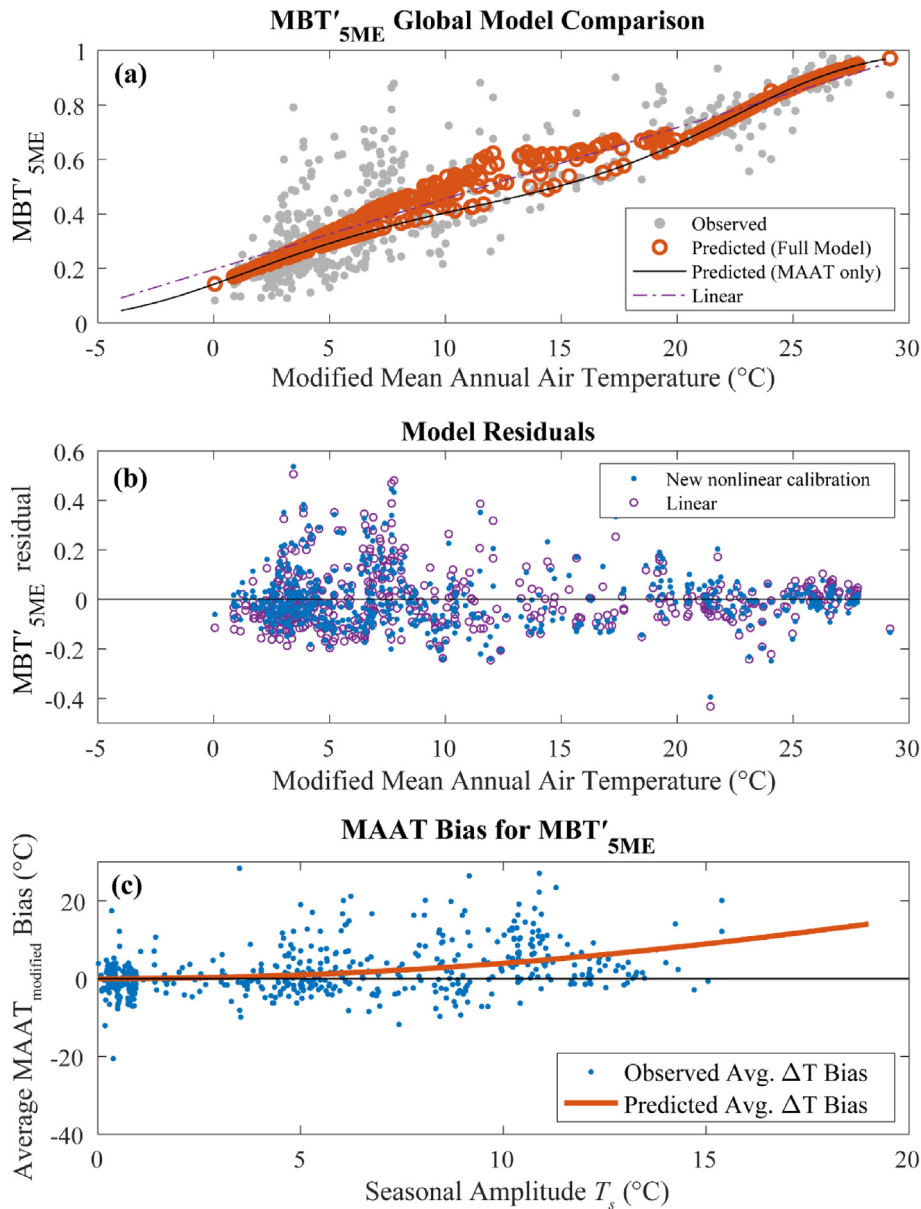


Fig. 5. Nonlinear model using global lacustrine brGDGT dataset. (a) Model outputs using a linear regression (violet dashed line), the nonlinear model without temperature seasonality (black curve), and the 'full model' incorporating non-linear and seasonal effects (red circles). Grey dots depict temperatures and MBT' _{5ME} in the global lake surface sediment dataset. (b) Comparison of the MBT' _{5ME} residuals (offsets between predicted and measured MBT' _{5ME}) for linear and nonlinear models. (c) The scatter plots show the average temperature bias in the full model associated with temperature seasonality (T_s).

Table 2
Temperature and elevation information for the tropical and the Arctic lakes shown in Fig. 6.

Regions	Numbers	MAAT (°C)	MAF (°C)	Elevations (m)	Sources
Tropical	54	5.2	5.2	4132	This study, Russell et al. (2018), Baxter et al. (2019), Martínez-Sosa et al. (2021)
Arctic	69	−2.4	5.9	303	Raberg et al. (2021), Martínez-Sosa et al. (2021), Zhao et al. (2021b)

of tropical and Arctic MAF temperatures (Table 2) are significantly different at the 0.05 level according to the one-way ANOVA analysis and tropical lakes tend to have slightly higher MBT' _{5ME} values at a given MAF (Fig. 6b). A unified calibration of MBT' _{5ME} to MAF would thus overestimate temperature in the tropical sites as observed in our data (Fig. 4). Meanwhile, on the cold end, this approach likely underestimates temperatures from Arctic lakes. Although using MAF could introduce artifacts, it significantly reduces uncertainties

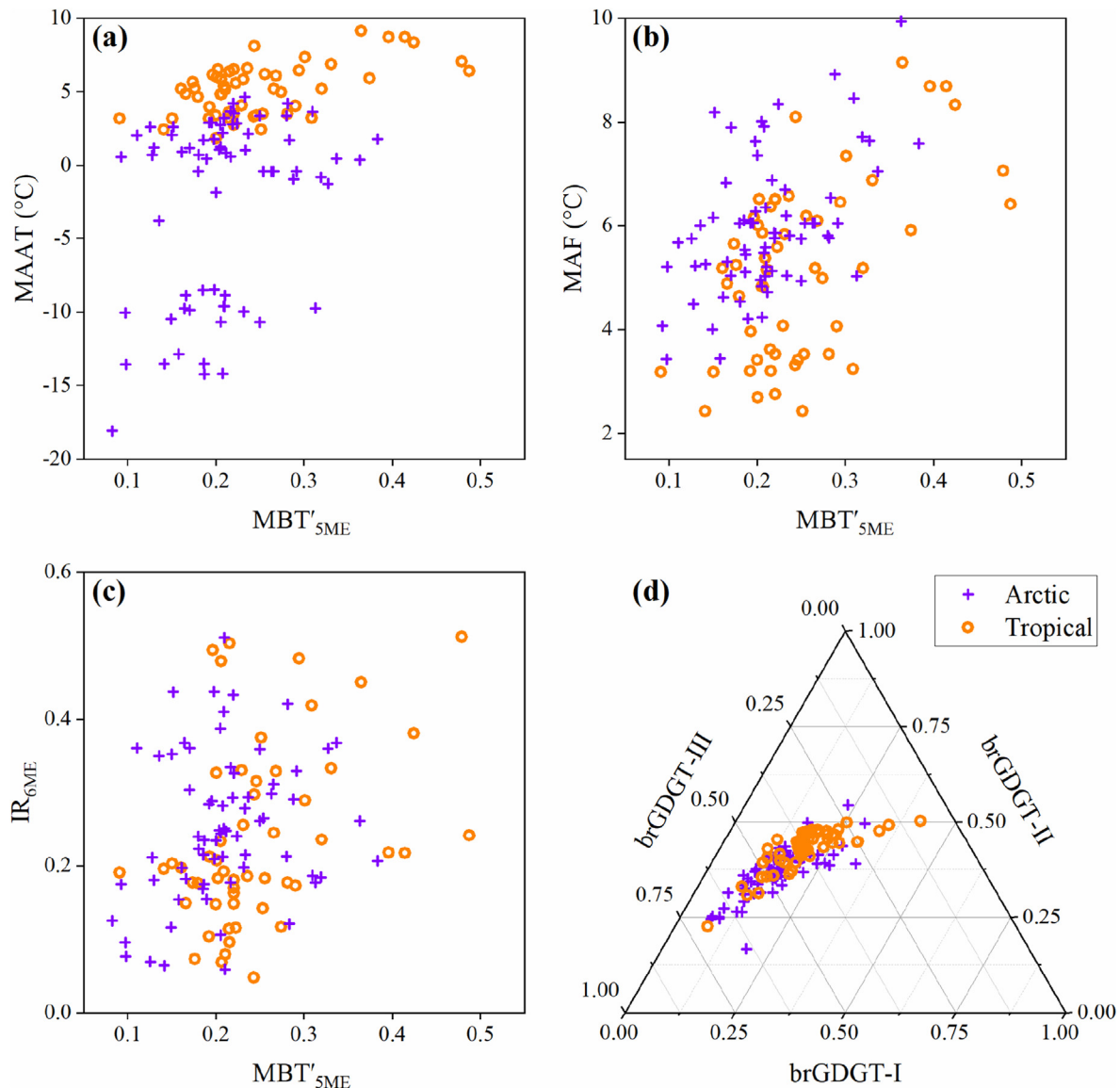


Fig. 6. Characteristics of brGDGTs from cold regions, including the Arctic, and tropics with high elevations. The comparison between MBT'5ME with MAAT (a), MAF (b), and IR6ME (c). (d) Ternary plot showing the comparison of the brGDGTs from different regions.

in temperature calibrations in the mid- and high latitude lakes (Martínez-Sosa et al., 2021; Raberg et al., 2021).

4.2. Determining the brGDGT bias due to temperature seasonality

While temperature is arguably the dominant factor controlling MBT'5ME, the response of MBT'5ME to temperature varies among different climatic regions with different mean annual and seasonal temperatures. To investigate these relationships, we use a nonlinear lacustrine brGDGT model that explicitly models the effects of temperature seasonality in the global lacustrine brGDGT data (Fig. 5). The model indicates that strong temperature seasonality will cause bias in the temperature reconstructions, especially in mid-latitude regions.

Previous application of the model in soil samples showed that temperature seasonality plays an important role in explaining variation in MBT'5ME in soil samples (Zhao et al., 2022). We find similar patterns in our global lake dataset. For the lakes that have a relatively small amplitude of temperature seasonality, i.e. most

lakes located in the regions with MAAT_{modified} below 5 or above 20 °C, the linear and nonlinear models of MBT'5ME on MAAT_{modified} have similar slopes and intercepts (Fig. 5). There is a more substantial difference in lakes with temperatures between ~10 and 20 °C, which are mostly mid-latitude lakes where seasonality is highest. Notably, including T_s improves model performance at the cold sites, and eliminates the bias between observed and estimated temperatures at sites with seasonal temperature amplitudes of less than 5 °C (tropical and many Arctic sites). At sites with a temperature seasonality of 15 °C, the predicted MAAT_{modified} may be biased by more than ~10 °C (Fig. 5c). These results suggest that if seasonality is not taken into consideration, MBT'5ME inferred temperature records from lakes with large seasonal temperature changes (10–15 °C) may have a substantial warm bias of ~5–10 °C (Fig. 5c).

The temperature seasonality term m_s has a value of -3.08×10^{-3} , indicating a large component of seasonal temperature fluctuation is included in the full model (Table 1). For comparison, m_s has a value of -1.84×10^{-3} in the nonlinear soil brGDGT model (Zhao et al., 2022), implying the temperature

seasonality has a stronger influence on the lacustrine MBT'_{SME} index than soil MBT'_{SME} when the T_s values in soils and lakes at the same latitudes are similar. Notably, at high latitudes the T_s of soils are greater than those of lakes because the lake water buffers against the negative air temperatures. Taking the product of m_s and T_s , as done in the calibration, seasonal temperatures play a more important role in explaining variations in soil MBT'_{SME} at high latitudes.

The nonlinear full model applied to our lake samples has a different curvature than the nonlinear soil brGDGT model (Zhao et al., 2022). For soil brGDGTs, the relationship between MBT'_{SME} and MAAT becomes saturated at the coldest and warmest temperatures (Zhao et al., 2022) whereas for lacustrine brGDGTs, the model predicts a distinct 'plateau' at sites with temperatures ranging from 10 to 20 °C (Fig. 5a). This finding suggests the sensitivity of MBT'_{SME} could be limited in mid-latitude lakes. Interestingly, the most recent culture experiments demonstrate that MBT'_{SME} is sensitive at temperatures from 10 to 25 °C in lab settings (Chen et al., 2022), similar to the soil brGDGTs. This mismatch implies that other factors potentially alter lacustrine MBT'_{SME} signals in addition to temperature. One possibility is that the lacustrine model assumes that brGDGT production is evenly distributed each month throughout the year. However, field observations show that a high fraction of lacustrine brGDGTs are produced when lakes experience mixing events as biological productivity peaks (e.g., Loomis et al., 2014b). This could bias the temperature estimates toward an average mixing temperature, often 4–8 °C in mid-latitudes, suppressing the MBT'_{SME} response. However, field observations of seasonal brGDGT fluxes are limited, suggesting the need for future work to explore the relationship between seasonal temperatures and brGDGT production, especially in mid-latitude lakes where mixing dynamics and temperatures have substantial seasonality (Liang et al., 2022).

As with global lacustrine brGDGT calibrations, lakes with cold temperatures cluster separately in our nonlinear lacustrine brGDGT model with and without seasonality (Fig. S2). Although MAAT_{modified} is better than MAF in predicting temperature at these sites, the cold tropical lakes are not fully blended with high latitude lakes even with a nonlinear model approach (Fig. S2). This implies the need to analyze brGDGTs based on latitudinal locations to develop more accurate temperature calibrations.

4.3. Calibrating brGDGTs in tropical lakes to MAAT

Due to the different responses of brGDGTs at sites with different temperature seasonality, we argue that brGDGTs from tropical and mid-to high latitude regions should be analyzed and calibrated separately to generate the most accurate brGDGT calibrations. Tropical lakes experience minimal temperature seasonality, and regression analysis indicates that MBT'_{SME} is significantly correlated with MAAT in our tropical lake data (Fig. 7a). We therefore develop a new brGDGT calibration for reconstructing MAAT in tropical lakes:

$$\text{MAAT} = -1.78 (\pm 0.42) + 31.01 (\pm 0.60) \times \text{MBT}'_{\text{SME}} \quad (8)$$

This calibration has an RMSE of 2.26 °C ($n = 187$, $r = 0.97$, Adj. $R^2 = 0.93$, $p < 10^{-110}$). This RMSE is smaller compared to the RMSE of the previous calibration based on East Africa lakes alone (RMSE = 2.44 °C). Importantly, data from all of our tropical samples (South America, Africa, and Asia) all display similar responses of MBT'_{SME} to temperature, suggesting little to no effect of continental setting on this relationship.

We also develop a new calibration using best subset selection, which is a multivariate linear regression (MLR) of individual

brGDGT abundances on MAAT. The regression starts with all possible combinations of different brGDGTs and identifies a model that has the highest correlation coefficient with a minimum number of predictors in which all coefficients and intercepts pass both a t -test and F -test. This MLR approach has been shown to significantly improve the precision and applicability of brGDGT calibrations (Loomis et al., 2012; Russell et al., 2018). The MLR calibration is:

$$\text{MAAT} = -4.11 + 31.63 \times f(\text{Ia}) + 64.50 \times f(\text{Ib}) + 32.28 \times f(\text{IIa}') \quad (9)$$

As expected, the MLR calibration shows a smaller RMSE (2.13 °C) compared to the MBT'_{SME} calibration (Eq. (8)), and the adjusted R^2 of the MLR calibration is higher (Adj. $R^2 = 0.94$). This indicates that the MLR model captures more variance in MAAT than the model based on MBT'_{SME} alone.

We examine the performance of both regression models by comparing the reconstructed and observed MAAT of the tropical brGDGTs dataset (Fig. 8). In both calibrations, the residuals (Fig. 8b, d) generally have less systematic biases compared to temperature estimates using the global calibrations (Fig. 4b, d, f). This supports the hypothesis that lacustrine brGDGTs from different climatic regions should be grouped separately due to the important variance in temperature seasonality. By removing the mid- and high latitude brGDGT data, our calibrations minimize the systematic bias introduced by calibrations to MAF. The MLR calibration shows slightly less scatter, as expected from the lower RMSE values.

These new calibrations are consistent with the RDA results. PC1 demonstrates that the degree of methylation of brGDGTs relates to temperature (Fig. 3a). brGDGT-Ia and Ib load positively on PC1 and are included in our MLR calibration (Eq. (9)), as well as in the MBT'_{SME} calibration because those two compounds are essential parameters in the MBT'_{SME} formula (Eq. (1)). Previous studies showed that 6-methyl isomers are widely found in lacustrine brGDGTs and their production is likely related to lake water oxygenation (Weber et al., 2018). In Fig. 3a, our RDA results show that brGDGT-IIa' and IIb' have strong positive scores on PC2, which is associated with lake depth and surface area (Fig. 3a). Dissolved oxygen is not included in our analysis as the data are lacking in some of our study lakes; however, the RDA results could imply that *in situ* brGDGT productions are linked to lake morphometry and lake chemistry. For example, lake depth should influence hypolimnetic oxygenation. The inclusion of IIa' in our new MLR model could reflect interactions among these variables and temperature. More observations of brGDGT abundances and better limnological datasets are needed to evaluate these relationships.

We test our new calibrations on two previously published brGDGT records and compare them with the original temperature reconstructions (Garelick et al., 2022; Parish et al., 2023) (Fig. 9). The brGDGT records are from two different lakes: Lake Mahoma is an alpine lake from eastern equatorial Africa, and Lake Towuti is from Indonesia with an elevation of 318 m a.s.l.. For Lake Mahoma, reconstructions using MBT'_{SME} calibrations of Russell et al. (2018) and this study (Eq. (8)), and MLR calibration in this study (Eq. (9)) show similar patterns marked by warming during the last deglaciation, a warm early to mid-Holocene, and cooling trend during the late Holocene (Fig. 9a). It is not surprising that both MBT'_{SME}-based temperature reconstructions show identical patterns with a consistent offset, as our new MBT'_{SME}-based calibration differs only slightly from that of Russell et al. (2018). The MLR-based reconstructions also capture a similar set of temperature variations, though with a smaller warming during the last deglaciation (Fig. 9a). As discussed in Garelick et al. (2022) and Doughty et al. (2023), the trends in temperature at Lake Mahoma align qualitatively and quantitatively with inferences from tropical mountain

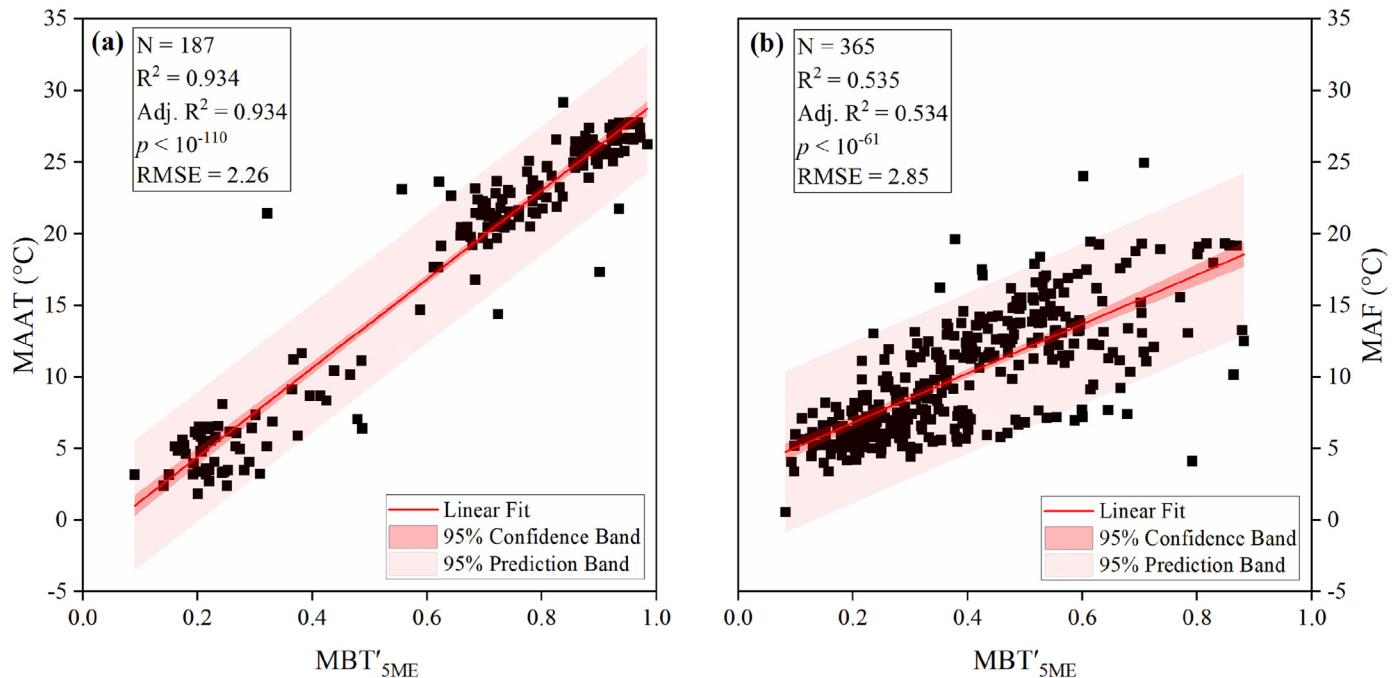


Fig. 7. Regression models between MBT'5ME and temperatures. (a) New lacustrine brGDGT calibration for MAAT from tropical regions (b) New lacustrine brGDGT calibration for MAF from mid-to high latitude regions.

glaciers and fossil pollen, supporting the use of our new calibrations.

The MBT'5ME-based temperature reconstructions from Lake Towuti are relatively flat. As discussed in Parish et al. (2023), brGDGTs in Lake Towuti appear to respond to both temperature and water chemistry, requiring the use of calibrations that limit the effects of brGDGT cyclization. In contrast to the MBT'5ME-based reconstruction, our new MLR-based reconstructions show a clear Glacial-Interglacial pattern (Fig. 9b). In particular, we observe a stable and relatively cool temperature during the Last Glacial Maximum at around 20 cal ka BP, followed by warming during the deglaciation and a stable Holocene temperature (Fig. 9b). Our new MLR-based reconstruction produces temperature estimates that are less variable and more accurate at Lake Towuti than the previous multiple linear regression model. Our model estimates late Holocene temperatures were ~29 °C relative to observed temperatures of ~30 °C, whereas the SFS model of Russell et al. (2018) estimated temperatures of 36 °C. The improved accuracy of our model could result from incorporation of more warm lakes as well as sites in Southeast Asia and South America with different water chemistries than those prevailing in East Africa. Together, these two case studies demonstrate the robustness and amelioration associated with our new pan-tropical calibrations.

The MBT'5ME calibration is solely based on 5-methyl brGDGTs (Eq. (1)) while the MLR calibration depends on both 5 and 6-methyl brGDGTs, especially brGDGT-Ia, Ib, and IIa'. Although the factors controlling 6-methyl brGDGTs are not well-known, these brGDGTs were found to be linked with pH (De Jonge et al., 2014a; Naafs et al., 2017b; Raberg et al., 2022), temperature (Dang et al., 2018; Liang et al., 2022), and salinity (Wang et al., 2021). Due to a lack of chemical data in our new lakes, particularly those from tropical South America, we were not able to examine the response of 6-methyl isomers to pH and salinity. Our RDA analysis suggests that MBT'5ME has a better relationship with MAAT than 6-methyl isomers and associated indices, such as IR6ME or MBT'6ME (Fig. 3a). However, it is worth noting that 6-methyl brGDGTs can be

important for temperature reconstruction in some lakes. For example, they appear to be crucial for the extraction of a temperature record from Lake Chala (Baxter et al., 2021). Since the MLR calibration has only a slightly better correlation with MAAT than MBT'5ME alone, we suggest that both calibrations could be applied in paleoclimate studies. Given that 6-methyl isomers may characterize environmental information other than temperature, we suggest that the MLR calibration is especially suitable for lakes in which fluctuations in pH, salinity, oxygenation, and other chemical variables are expected to be small. Parallel multiproxy reconstructions, which provide multiple lines of evidence to constrain paleoenvironmental changes, are helpful to better interpret brGDGT records.

Our MBT'5ME calibration has a very similar slope and intercept compared to the previous East African brGDGT calibration (Eq. (4)) (Russell et al., 2018). Although slight differences appear, our results suggest that the relationship between brGDGT distributions and MAAT is similar and strong across the tropics (Fig. 8). The brGDGT data are dominantly from Africa and South America ($n = 94$ and 63 , respectively), where sampling across elevation produces large temperature gradients. Unfortunately, we do not have enough brGDGT samples from high elevations to cover a large temperature gradient in Southeast Asia; the 13 samples we measured from Southeast Asian lakes have an average MAAT of 24 °C, and the brGDGT distributions cluster with the African and South American low elevation lakes (Fig. 8). Despite the different environmental and geological conditions and potential differences in the microbial communities that produce the brGDGTs on different continents, our findings clearly suggest that brGDGTs in tropical lake sediments are a powerful tool to reconstruct past temperature on all continents.

It is particularly important to validate the application of brGDGTs in tropical South American lakes because the Amazon rainforest plays a key role in carbon stores in ecosystems (Melillo et al., 1993) and is thus an extremely important region for climate-related research. Although temperature reconstructions

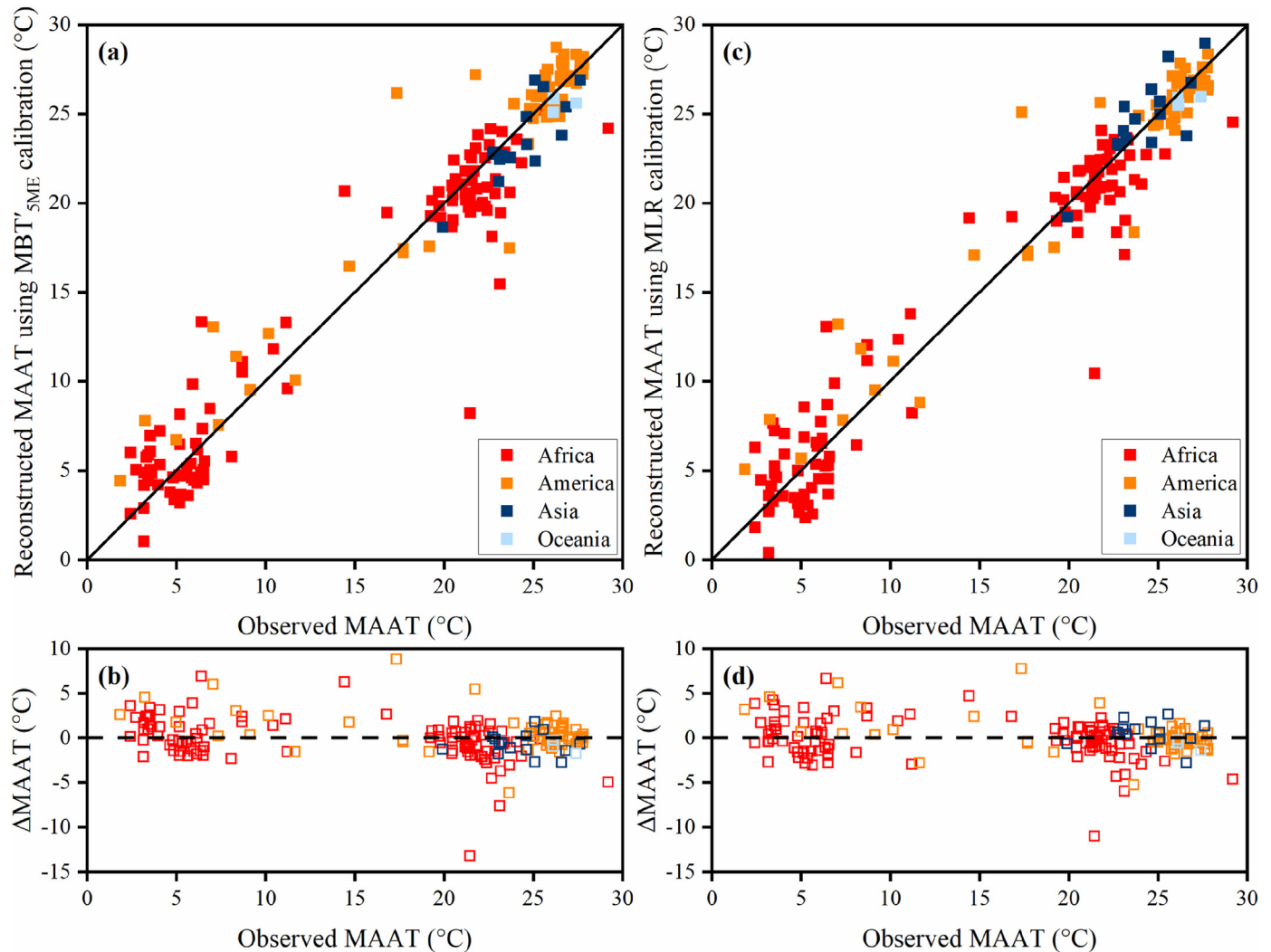


Fig. 8. Comparisons between observed MAAT and reconstructed MAAT for all tropical lakes using the MBT'5ME calibration (a) and MLR calibration (c). The corresponding offsets between reconstructions and observations are shown in (b) and (d).

from tropical South America are still rare (Baker and Fritz, 2015), our study indicates the applicability of lacustrine brGDGTs to reconstruct past temperatures in tropical South America. Such quantitative temperature records would help to better reveal the climatic variability and provide fundamental parameters for climate models, which were thought to be deficient in tropical South America (Baker and Fritz, 2015). Moreover, our new data from Amazonia expands the warm end of the previous East African calibration (Russell et al., 2018), as the warmest Amazon lakes (MAAT of ~25–28 °C) are warmer than the warmest East African ones (Fig. 8). Correspondingly, Amazon lakes have even lower brGDGT-III and brGDGT-II abundances than the East African samples (Fig. 2b), which yield a high MBT'5ME that is very close to saturation at 1. That said, and in contrast to the saturation of MBT'5ME at higher temperatures suggested by nonlinear modeling of brGDGT in soils (Zhao et al., 2022), our new data from the Amazon demonstrates a nearly linear relationship between MBT'5ME and temperature, and the MBT'5ME calibration will saturate close to a MAAT of 29.23 °C when MBT'5ME reaches 1.

Overall, our new calibrations show better statistical results and cover more extensive sampling sites, and thus should be used to reconstruct MAAT with sedimentary brGDGTs from all pan-tropical lakes.

4.4. Temperature calibration for mid- and high latitude lakes

A global brGDGT calibration would be valuable to improve the comparability of reconstructed global temperatures. However, separating more seasonal sites in the mid- and high latitudes from tropical sites produces more accurate temperature estimates in both regions, and therefore should improve global estimates.

brGDGTs from tropical lakes played an important role in previously published global calibrations (Martínez-Sosa et al., 2021; Raberg et al., 2021). In the Raberg et al. (2021) calibrations (Eqs. (5) and (6)), East African lakes (Russell et al., 2018) contributed all brGDGT data at sites with a MAF above 20 °C. In the BayMBT calibration (Martínez-Sosa et al., 2021), 50 tropical brGDGT sites out of a total of 52 samples had a MAF above 20 °C. Removal of these sites may limit the range of brGDGT calibrations, but on the other hand, because the tropical brGDGTs do not experience seasonality, including tropical brGDGTs could distort the calibrations for mid- and high latitudes. Indeed, in our global dataset, calibrations of MBT'5ME to MAAT in the tropics (where MAAT will equal MAF) have a different slope and intercept from calibration of MBT'5ME to MAF in mid- and high latitudes sites. Combining the two regional datasets worsens temperature estimates.

Focusing on mid- to high latitude sites, MBT'5ME is significantly

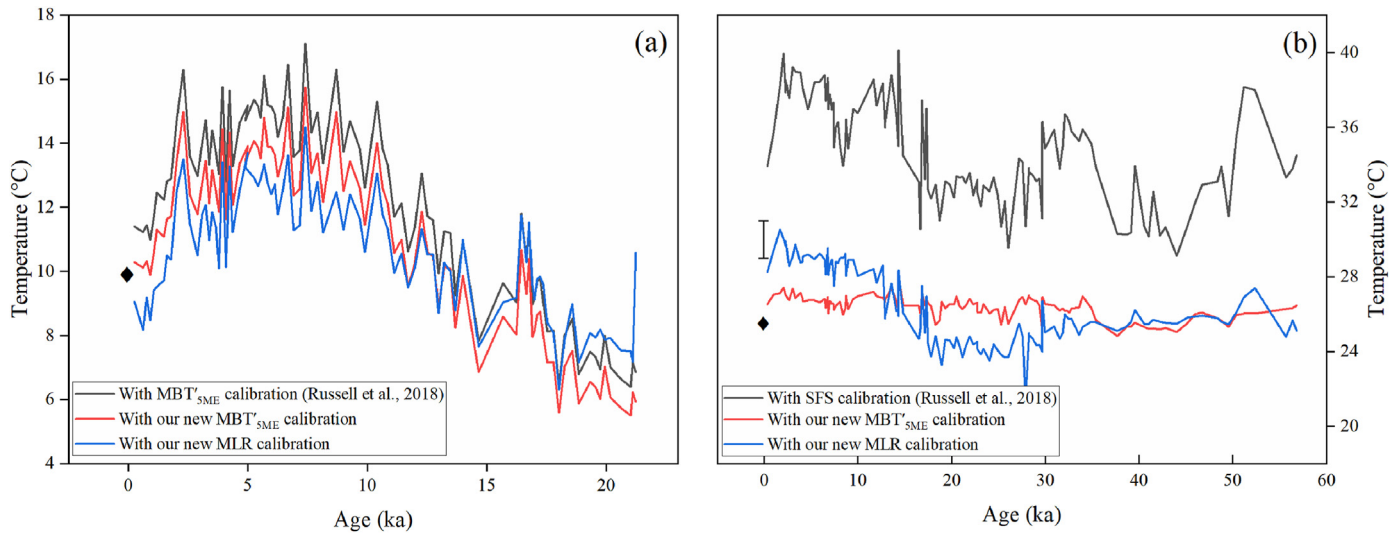


Fig. 9. Applying our new calibrations to the brGDGT records from two tropical lakes, a high elevation African lake, Lake Mahoma (a), and a low elevation Indonesian lake, Lake Towuti (b). (a) Black line is the original temperature reconstruction detailed by Garelick et al. (2022) using East Africa MBT_{SME} calibration (Russell et al., 2018). Red and Blue lines are the reconstructions with our new pan-tropical calibrations. The solid diamond denotes the modern annual air temperature of -10°C (Loomis et al., 2017). (b) Black line is the original temperature reconstruction detailed by Parish et al. (2023) using East Africa SFS calibration (Russell et al., 2018). Red and Blue lines are the reconstructions with our new pan-tropical calibrations. The solid diamond denotes the modern annual air temperature of -25.6°C (Fick and Hijmans, 2017), and the lake surface water temperature ranges from 29 to 31°C (Parish et al., 2023).

correlated with MAF with a slope that is significantly different from zero at the 0.05 level (Fig. 7b):

$$\text{MAF} = 3.36 (\pm 0.36) + 17.25 (\pm 0.84) \times \text{MBT}'_{\text{SME}} \quad (10)$$

This calibration has an RMSE of 2.85°C ($n = 365$, $r = 0.73$, Adj. $R^2 = 0.53$, $p < 10^{-61}$). This equation has a lower correlation coefficient than the global calibrations. The RMSE is slightly better than the BayMBT (Martínez-Sosa et al., 2021), but higher than the calibrations in Raberg et al. (2021). Similarly, the MLR approach was employed for the mid- and high latitude temperature and brGDGT data and the calibration for mid- and high latitudes is:

$$\text{MAF} = 1.44 + 15.88 \times f(\text{Ia}) + 66.92 \times f(\text{Ib}) + 8.33 \times f(\text{IIa}') + 7.02 \times f(\text{IIIa}') \quad (11)$$

This MLR calibration has a smaller RMSE of 2.27°C and the adjusted R^2 (0.70) is improved compared to the results from Eq. (10). In Fig. 10a, c, we present the relationship between reconstructed and observed MAF with both MBT_{SME} and MLR calibrations. Both calibration approaches produce temperature estimates that generally track observations (i.e., the data cluster around the 1:1 line) but the MBT_{SME} calibration displays a trend in the residuals in which it overestimates temperature at the coldest sites and underestimates temperature at the warmest ones. Overall, the model based on MBT_{SME} appears to be less sensitive than the MLR model. A small trend in residuals is also apparent in the MLR calibration, and the residuals are more symmetric than with MBT_{SME}, especially for the warm regions. Overall, the MLR calibration performs better than MBT_{SME} from a statistical perspective.

The RDA results for mid- and high latitude lakes (Fig. 3b) are harder to interpret than the data from the tropical lakes, possibly because the mid- and high latitude brGDGT data contains more chemically diverse lakes. For example, the data include some alkaline lakes from China and previous studies found that MBT_{6ME} is a better temperature indicator than MBT_{5ME} in those lakes (Dang et al., 2018; Liang et al., 2022). However, both RDA results share some similarities, and moreover, the MLR calibration (Eqs. (9) and

(11)) selects most of the same brGDGTs. MBT_{SME}, fractional abundances of brGDGT Ia, Ib, and Ic have positive scores on PC1, which is associated with MAF and MAAT, just as in tropical lakes (Fig. 3a). Interestingly, brGDGT-IIa', present in both MLR calibrations, shows different characteristics. In tropical lakes, brGDGT-IIa' tracks PC2 (Fig. 3a), whereas it is more aligned with PC1 (temperature) in mid- and high latitude lakes (Fig. 3b). brGDGT-IIIa' in Eq. (11) tracks PC2 in the mid- and high latitude lake data, and we speculate that in the mid- and high latitude MLR model, it plays a similar role as brGDGT-IIa' in the tropical MLR model. In cold regions, brGDGT distributions generally have a higher abundance of brGDGT-IIIa and IIIa' compared to warm settings; the average fractional abundances of brGDGT-IIIa' in tropical and mid-to high latitude lakes are 0.04 and 0.12, respectively. This may explain why brGDGT-IIIa' is present in Eq. (11) but is absent in Eq. (9).

Whereas our new tropical calibrations have better correlation statistics than previous calibrations (Martínez-Sosa et al., 2021; Russell et al., 2018), our calibrations for mid- and high latitude regions do not. This could be because the brGDGTs in tropical warm lakes (MAAT $> 20^{\circ}\text{C}$) show an excellent linear relationship with MAAT (Fig. 7a), and those brGDGT data anchor the warm end of previous global calibrations (Martínez-Sosa et al., 2021; Raberg et al., 2021). Although the separation of brGDGTs does not lead to a regression model with improved statistical results for mid- and high latitudes, our MBT_{SME} and MLR calibrations for mid- and high latitudes are robust and should more accurately capture MAF.

Taking all the above into consideration, we suggest that both MBT_{SME} and MLR calibrations are applicable in mid- and high latitude regions. The MLR calibration may provide a more accurate and precise reconstruction, but its application should be done with caution due to our presently insufficient understanding of the influence of lake environmental parameters lake, such as salinity, pH, and other variables on individual brGDGTs.

4.5. Global lacustrine brGDGT calibration

The slope of MBT_{SME} calibrations in tropical and mid-to high latitude regions are 31.01 and 17.25, respectively (Eqs. (8) and (10)).

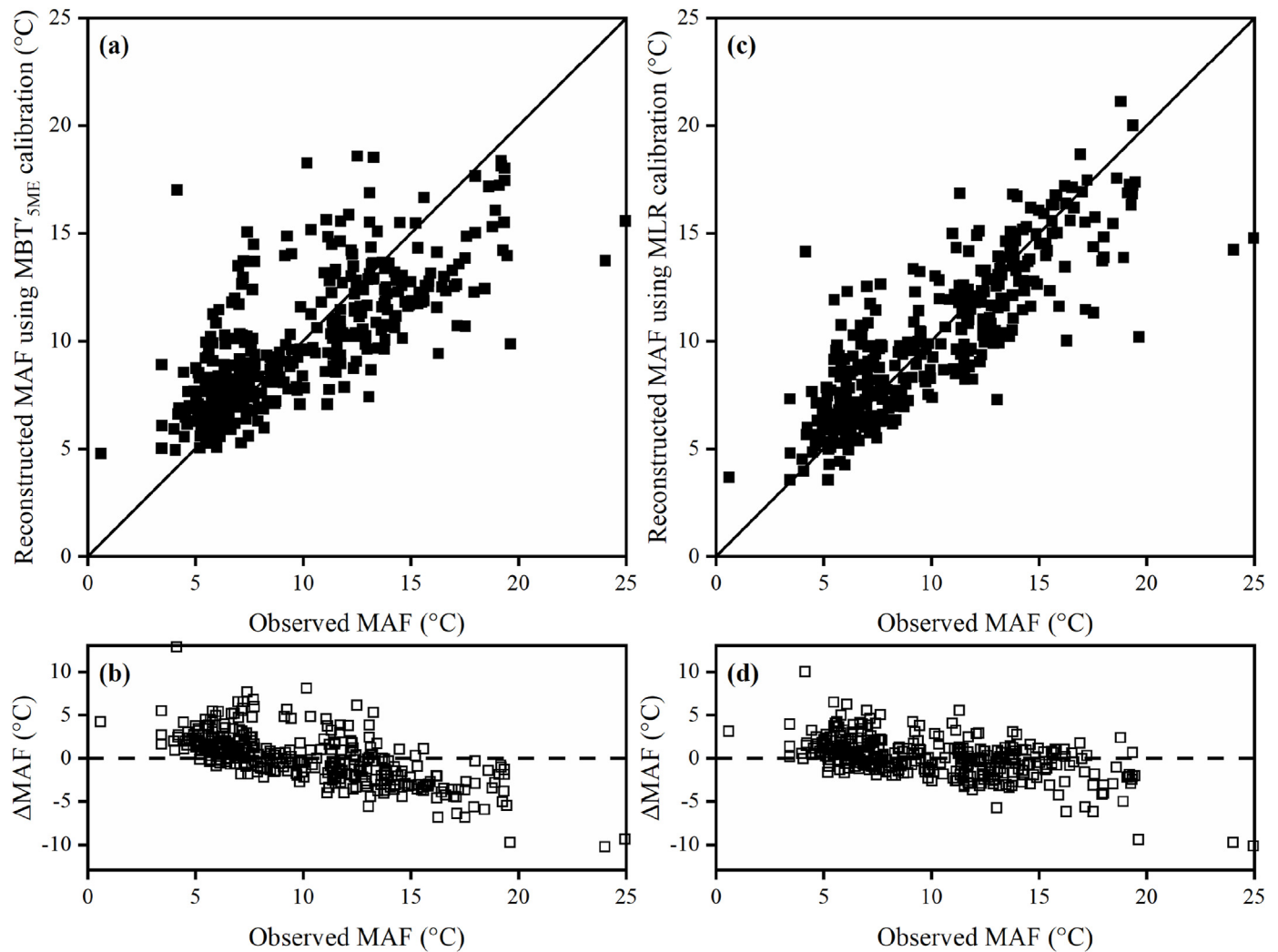


Fig. 10. Comparisons between observed MAF and reconstructed MAF for all mid-to high latitude lakes using the MBT'5ME calibration (a) and MLR calibration (c). The corresponding offsets between reconstructions and observations are shown in (b) and (d).

It is not surprising that the regression of MAF on global lacustrine MBT'5ME lies between the two calibrations from the tropics and mid- and high latitude:

$$\text{MAF} = 0.19 (\pm 0.29) + 26.49 (\pm 0.55) \times \text{MBT}'_{5\text{ME}} \quad (12)$$

This calibration has an RMSE of 3.13 °C ($n = 552$, $r = 0.90$, Adj. $R^2 = 0.81$, $p < 10^{-200}$). While it is possible to generate a global lake calibration for the global lake dataset, this calibration should be used with caution and when other calibrations are not applicable. For example, this calibration could be implemented in deeper time settings where temperature seasonality is poorly understood.

The differences in the calibrations for mid- and high latitudes compared to the tropical calibrations (Fig. 7) are puzzling, as there is no prior reason to expect a different response of brGDGTs to temperature in the two regions. Correlating MBT'5ME from mid- and high latitude lakes against MAAT did not ameliorate this divergence (Fig. S3); rather, it produced a worse adjusted R^2 and RMSE (0.34 and 5.63, respectively) compared to the regression model using MAF (Eq. (10), 0.53 and 2.85, respectively). The difference between low- and high-latitude calibrations may indicate remaining inaccuracies and biases through the use of MAF to reflect the temperatures experienced by brGDGT producers. In our nonlinear

lacustrine brGDGT model, we use a MAAT_{modified} in which 0 °C is used to replace all monthly temperatures that are below 0 °C to incorporate brGDGT production in winter. The winter brGDGT fluxes should reflect winter lake water temperatures that typically range from 0 to 4 °C, depending on the date and water depth. We tested different thresholds from 0 to 4 °C to see whether we could improve the correlation between temperatures with MBT'5ME in the mid- and high latitude lakes. The R^2 increases when the threshold moves from 0 to 4 °C with an increment of 0.01 °C and reaches the highest value of 0.477 when 4 °C is picked to be the threshold (Fig. S4). The slope and intercept covary monotonically with different thresholds. When the thresholds move from 0 °C to 4 °C, the slope decreases from 18.24 to 15.40, and the intercept increases from -0.18 to 2.64 (Fig. S5). The increase in R^2 with increasing temperature could reflect increasing brGDGT production rates with temperature, but the change in R^2 is subtle (0.469–0.477), and it is always smaller than 0.53 when the original MAF was employed. We therefore recommend reconstructing MAF using Eqs. (10) and (11) from mid- and high latitude lakes. Although field observations of brGDGT fluxes are still limited, we speculate that calibrations of brGDGTs to temperature will be improved by weighting monthly temperatures to capture varying seasonal brGDGT production in lakes.

Field observations have focused on the relationship between brGDGT distributions and temperatures but more consideration to water chemistry could substantially improve calibrations and applications of the proxy. It has been suggested that water column oxygenation strongly affects brGDGT production, and brGDGT distributions may vary along the oxygen gradient in lake water columns (van Bree et al., 2020; Weber et al., 2018; Wu et al., 2021). Although calibration studies suggest these effects are small on the sedimentary brGDGT pool (e.g., Russell et al., 2018), the oxygen gradient generally varies with lake depths and mixing regime, and the latter is linked to temperature making these effects difficult to parse from surface sediment studies alone. For example, water chemistry, rather than temperatures, controls the PC1 of 60,000-year brGDGT records from Lake Towuti, and may impact brGDGT distributions across the Pleistocene-Holocene transition (Parish et al., 2023). Long-term observations can help constrain these various influences on brGDGTs from a temporal perspective, which is missing in brGDGT temperature calibrations using 'space-for-time' substitution.

5. Conclusions

Using new brGDGT data in surface sediments from lakes across South America, East Africa, and Southeast Asia, we reexamine currently available lacustrine brGDGT data and develop regional-to-global temperature calibrations. We identify key issues that hinder brGDGT applications, and particularly temperature seasonality. The use of MAF in high-latitude settings to mitigate the effects of seasonal production improves temperature calibrations in those settings but introduces biases in tropical temperature calibrations and reconstructions. Substantial warm bias may appear if temperature seasonality is not considered in mid-latitude lacustrine brGDGT applications. Hence, we calibrate MBT_{5ME} to MAAT in the tropics and MAF in mid- and high latitude regions separately. Both calibrations are applicable, and our new tropical calibration demonstrates a uniform brGDGT response to temperature across the tropics. We use multivariate linear regression (MLR) to calibrate brGDGT distributions to temperature in the tropics and mid-to-high latitudes. Both the MLR calibrations have better statistical fit than corresponding MBT_{5ME} calibrations, and we show that they hold promise in applications in sediment sequences from tropical lakes. However, it should be noted that the MLR regressions lack a well-defined underlying biophysiological mechanism, and they therefore may be more suitable for lakes that do not have extreme values of physical or chemical parameters.

Our findings substantially improve the brGDGT-based temperature calibration. We stress that future study focusing on temporal brGDGT fluxes and their linkage to water temperatures is essential. This could further improve the accuracy of lacustrine brGDGTs-based temperature reconstructions in the mid-and high latitude regions.

Author contributions

Boyang Zhao: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization, James M. Russell: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition, Victor C. Tsai: Methodology, Formal analysis, Investigation, Writing - Review & Editing, Visualization, Ansis Blaus: Investigation, Resources, Writing - Review & Editing, Meredith C. Parish: Resources, Writing - Review & Editing, Jie Liang: Investigation, Writing - Review & Editing, Alexander Wilk: Resources, Writing - Review & Editing, Xiaojing Du: Resources, Writing - Review & Editing, Mark B. Bush:

Investigation, Resources, Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Datasets related to this article can be found in Supplementary materials.

Acknowledgments

We thank the Editor and two anonymous reviewers for their comments that helped improve this paper. This work was supported by U.S. National Science Foundation (DEB-2029614 award to J.M.R.; EAR-1903348 award to J.M.R.; DEB-2029649 award to M.B.B.; DEB-1260983 award to M.B.B.; P2C2-2202746 award to X.D.).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.quascirev.2023.108124>.

References

- Baker, P.A., Fritz, S.C., 2015. Nature and causes of Quaternary climate variation of tropical South America. *Quat. Sci. Rev.* 124, 31–47. <https://doi.org/10.1016/j.quascirev.2015.06.011>.
- Baxter, A.J., Hopmans, E.C., Russell, J.M., Sinninghe Damsté, J.S., 2019. Bacterial GMGTs in East African lake sediments: their potential as palaeotemperature indicators. *Geochim. Cosmochim. Acta* 259, 155–169. <https://doi.org/10.1016/j.gca.2019.05.039>.
- Baxter, A.J., van Bree, L.G.J., Peterse, F., Hopmans, E.C., Villanueva, L., Verschuren, D., Sinninghe Damsté, J.S., 2021. Seasonal and multi-annual variation in the abundance of isoprenoid GDGT membrane lipids and their producers in the water column of a meromictic equatorial crater lake (Lake Chala, East Africa). *Quat. Sci. Rev.* 273, 107263. <https://doi.org/10.1016/j.quascirev.2021.107263>.
- Bechtel, A., Smittenberg, R.H., Bernasconi, S.M., Schubert, C.J., 2010. Distribution of branched and isoprenoid tetraether lipids in an oligotrophic and a eutrophic Swiss lake: insights into sources and GDGT-based proxies. *Org. Geochem.* 41, 822–832. <https://doi.org/10.1016/j.orggeochem.2010.04.022>.
- Blaga, C.I., Reichert, G.J., Heiri, O., Sinninghe Damsté, J.S., 2009. Tetraether membrane lipid distributions in water-column particulate matter and sediments: a study of 47 European lakes along a north-south transect. *J. Paleolimnol.* 41, 523–540. <https://doi.org/10.1007/s10933-008-9242-2>.
- Blaga, C.I., Reichert, G.J., Schouten, S., Lotter, A.F., Werne, J.P., Kosten, S., Mazzeo, N., Lacerot, G., Sinninghe Damsté, J.S., 2010. Branched glycerol dialkyl glycerol tetraethers in lake sediments: can they be used as temperature and pH proxies? *Org. Geochem.* 41, 1225–1234. <https://doi.org/10.1016/j.orggeochem.2010.07.002>.
- Buckles, L.K., Weijers, J.W.H., Verschuren, D., Sinninghe Damsté, J.S., 2014. Sources of core and intact branched tetraether membrane lipids in the lacustrine environment: anatomy of Lake Challa and its catchment, equatorial East Africa. *Geochim. Cosmochim. Acta* 140, 106–126. <https://doi.org/10.1016/j.gca.2014.04.042>.
- Cao, J., Rao, Z., Shi, F., Jia, G., 2020. Ice formation on lake surfaces in winter causes warm-season bias of lacustrine brGDGT temperature estimates. *Biogeosciences* 17, 2521–2536. <https://doi.org/10.5194/bg-17-2521-2020>.
- Carroll, R.J., Ruppert, D., Stefanski, L.A., Crainiceanu, C.M., 2006. Measurement Error in Nonlinear Models, Measurement Error in Nonlinear Models. Chapman and Hall/CRC. <https://doi.org/10.1201/9781420010138>.
- Castañeda, I.S., Schouten, S., 2011. A review of molecular organic proxies for examining modern and ancient lacustrine environments. *Quat. Sci. Rev.* 30, 2851–2891. <https://doi.org/10.1016/j.quascirev.2011.07.009>.
- Chen, Y., Zheng, F., Yang, H., Yang, W., Wu, R., Liu, X., Liang, H., Chen, H., Pei, H., Zhang, C., Pancost, R.D., Zeng, Z., 2022. The production of diverse brGDGTs by an Acidobacterium providing a physiological basis for paleoclimate proxies. *Geochim. Cosmochim. Acta*. <https://doi.org/10.1016/j.gca.2022.08.033>.
- Colcord, D.E., Cadieux, S.B., Brassell, S.C., Castañeda, I.S., Pratt, L.M., White, J.R., 2015. Assessment of branched GDGTs as temperature proxies in sedimentary records from several small lakes in southwestern Greenland. *Org. Geochem.* 82, 33–41. <https://doi.org/10.1016/j.orggeochem.2015.02.005>.

- Dang, X., Ding, W., Yang, H., Pancost, R.D., Naafs, B.D.A., Xue, J., Lin, X., Lu, J., Xie, S., 2018. Different temperature dependence of the bacterial brGDGT isomers in 35 Chinese lake sediments compared to that in soils. *Org. Geochem.* 119, 72–79. <https://doi.org/10.1016/j.orggeochem.2018.02.008>.
- Dang, X., Yang, H., Naafs, B.D.A., Pancost, R.D., Xie, S., 2016. Evidence of moisture control on the methylation of branched glycerol dialkyl glycerol tetraethers in semi-arid and arid soils. *Geochim. Cosmochim. Acta* 189, 24–36. <https://doi.org/10.1016/j.gca.2016.06.004>.
- De Jonge, C., Hopmans, E.C., Zell, C.I., Kim, J.H., Schouten, S., Sinninghe Damsté, J.S., 2014a. Occurrence and abundance of 6-methyl branched glycerol dialkyl glycerol tetraethers in soils: implications for palaeoclimate reconstruction. *Geochim. Cosmochim. Acta* 141, 97–112. <https://doi.org/10.1016/j.gca.2014.06.013>.
- De Jonge, C., Radujković, D., Sigurdsson, B.D., Weedon, J.T., Janssens, I., Peterse, F., 2019. Lipid biomarker temperature proxy responds to abrupt shift in the bacterial community composition in geothermally heated soils. *Org. Geochem.* 137, 103897. <https://doi.org/10.1016/j.orggeochem.2019.07.006>.
- De Jonge, C., Stadnitskaia, A., Hopmans, E.C., Cherkashov, G., Fedotov, A., Sinninghe Damsté, J.S., 2014b. In situ produced branched glycerol dialkyl glycerol tetraethers in suspended particulate matter from the Yenisei River, Eastern Siberia. *Geochim. Cosmochim. Acta* 125, 476–491. <https://doi.org/10.1016/j.gca.2013.10.031>.
- Dearing Crampton-Flood, E., Tierney, J.E., Peterse, F., Kirkels, F.M.S.A., Sinninghe Damsté, J.S., 2020. BayMBT: a Bayesian calibration model for branched glycerol dialkyl glycerol tetraethers in soils and peats. *Geochim. Cosmochim. Acta* 268, 142–159. <https://doi.org/10.1016/j.gca.2019.09.043>.
- Dearing Crampton-Flood, E., van der Weijst, C.M.H., van der Molen, G., Bouquet, M., Yedema, Y., Donders, T.H., Sangiorgi, F., Sluijs, A., Sinninghe Damsté, J.S., Peterse, F., 2021. Identifying marine and freshwater overprints on soil-derived branched GDGT temperature signals in Pliocene Mississippi and Amazon River fan sediments. *Org. Geochem.* 154, 104200. <https://doi.org/10.1016/j.orggeochem.2021.104200>.
- Donders, T.H., Weijers, J.W.H., Munsterman, D.K., Kloosterboer-van Hoeve, M.L., Buckles, L.K., Pancost, R.D., Schouten, S., Sinninghe Damsté, J.S., Brinkhuis, H., 2009. Strong climate coupling of terrestrial and marine environments in the Miocene of northwest Europe. *Earth Planet. Sci. Lett.* 281, 215–225. <https://doi.org/10.1016/j.epsl.2009.02.034>.
- Doughty, A.M., Kelly, M.A., Russell, J.M., Jackson, M.S., Anderson, B.M., Chipman, J., Nakileza, B.R., 2023. Last glacial maximum reconstructions of Rwenzori mountain glaciers. *Paleoceanogr. Paleoclimatol.* 38. <https://doi.org/10.1029/2022PA004527>.
- Duguay, C.R., Flato, G.M., Jeffries, M.O., Ménard, P., Morris, K., Rouse, W.R., 2003. Ice-cover variability on shallow lakes at high latitudes: model simulations and observations. *Hydrol. Process.* 17, 3465–3483. <https://doi.org/10.1002/hyp.1394>.
- Eiler, J.M., 2011. Paleoclimate reconstruction using carbonate clumped isotope thermometry. *Quat. Sci. Rev.* 30, 3575–3588. <https://doi.org/10.1016/j.quascirev.2011.09.001>.
- Ernst, R., Ejlsing, C.S., Antonny, B., 2016. Homeoviscous adaptation and the regulation of membrane lipids. *J. Mol. Biol.* 428, 4776–4791. <https://doi.org/10.1016/j.jmb.2016.08.013>.
- Feng, X., Zhao, C., D'Andrea, W.J., Liang, J., Zhou, A., Shen, J., 2019. Temperature fluctuations during the Common Era in subtropical southwestern China inferred from brGDGTs in a remote alpine lake. *Earth Planet. Sci. Lett.* 510, 26–36. <https://doi.org/10.1016/j.epsl.2018.12.028>.
- Fick, S.E., Hijmans, R.J., 2017. WorldClim 2: new 1-km spatial resolution climate surfaces for global land areas. *Int. J. Climatol.* 37, 4302–4315. <https://doi.org/10.1002/joc.5086>.
- Fréchette, B., de Vernal, A., Guiot, J., Wolfe, A.P., Miller, G.H., Fredskild, B., Kerwin, M.W., Richard, P.J.H., 2008. Methodological basis for quantitative reconstruction of air temperature and sunshine from pollen assemblages in Arctic Canada and Greenland. *Quat. Sci. Rev.* 27, 1197–1216. <https://doi.org/10.1016/j.quascirev.2008.02.016>.
- Garellick, S., Russell, J., Richards, A., Smith, J., Kelly, M., Anderson, N., Jackson, M.S., Doughty, A., Nakileza, B., Ivory, S., Dee, S., Marshall, C., 2022. The dynamics of warming during the last deglaciation in high-elevation regions of Eastern Equatorial Africa. *Quat. Sci. Rev.* 281, 107416. <https://doi.org/10.1016/j.quascirev.2022.107416>.
- Halamka, T.A., Raberg, J.H., McFarlin, J.M., Younkin, A.D., Mulligan, C., Liu, X.L., Kopf, S.H., 2023. Production of diverse brGDGTs by *Acidobacterium Solibacter usitatus* in response to temperature, pH, and O₂ provides a culturing perspective on brGDGT proxies and biosynthesis. *Geobiology* 21, 102–118. <https://doi.org/10.1111/gbi.12525>.
- Hamilton, P.B., Gajewski, K., Atkinson, D.E., Lean, D.R.S., 2001. Physical and chemical limnology of 204 lakes from the Canadian Arctic Archipelago. *Hydrobiologia* 457, 133–148. <https://doi.org/10.1023/A:1012275316543>.
- Herbert, T.D., Peterson, L.C., Lawrence, K.T., Liu, Z., 2010. Tropical Ocean temperatures over the past 3.5 million years. *Science* 80 328, 1530–1534. <https://doi.org/10.1126/science.1185435>.
- Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2016. The effect of improved chromatography on GDGT-based palaeoproxies. *Org. Geochem.* 93, 1–6. <https://doi.org/10.1016/j.orggeochem.2015.12.006>.
- Hopmans, E.C., Weijers, J.W.H., Schefuß, E., Herfort, L., Sinninghe Damsté, J.S., Schouten, S., 2004. A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids. *Earth Planet. Sci. Lett.* 224, 107–116. <https://doi.org/10.1016/j.epsl.2004.05.012>.
- Inglis, G.N., Bhattacharya, T., Hemingway, J.D., Hollingsworth, E.H., Feakins, S.J., Tierney, J.E., 2022. Biomarker approaches for reconstructing terrestrial environmental change. *Annu. Rev. Earth Planet. Sci.* 50, 369–394. <https://doi.org/10.1146/annurev-earth-032320-095943>.
- Lear, C.H., Elderfield, H., Wilson, P.A., 2000. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* 287, 269–272. <https://doi.org/10.1126/science.287.5451.269>.
- Li, J., Naafs, B.D.A., Pancost, R.D., Yang, H., Liu, D., Xie, S., 2017. Distribution of branched tetraether lipids in ponds from Inner Mongolia, NE China: insight into the source of brGDGTs. *Org. Geochem.* 112, 127–136. <https://doi.org/10.1016/j.orggeochem.2017.07.005>.
- Liang, J., Guo, Y., Richter, N., Xie, H., Vachula, R.S., Lupien, R.L., Zhao, B., Wang, M., Yao, Y., Hou, J., Liu, J., Russell, J.M., 2022. Calibration and application of branched GDGTs to Tibetan lake sediments: the influence of temperature on the fall of the guge kingdom in western tibet, China. *Paleoceanogr. Paleoclimatol.* 37, 1–23. <https://doi.org/10.1029/2021PA004393>.
- Livingstone, D.M., Lotter, A.F., Walkery, I.R., 1999. The decrease in summer surface water temperature with altitude in Swiss alpine lakes: a comparison with air temperature lapse rates. *Arctic Antarct. Alpine Res.* 31, 341–352. <https://doi.org/10.1080/15230430.1999.12003319>.
- Loomis, S.E., Russell, J.M., Eggermont, H., Verschuren, D., Sinninghe Damsté, J.S., 2014a. Effects of temperature, pH and nutrient concentration on branched GDGT distributions in East African lakes: implications for paleoenvironmental reconstruction. *Org. Geochem.* 66, 25–37. <https://doi.org/10.1016/j.orggeochem.2013.10.012>.
- Loomis, S.E., Russell, J.M., Heurieux, A.M., D'Andrea, W.J., Sinninghe Damsté, J.S., 2014b. Seasonal variability of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in a temperate lake system. *Geochim. Cosmochim. Acta* 144, 173–187. <https://doi.org/10.1016/j.gca.2014.08.027>.
- Loomis, S.E., Russell, J.M., Ladd, B., Street-Perrott, F.A., Sinninghe Damsté, J.S., 2012. Calibration and application of the branched GDGT temperature proxy on East African lake sediments. *Earth Planet. Sci. Lett.* 357–358, 277–288. <https://doi.org/10.1016/j.epsl.2012.09.031>.
- Loomis, S.E., Russell, J.M., Sinninghe Damsté, J.S., 2011. Distributions of branched GDGTs in soils and lake sediments from western Uganda: implications for a lacustrine paleothermometer. *Org. Geochem.* 42, 739–751. <https://doi.org/10.1016/j.orggeochem.2011.06.004>.
- Loomis, S.E., Russell, J.M., Verschuren, D., Morrill, C., De Cort, G., Sinninghe Damsté, J.S., Olago, D., Eggermont, H., Street-Perrott, F.A., Kelly, M.A., 2017. The tropical lapse rate steepened during the Last Glacial Maximum. *Sci. Adv.* 3, 1–8. <https://doi.org/10.1126/sciadv.1600815>.
- Martínez-Sosa, P., Tierney, J.E., Meredith, L.K., 2020. Controlled lacustrine microcosms show a brGDGT response to environmental perturbations. *Org. Geochem.* 145, 104041. <https://doi.org/10.1016/j.orggeochem.2020.104041>.
- Martínez-Sosa, P., Tierney, J.E., Stefanescu, I.C., Dearing Crampton-Flood, E., Shuman, B.N., Routson, C., 2021. A global Bayesian temperature calibration for lacustrine brGDGTs. *Geochim. Cosmochim. Acta* 305, 87–105. <https://doi.org/10.1016/j.gca.2021.04.038>.
- Medeiros, A.S., Chipman, M.L., Francis, D.R., Hamerlik, L., Langdon, P., Puleo, P.J.K., Schellinger, C., Steigleder, R., Walker, I.R., Woodroffe, S., Axford, Y., 2022. A continental-scale chironomid training set for reconstructing Arctic temperatures. *Quat. Sci. Rev.* 294, 107728. <https://doi.org/10.1016/j.quascirev.2022.107728>.
- Melillo, J.M., McGuire, A.D., Kicklighter, D.W., Moore, B., Vorosmarty, C.J., Schloss, A.L., 1993. Global climate change and terrestrial net primary production. *Nature* 363, 234–240. <https://doi.org/10.1038/363234a0>.
- Miller, D.R., Helen Habicht, M., Keisling, B.A., Castañeda, I.S., Bradley, R.S., 2018. A 900-year New England temperature reconstruction based on in situ seasonally produced branched glycerol dialkyl glycerol tetraethers (brGDGTs). *Clim. Past* 14, 1653–1667. <https://doi.org/10.5194/cp-14-1653-2018>.
- Naafs, B.D.A., Gallego-Sala, A.V., Inglis, G.N., Pancost, R.D., 2017a. Refining the global branched glycerol dialkyl glycerol tetraether (brGDGT) soil temperature calibration. *Org. Geochem.* 106, 48–56. <https://doi.org/10.1016/j.orggeochem.2017.01.009>.
- Naafs, B.D.A., Inglis, G.N., Zheng, Y., Amesbury, M.J., Biester, H., Bindler, R., Blewett, J., Burrows, M.A., del Castillo Torres, D., Chambers, F.M., Cohen, A.D., Evershed, R.P., Feakins, S.J., Gaika, M., Gallego-Sala, A., Gandois, L., Gray, D.M., Hatcher, P.G., Honorio Coronado, E.N., Hughes, P.D.M., Hugué, A., Könönen, M., Laggoun-Défarge, F., Lähdenoja, O., Lamentowicz, M., Marchant, R., McClymont, E., Pontevedra-Pombal, X., Ponton, C., Pourmand, A., Rizzuti, A.M., Rochefort, L., Schellekens, J., De Vleeschouwer, F., Pancost, R.D., 2017b. Introducing global peat-specific temperature and pH calibrations based on brGDGT bacterial lipids. *Geochim. Cosmochim. Acta* 208, 285–301. <https://doi.org/10.1016/j.gca.2017.01.038>.
- Ning, D., Zhang, E., Shulmeister, J., Chang, J., Sun, W., Ni, Z., 2019. Holocene mean annual air temperature (MAAT) reconstruction based on branched glycerol dialkyl glycerol tetraethers from Lake Ximenglongtan, southwestern China. *Org. Geochem.* 133, 65–76. <https://doi.org/10.1016/j.orggeochem.2019.05.003>.
- Parish, M.C., Du, X., Bjaksana, S., Russell, J.M., 2023. A brGDGT-based reconstruction of terrestrial temperature from the maritime continent spanning the last glacial maximum. *Paleoceanogr. Paleoclimatol.* 38, 1–17. <https://doi.org/10.1029/2022PA004501>.
- Peterse, F., Kim, J.H., Schouten, S., Kristensen, D.K., Koç, N., Sinninghe Damsté, J.S., 2009. Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway). *Org. Geochem.* 40, 692–699. <https://doi.org/10.1016/j.orggeochem.2009.03.004>.

- Peterse, F., van der Meer, J., Schouten, S., Weijers, J.W.H., Fierer, N., Jackson, R.B., Kim, J.H., Sinninghe Damsté, J.S., 2012. Revised calibration of the MBT-CBT paleotemperature proxy based on branched tetraether membrane lipids in surface soils. *Geochim. Cosmochim. Acta* 96, 215–229. <https://doi.org/10.1016/j.gca.2012.08.011>.
- Qian, S., Yang, H., Dong, C., Wang, Y., Wu, J., Pei, H., Dang, X., Lu, J., Zhao, S., Xie, S., 2019. Rapid response of fossil tetraether lipids in lake sediments to seasonal environmental variables in a shallow lake in central China: implications for the use of tetraether-based proxies. *Org. Geochem.* 128, 108–121. <https://doi.org/10.1016/j.orggeochem.2018.12.007>.
- Raberg, J.H., Harning, D.J., Crump, S.E., de Wet, G., Blumm, A., Kopf, S., Geirsdóttir, Á., Miller, G.H., Sepúlveda, J., 2021. Revised fractional abundances and warm-season temperatures substantially improve brGDGT calibrations in lake sediments. *Biogeosciences* 18, 3579–3603. <https://doi.org/10.5194/bg-18-3579-2021>.
- Raberg, J.H., Miller, G.H., Geirsdóttir, Á., Sepúlveda, J., 2022. Near-universal trends in brGDGT lipid distributions in nature. *Sci. Adv.* 8, 1–13. <https://doi.org/10.1126/sciadv.abm7625>.
- Russell, J.M., Hopmans, E.C., Loomis, S.E., Liang, J., Sinninghe Damsté, J.S., 2018. Distributions of 5- and 6-methyl branched glycerol dialkyl glycerol tetraethers (brGDGTs) in East African lake sediment: effects of temperature, pH, and new lacustrine paleotemperature calibrations. *Org. Geochem.* 117, 56–69. <https://doi.org/10.1016/j.orggeochem.2017.12.003>.
- Shanahan, T.M., Huguen, K.A., Van Mooy, B.A.S., 2013. Temperature sensitivity of branched and isoprenoid GDGTs in Arctic lakes. *Org. Geochem.* 64, 119–128. <https://doi.org/10.1016/j.orggeochem.2013.09.010>.
- Sinensky, M., 1974. Homeoviscous adaptation—a homeostatic process that regulates the viscosity of membrane lipids in *Escherichia coli*. *Proc. Natl. Acad. Sci. USA* 71, 522–525. <https://doi.org/10.1073/pnas.71.2.522>.
- Sinninghe Damsté, J.S., Hopmans, E.C., Pancost, R.D., Schouten, S., Geenevasen, J.A.J., 2000. Newly discovered non-isoprenoid glycerol dialkyl glycerol tetraether lipids in sediments. *Chem. Commun.* 1683–1684. <https://doi.org/10.1039/b004517i>.
- Sinninghe Damsté, J.S., Ossebaer, J., Abbas, B., Schouten, S., Verschuren, D., 2009. Fluxes and distribution of tetraether lipids in an equatorial African lake: constraints on the application of the TEX86 palaeothermometer and BIT index in lacustrine settings. *Geochim. Cosmochim. Acta* 73, 4232–4249. <https://doi.org/10.1016/j.gca.2009.04.022>.
- Sinninghe Damsté, J.S., Rijpstra, W.I.C., Foesel, B.U., Huber, K.J., Overmann, J., Nakagawa, S., Kim, J.J., Dunfield, P.F., Dedysh, S.N., Villanueva, L., 2018. An overview of the occurrence of ether- and ester-linked iso-diabolic acid membrane lipids in microbial cultures of the Acidobacteria: implications for brGDGT paleoproxies for temperature and pH. *Org. Geochem.* 124, 63–76. <https://doi.org/10.1016/j.orggeochem.2018.07.006>.
- Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Weijers, J.W.H., Foesel, B.U., Overmann, J., Dedysh, S.N., 2011. 13,16-Dimethyl octacosanedioic acid (iso-diabolic acid), a common membrane-spanning lipid of Acidobacteria subdivisions 1 and 3. *Appl. Environ. Microbiol.* 77, 4147–4154. <https://doi.org/10.1128/AEM.00466-11>.
- Tierney, J.E., Russell, J.M., 2009. Distributions of branched GDGTs in a tropical lake system: implications for lacustrine application of the MBT/CBT paleoproxy. *Org. Geochem.* 40, 1032–1036. <https://doi.org/10.1016/j.orggeochem.2009.04.014>.
- Tierney, J.E., Russell, J.M., Eggermont, H., Hopmans, E.C., Verschuren, D., Sinninghe Damsté, J.S., 2010. Environmental controls on branched tetraether lipid distributions in tropical East African lake sediments. *Geochim. Cosmochim. Acta* 74, 4902–4918. <https://doi.org/10.1016/j.gca.2010.06.002>.
- Tierney, J.E., Schouten, S., Pitcher, A., Hopmans, E.C., Sinninghe Damsté, J.S., 2012. Core and intact polar glycerol dialkyl glycerol tetraethers (GDGTs) in Sand Pond, Warwick, Rhode Island (USA): insights into the origin of lacustrine GDGTs. *Geochim. Cosmochim. Acta* 77, 561–581. <https://doi.org/10.1016/j.gca.2011.10.018>.
- van Bree, L.G.J., Peterse, F., Baxter, A.J., De Crop, W., van Grinsven, S., Villanueva, L., Verschuren, D., Sinninghe Damsté, J.S., 2020. Seasonal variability and sources of in situ brGDGT production in a permanently stratified African crater lake. *Biogeosciences* 17, 5443–5463. <https://doi.org/10.5194/bg-17-5443-2020>.
- Volkman, J.K., Eglinton, Geoffrey, Eric, D.S., Corner, Forsberg, T.E.V., 1980. Long-chain alkenes and alkenones in the marine coccolithophorid. *Phytochemistry* 19, 2619–2622.
- Wang, H., An, Z., Lu, H., Zhao, Z., Liu, W., 2020. Calibrating bacterial tetraether distributions towards in situ soil temperature and application to a loess-paleosol sequence. *Quat. Sci. Rev.* 231, 106172. <https://doi.org/10.1016/j.quascirev.2020.106172>.
- Wang, H., Chen, W., Zhao, H., Cao, Y., Hu, J., Zhao, Z., Cai, Z., Wu, S., Liu, Z., Liu, W., 2023. Biomarker-based quantitative constraints on maximal soil-derived brGDGTs in modern lake sediments. *Earth Planet. Sci. Lett.* 602, 117947. <https://doi.org/10.1016/j.epsl.2022.117947>.
- Wang, H., Liu, W., He, Y., Zhou, A., Zhao, H., Liu, H., Cao, Y., Hu, J., Meng, B., Jiang, J., Kolpakova, M., Krivonogov, S., Liu, Z., 2021. Salinity-controlled isomerization of lacustrine brGDGTs impacts the associated MBT 5ME' terrestrial temperature index. *Geochim. Cosmochim. Acta* 305, 33–48. <https://doi.org/10.1016/j.gca.2021.05.004>.
- Wang, H., Liu, W., Zhang, C.L., Wang, Z., Wang, J., Liu, Z., Dong, H., 2012. Distribution of glycerol dialkyl glycerol tetraethers in surface sediments of Lake Qinghai and surrounding soil. *Org. Geochem.* 47, 78–87. <https://doi.org/10.1016/j.orggeochem.2012.03.008>.
- Weber, Y., De Jonge, C., Rijpstra, W.I.C., Hopmans, E.C., Stadnitskaia, A., Schubert, C.J., Lehmann, M.F., Sinninghe Damsté, J.S., Niemann, H., 2015. Identification and carbon isotope composition of a novel branched GDGT isomer in lake sediments: evidence for lacustrine branched GDGT production. *Geochim. Cosmochim. Acta* 154, 118–129. <https://doi.org/10.1016/j.gca.2015.01.032>.
- Weber, Y., Sinninghe Damsté, J.S., Zopfi, J., De Jonge, C., Gilli, A., Schubert, C.J., Lepori, F., Lehmann, M.F., Niemann, H., 2018. Redox-dependent niche differentiation provides evidence for multiple bacterial sources of glycerol tetraether lipids in lakes. *Proc. Natl. Acad. Sci. USA* 115, 10926–10931. <https://doi.org/10.1073/pnas.1805186115>.
- Weijers, J.W.H., Schouten, S., Hopmans, E.C., Geenevasen, J.A.J., David, O.R.P., Coleman, J.M., Pancost, R.D., Sinninghe Damsté, J.S., 2006. Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits. *Environ. Microbiol.* 8, 648–657. <https://doi.org/10.1111/j.1462-2920.2005.00941.x>.
- Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S., 2007. Environmental controls on bacterial tetraether membrane lipid distribution in soils. *Geochim. Cosmochim. Acta* 71, 703–713. <https://doi.org/10.1016/j.gca.2006.10.003>.
- Weijers, J.W.H., Steinmann, P., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2011. Bacterial tetraether membrane lipids in peat and coal: testing the MBT-CBT temperature proxy for climate reconstruction. *Org. Geochem.* 42, 477–486. <https://doi.org/10.1016/j.orggeochem.2011.03.013>.
- Wu, J., Yang, H., Pancost, R.D., Naafs, B.D.A., Qian, S., Dang, X., Sun, H., Pei, H., Wang, R., Zhao, S., Xie, S., 2021. Variations in dissolved O₂ in a Chinese lake drive changes in microbial communities and impact sedimentary GDGT distributions. *Chem. Geol.* 579, 120348. <https://doi.org/10.1016/j.chemgeo.2021.120348>.
- Yang, H., Lü, X., Ding, W., Lei, Y., Dang, X., Xie, S., 2015. The 6-methyl branched tetraethers significantly affect the performance of the methylation index (MBT) in soils from an altitudinal transect at Mount Shennongjia. *Org. Geochem.* 82, 42–53. <https://doi.org/10.1016/j.orggeochem.2015.02.003>.
- Zhang, Y.-M., Rock, C.O., 2008. Membrane lipid homeostasis in bacteria. *Nat. Rev. Microbiol.* 6, 222–233. <https://doi.org/10.1038/nrmicro1839>.
- Zhao, B., 2021. Organic Biomarker Based Climate Reconstruction in Southern Greenland and its Relationship to the Demise of Norse Settlements. University of Massachusetts Amherst. <https://doi.org/10.7275/24528222>.
- Zhao, B., Castaneda, I., Miller, D., Habicht, M., Keisling, B., Salacup, J., Bradley, R., 2021a. High seasonal variability in branched GDGT concentrations and distributions in settling particulate matter from Basin Pond, Maine, Northeastern USA. In: *AGU Fall Meeting Abstracts*. PP25D-0950.
- Zhao, B., Castañeda, I.S., Bradley, R.S., Salacup, J.M., de Wet, G.A., Daniels, W.C., Schneider, T., 2021b. Development of an in situ branched GDGT calibration in Lake 578, southern Greenland. *Org. Geochem.* 152, 104168. <https://doi.org/10.1016/j.orggeochem.2020.104168>.
- Zhao, B., Castañeda, I.S., Salacup, J.M., Thomas, E.K., Daniels, W.C., Schneider, T., de Wet, G.A., Bradley, R.S., 2022. Prolonged drying trend coincident with the demise of Norse settlement in southern Greenland. *Sci. Adv.* 8. <https://doi.org/10.1126/sciadv.abm4346>.
- Zhao, J., Huang, Y., Yao, Y., An, Z., Zhu, Y., Lu, H., Wang, Z., 2020. Calibrating branched GDGTs in bones to temperature and precipitation: application to Alaska chronological sequences. *Quat. Sci. Rev.* 240, 106371. <https://doi.org/10.1016/j.quascirev.2020.106371>.
- Zhao, J., Tsai, V.C., Huang, Y., 2022. A nonlinear model for resolving the temperature bias of branched glycerol dialkyl glycerol tetraether (brGDGT) temperature proxies. *Geochim. Cosmochim. Acta* 327, 158–169. <https://doi.org/10.1016/j.gca.2022.04.022>.