

A lacustrine GDGT-temperature calibration from the Scandinavian Arctic to Antarctic: Renewed potential for the application of GDGT-paleothermometry in lakes

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Abstract

Quantitative climate reconstructions are fundamental to understand long-term trends in natural climate variability and to test climate models used to predict future climate change. Recent advances in molecular geochemistry have led to calibrations using glycerol dialkyl glycerol tetraethers (GDGTs), a group of temperature-sensitive membrane lipids found in Archaea and bacteria. GDGTs have been used to construct temperature indices for oceans (TEX₈₆ index) and soils (MBT/CBT index). The aim of this study is to examine GDGT-temperature relationships and assess the potential of constructing a GDGT-based palaeo-thermometer for lakes. We examine GDGT-temperature relationships using core top sediments from 90 lakes across a north–south transect from the Scandinavian Arctic to Antarctica including sites from Finland, Sweden, Siberia, the UK, Austria, Turkey, Ethiopia, Uganda, Chile, South Georgia and the Antarctic Peninsula. We examine a suite of 15 GDGTs, including compounds used in the TEX₈₆ and MBT/CBT indices and reflecting the broad range of GDGT inputs to small lake systems.

GDGTs are present in varying proportions in all lakes examined. The TEX₈₆ index is not applicable to our sites because of the large relative proportions of soil derived and methanogenic components. Similarly, the MBT/CBT index is also not applicable and predicts temperatures considerably lower than those measured. We examine relationships between individual GDGT compounds and temperature, pH, conductivity and water depth. Temperature accounts for a large and statistically independent fraction of variation in branched GDGT composition. We propose a GDGT-temperature regression model with high accuracy and precision ($R^2 = 0.88$; RMSE = 2.0 °C; RMSEP = 2.1 °C) for use in lakes based on a subset of branched GDGT compounds and highlight the potential of this new method for reconstructing past temperatures using lake sediments. © 2011 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Lake sediments are useful archives of past environmental and climate change. However, to date there is no robust method for directly reconstructing past temperatures using lake sediments since most methods rely on biological

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proxies (e.g. pollen, chironomids, diatoms) which are influenced by changes in catchment or water chemistry that confound the temperature signal (e.g. Anderson, 2000; Velle et al., 2010). Palaeotemperature proxies based on molecular biomarkers are promising since environmental controls on membrane lipid distributions are thought to be relatively uncomplicated (Tierney et al., 2010). Calibrations using temperature dependent alkenones (di-, tri- and tetra-unsaturated methyl ketones) have been examined using lake sediments (e.g. Zink et al., 2001; Sun et al., 2004; Chu et al., 2005; Pearson et al., 2008). However, these studies show that alkenones are not present in all lakes, lacustrine distributions are also influenced by salinity and brine type and that in lakes, unlike in marine environments, alkenones originate from a variety of source organisms, many of which are unknown. These factors make it difficult to construct an alkenone-temperature calibration that is universally appropriate and applicable to lacustrine sediment cores. More recently, an alternative approach using glycerol dialkyl glycerol tetraethers (GDGTs) as temperature indicators in lakes has been examined.

1.1. Lacustrine GDGT temperature studies

1.1.1. TEX_{86}

In marine systems the composition of glycerol dialkyl glycerol tetraether (GDGT) cell membrane lipids of Thaumarchaeota (a phylum of the domain Archaea, formerly known as Crenarchaeota; see Spang et al., 2010) is strongly dependent on growth temperature and this relationship has been quantified in the TEX_{86} index (TetraEther indeX of tetraethers consisting of 86 carbon atoms; Schouten et al., 2002) and used to create marine TEX_{86} -temperature calibrations (e.g. see Kim et al., 2010). The isoprenoid GDGTs used in TEX_{86} (Eq. 1) are produced by predominantly mesophilic (aquatic) Thaumarchaeota (GDGT-IV and GDGT-IV' – see Fig. 1 for structures) but also include a more widespread, universal array of Archaea including methanogens, methane oxidisers and halophiles (e.g. GDGT-V, GDGT-VI, GDGT-VII and GDGT-VIII).

$$TEX_{86} = \frac{(\text{GDGT-VII} + \text{GDGT-VIII} + \text{GDGT-IV}')}{(\text{GDGT-VI} + \text{GDGT-VII} + \text{GDGT-VIII} + \text{GDGT-IV}')} \quad (1)$$

These GDGTs have also been found in lakes and used to create lacustrine TEX_{86} calibrations (e.g. Powers et al., 2004, 2010; Blaga et al., 2009; Zink et al., 2010). However, these studies have met with limited success due, in part, to (1) the usually low abundance of the isoprenoid compounds, (notably the crenarchaeol isomer, GDGT-IV') in many lakes, and (2) dominant inputs of branched GDGTs (e.g. GDGT-I, GDGT-II, GDGT-III) which are thought to be derived predominantly from catchment soil bacteria which can confound the TEX_{86} temperature signal (Sinninghe Damsté et al., 2000; Hopmans et al., 2004; Weijers et al., 2006). The Branched Isoprenoid Tetraether (BIT) index (Eq. 2; Hopmans et al., 2004) can be used to assess relative inputs of branched GDGTs to sediments and provides a means to identify sites with large inputs of soil organic

matter and where the TEX_{86} -temperature relationship is likely to be unreliable (Hopmans et al., 2004; Weijers et al., 2006).

$$\text{BIT} = \frac{(\text{GDGT-III} + \text{GDGT-II} + \text{GDGT-I})}{(\text{GDGT-III} + \text{GDGT-II} + \text{GDGT-I} + \text{GDGT-IV})} \quad (2)$$

Removal of samples with high BIT values from calibration datasets has improved calibrations but results in datasets with few samples. For example, Blaga et al. (2009) excluded lakes with $\text{BIT} > 0.4$ resulting in 9 out of 47 lakes showing potential for TEX_{86} and Powers et al. (2010) excluded samples with $\text{BIT} > 0.5$, using only 12 out of 46 samples. Bechtel et al. (2010) also found most promise in applying the calibration of Powers et al. (2010) to samples with $\text{BIT} < 0.3$.

The application of TEX_{86} is also problematic in lakes with high rates of anaerobic oxidation of methane and high proportions of GDGT-V, GDGT-VI and GDGT-VII which are derived from anaerobic methanotrophic Archaea (Pancost et al., 2001; Wakeham et al., 2003). This means that where GDGT-V is found in abundance alongside branched GDGTs, GDGT-V is likely to be derived from a different source, most likely methanogenic Archaea (Hopmans et al., 2004) such as methanogenic Euryarchaeota which can contribute large amounts of GDGT-V to the microbial soil community (Koga et al., 1993). In Thaumarchaeota the GDGT-V/crenarchaeol (GDGT-IV) ratio typically varies between 0.2 and 2 (Schouten et al., 2002) and a ratio > 2 indicates a substantial methanogenic origin for GDGT-V (Blaga et al., 2009) because methanogens synthesise GDGT-V but not crenarchaeol. Since methanogenesis is the dominant anaerobic mineralisation process in lake sediments, methanogenic Archaea may be an important source of GDGTs in lakes (Blaga et al., 2009). Recent studies (e.g. Blaga et al., 2009; Bechtel et al., 2010) indicate that TEX_{86} should only be applied in lakes with sufficient production of GDGTs by aquatic Thaumarchaeota relative to isoprenoid GDGTs derived from catchment soils or other sources such as methanotrophs. Therefore, while TEX_{86} is a promising tool for palaeotemperature reconstruction in some lake sediments, careful screening is required and the factors discussed above limit its general applicability as a continental lacustrine palaeotemperature proxy.

1.1.2. MBT/CBT

In their global soil survey Weijers et al. (2007) found that the cyclisation ratio of branched tetraethers (CBT; Eq. 3) showed a significant relationship with soil pH (Eq. 4) and that the degree of methylation (expressed by the MBT index; Eq. 5) combined with the CBT index was significantly correlated with mean annual air temperature (MAAT; Eq. 6).

$$\text{CBT} = -\log((\text{GDGT-Ib} + \text{GDGT-IIb})/(\text{GDGT-I} + \text{GDGT-II})) \quad (3)$$

$$\text{CBT} = 3.33 - 0.38 \cdot \text{pH} \quad (4)$$

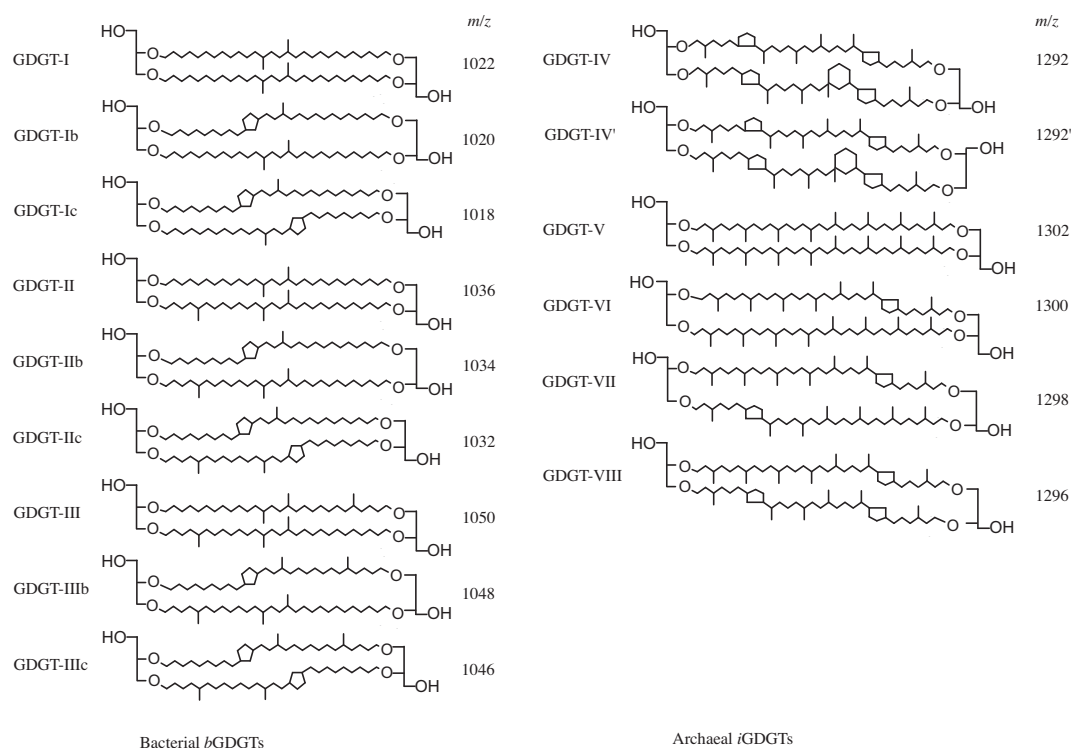


Fig. 1. Chemical structures of the glycerol dialkyl glycerol tetraether (GDGT) membrane lipids discussed in the text.

$$\begin{aligned} \text{MBT} = & (\text{GDGT-I} + \text{GDGT-Ib} + \text{GDGT-Ic}) \\ & / ((\text{GDGT-I} + \text{GDGT-Ib} + \text{GDGT-Ic}) \\ & + (\text{GDGT-II} + \text{GDGT-IIb} + \text{GDGT-IIc}) \\ & + (\text{GDGT-III} + \text{GDGT-IIIb} \\ & + \text{GDGT-IIIc})) \end{aligned} \quad (5)$$

$$\text{MBT} = 0.122 + 0.187 \cdot \text{CBT} + 0.020 \cdot \text{MAAT} \quad (6)$$

This MBT/CBT index may be more applicable to lake systems than the marine derived TEX₈₆ index and, in particular, to small and shallow lakes with high proportions of catchment/soil derived GDGT inputs. Moreover, while branched GDGTs were first thought to derive predominantly from peat and soil bacterial lipids (e.g. [Sinninghe Damsté et al., 2000](#); [Weijers et al., 2006, 2007](#)), more recent studies have suggested that branched GDGTs can also originate from within the water column, although in most lakes these GDGTs will derive from a combination of the two sources ([Tierney and Russell, 2009](#); [Sinninghe Damsté et al., 2009](#)).

Some authors have applied the MBT/CBT index to lake sediments ([Blaga et al., 2010](#); [Tierney et al., 2010](#); [Zink et al., 2010](#); [Sun et al., 2011](#)) but in all cases, though a correlation was found between MBT/CBT and temperature, the MBT/CBT-inferred temperatures considerably underestimated measured values. Application of the MBT/CBT index to core material from a eutrophic lake by [Bechtel et al. \(2010\)](#) also underestimated temperatures when compared with the instrumental record although the method showed more promise when applied

to a core from an oligotrophic lake. This problem has led to alternative, weighted calibration approaches being used (e.g. [Tierney et al., 2010](#)).

1.1.3. This study

In this study we investigate relationships between all fifteen GDGT compounds used in the TEX₈₆ and MBT/CBT indices and quantify their responses to temperature and other key limnological variables. Our motivation for examining all GDGTs is that the TEX₈₆ index, which was originally derived from marine environments, is not directly applicable due to relatively large proportions of branched GDGTs which may confound the TEX₈₆ signal in small lakes with large terrestrial inputs. Similarly, the MBT/CBT index is also not directly applicable because it was calibrated using soils rather than aquatic sediments. Since lacustrine sediments, especially in relatively small lakes, contain GDGTs derived from aquatic and terrestrial sources we examine the full suite of GDGTs from both of these sources.

To date lacustrine GDGT studies have predominantly examined groups of lakes within discrete or regional geographical locations. Here we examine the GDGT composition of 90 lakes spanning a latitudinal gradient from the Scandinavian Arctic to the Antarctic Peninsula. While regional datasets are often limited by a narrow temperature gradient as well as geographical range, our north-south transect spans a wide temperature range from ~1–31 °C and provides potential to examine GDGT distributions

and relationships with temperature at a much larger geographical scale than previous studies. Our principal aim is to examine GDGT-temperature relationships and assess the potential of constructing a GDGT-temperature calibration for use in lakes.

2. SAMPLES AND METHODS

2.1. Study sites

Surface sediments (0–2 cm) were collected from 90 lakes during various field campaigns and span a wide temperature, as well as geographical, gradient from within the Arctic Circle in Finland and Sweden to Siberia, the UK, Austria, Turkey, Ethiopia, Uganda, Chile, South Georgia and the Antarctic Peninsula (Fig. 2). Our sample set includes lakes of various sizes (from 0.01 to >3000 km²) and from a wide range of environments (e.g. alpine, forest, plantation, national park, boreal, tundra, mountain, polar, oceanic islands), elevations (2.5–2260 m), depths (<1–141 m), and water chemistries (e.g. conductivity 10.6 $\mu\text{S cm}^{-1}$ –74.1 mS cm^{-1} , pH 4.5–10.7). A summary of some of the major lake features are listed in Table 1.

2.2. Experimental procedures

GDGTs were extracted from freeze-dried and homogenised samples (0.1–2 g) using 15 ml DCM/methanol (3:1) and a MARS 5 microwave assisted solvent extraction sys-

tem (CEM Microwave Technology Ltd. UK). We used a temperature programme that heated to 70 °C in 2 min and held at 70 °C for 5 min (e.g. see Kornilova and Rosell-Melé, 2003). Sample extracts were saponified with 6% KOH and the neutral fraction (containing GDGTs) extracted using hexane. The dried extract was dissolved in 99:1 hexane:propan-2-ol and filtered through a 0.45 μm PTFE filter prior to analysis.

GDGTs were analysed by normal-phase LC/MSⁿ using a Surveyor HPLC system (ThermoFinnigan, Hemel Hempstead, UK) interfaced to a ThermoFinnigan LCQ ion trap mass spectrometer. The HPLC system was fitted with a Grace Prevail Cyano HPLC column (3 μm , 150 \times 2.1 mm i.d.) and a guard column of the same material. Separation was achieved at 30 °C with a flow-rate of 0.2 ml min^{-1} and the following gradient profile: 50% A, 50% B (0–5 min); 10% A, 90% B (at 25 min); 100% C (at 30 min, hold 10 min) then return to starting conditions and allow to equilibrate for 20 min (where A = Hexane, B = 2% propan-2-ol in Hexane, C = 10% propan-2-ol in Hexane; all HPLC grade purchased from Fisher [Loughborough, UK]).

The ThermoFinnigan LCQ MS was equipped with an atmospheric pressure chemical ionisation interface (APCI) source operated in positive ion mode. LC/MS settings were as follows: Vaporiser 400 °C, capillary temperature 200 °C, discharge current 5 μA , sheath gas flow 40 and auxiliary gas 6 (arbitrary units). Detection of GDGTs was achieved using the mass ranges m/z 1280–1310 for isoprenoid GDGTs and m/z 1015–1055 for branched GDGTs.

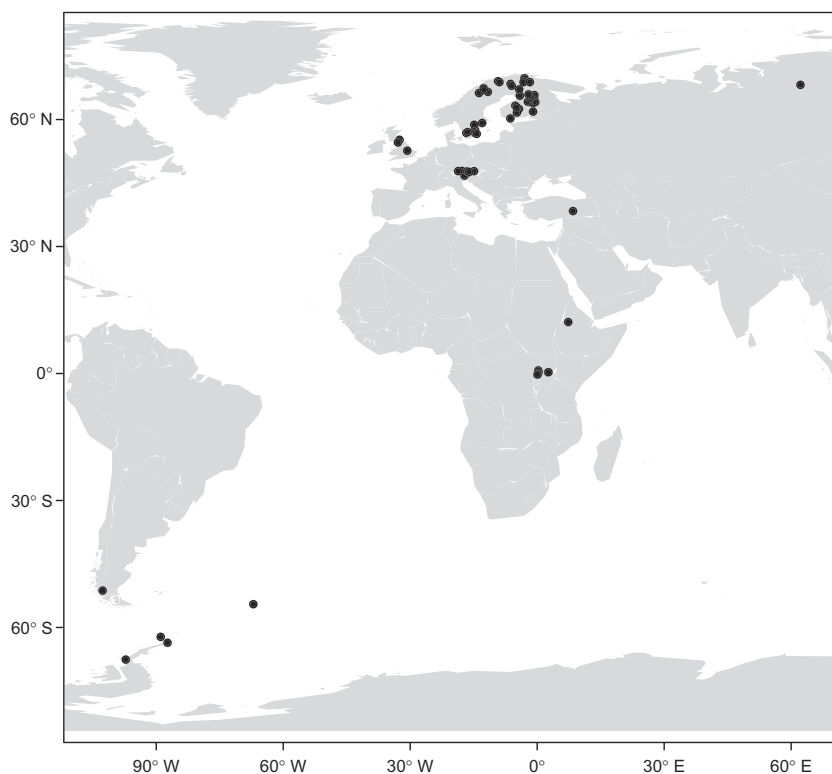


Fig. 2. Map showing location of study sites.

Table 1
Lake temperature and environmental characteristics summarised by region.

Country	Dataset Code	Number of lakes	Temperature °C		Latitude		Longitude		Water Depth m		Altitude m		Conductivity $\mu\text{S}/\text{cm}$		pH	
			Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	max
Antarctic Peninsula	AN	6	1.6	6.5	S 62.21	S 67.21	W 57.34	W 67.21	4.0	26.0	2.5	34.0	93.7	250.0	6.54	8.61
Austria	AU	13	9.4	21.6	N 46.79	N 47.87	E 11.29	E 15.05	7.3	78.0	470.0	2260.0	121.0	460.0	7.70	8.70
Chile	CH	1	11.8	11.8	S 51.30	S 51.30	W 72.67	W 72.67	4.4	4.4	50.0	50.0	246.0	246.0	8.81	8.81
Ethiopia	ET	1	20.0	20.0	N 12.17	N 12.17	E 37.33	E 37.33	14.0	14.0	1830.0	1830.0	220.0	220.0	8.40	8.40
Northern Finland	NF	21	10.9	15.9	N 64.12	N 69.76	E 20.79	E 29.55	1.3	20.0	74.7	473.0	18.0	36.0	5.48	7.36
Southern Finland	SF	8	15.4	17.1	N 60.28	N 63.86	E 23.68	E 29.14	6.2	24.0	53.9	180.6	15.0	120.0	6.30	7.70
South Georgia	SG	1	4.6	4.6	S 54.5	S 54.50	W 37.05	W 37.05	17.5	17.5	94.0	94.0	38.0	38.0	8.07	8.07
Siberia	SI	1	11.8	11.8	N 68.17	N 68.17	E 92.173	E 92.173	8.1	8.1	569.0	569.0	22.0	22.0	7.00	7.28
Southern Sweden	SS	7	14.6	15.9	N 56.59	N 59.18	E 13.24	E 17.02	2.3	15.5	98.4	237.0	34.1	70.1	4.50	6.82
Northern Sweden	SW	12	7.5	14.3	N 66.29	N 67.45	E 16.29	E 18.36	3.2	21.3	304.0	1250.0	10.6	82.3	5.91	7.01
Turkey	TU	1	27.7	27.7	N 38.38	N 38.38	E 38.46	E 38.46	26.0	26.0	1363.0	1363.0	4000.0	4000.0	8.00	8.00
Uganda	UG	15	21.8	31.2	S 0.10	N 0.70	E 30.03	E 32.65	0.9	141.0	120.0	1520.0	119.0	74100.0	6.63	10.66
UK	UK	3	15.0	20.0	N 52.65	N 55.18	W 0.66	W 2.89	10.5	25.3	85.0	184.0				
Total lakes		90	1.6	31.2					0.9	141.0	2.5	2260.0	10.6	74100.0	4.50	10.66

2.3. Temperature data and numerical analysis

Tight coupling between air and lake water temperature (e.g. Edinger et al., 1968; Webb and Nobilis, 1997; Livingstone and Dokulil, 2001) means that air temperatures are generally considered to be a reliable and robust surrogate for water temperatures in limnological studies. Air temperatures have also been shown to improve the performance of paleolimnological transfer functions that previously relied on surface-water temperature data (see Livingstone and Lotter, 1998; Brooks, 2006). Where possible in this study summer air temperature data was obtained from the nearest climate station and was lapse rate corrected (Laaksonen, 1976). Where we did not have climate station air temperature data we used water temperature data that we consider to be the most reliable long-term *in situ* measurements of temperature (e.g. averaged over several summer field seasons or obtained from thermistors installed within lakes for long-term monitoring) or published data. All reference to measured temperature data in our discussion reflects mean summer temperature data. We use summer temperature data, rather than mean annual data, for two reasons. First, mean annual temperature data does not exist for many of the lakes in our dataset as they have been monitored during the summer which is common for biological proxy studies (e.g. Rosén et al., 2001; Huber et al., 2010; Schmidt et al., 2004). Furthermore, many lakes in our dataset are ice-covered for substantial periods of the year and not easily accessible outside of summer. Second, mean annual temperature is not a biologically relevant parameter for those sites which experience large seasonal fluctuations in temperature and long periods of ice cover. For these lakes it is more meaningful to relate GDGT composition to the temperature when lake (and GDGT) productivity will be greatest (e.g. Sun et al., 2011).

We explore relationships between GDGT composition, water chemistry and environmental parameters using ternary plots, redundancy analysis (RDA), variance partitioning and regressions of individual compounds with environmental parameters. RDA is a form of constrained principal components analysis in which the components are constrained to be linear combinations of one or more explanatory variables (ter Braak, 1994). As such, RDA provides an ordination in which variation in GDGT composition is directly related to lake physico-chemical characteristics, namely pH, conductivity, lake depth and temperature. The relative strength and statistical independence of each explanatory variable was assessed using a series of RDAs and partial RDAs to partition the variance in the GDGT compositional data into components related to (a) the marginal or total effect, and (b) the unique or independent effect of each variable (cf. Borcard et al., 1992). The significance of each component of variation was assessed using a Monte-Carlo permutation test (Manly, 2006) and the explained variance adjusted for the number of predictors according to Peres-Neto et al. (2006). GDGTs were expressed as relative abundances (percentages) prior to all analyses because we are interested in *compositional* rather than *concentration* differences between sites. It is also thought that although environmental factors other than

temperature might affect absolute concentrations they are less likely to affect relative abundance of GDGTs (Schouten et al., 2002). Lake water conductivity and depth showed right-skewed distributions and were log10 and square-root transformed respectively. All numerical analyses were performed using R software for statistical computing and graphics (R Development Core Team, 2010) with the vegan package (Oksanen et al., 2010).

3. RESULTS AND DISCUSSION

3.1. Exploratory analysis of GDGT occurrence, composition and environmental controls

GDGT compositions varied between samples with both isoprenoid and branched GDGTs found in all samples apart from 8 Swedish sites in which some isoprenoid compounds were below the detection limit. Fig. 3 illustrates some of the variations in dominant GDGTs and GDGT compositions found in our dataset (see Fig. 1 for structures). The variation in GDGT composition and dominance is summarised in Table 2 and is comparable to that found in the lakes studied by Blaga et al. (2009).

Fig. 4 illustrates relationships between the relative proportions of the three dominant GDGT compound groups: crenarchaeol (GDGT-IV), GDGT-V and branched-GDGTs. Although branched (bacterial) GDGTs tend to dominate our samples, a number of lakes also contain high relative abundances of GDGT-V, a “general” GDGT which occurs in methanogenic Archaea, thermophilic, and planktonic non-thermophilic Thaumarchaeota, and is also synthesised by soil Thaumarchaeota (e.g. Leininger et al., 2006; Schouten et al., 2000, 2002; Pitcher et al., 2011). Similarly to Blaga et al. (2009), crenarchaeol (a specific GDGT for aquatic Thaumarchaeota) was found in all our lakes (cf. Powers et al., 2010 who suggest Thaumarchaeota are present at only low concentrations or are absent in most small lakes). However, concentrations varied between 0.02% and 38% of total GDGTs in our study; only four lakes contained >20% crenarchaeol, and these lakes (which also had the lowest BIT values, see below) include two of the deepest lakes in our dataset (Grundlsee, 64 m; and Vorderer Lahngangsee, 78 m, both from Austria), and Lake Tana, Ethiopia (14 m depth). Blaga et al. (2009) also found crenarchaeol to be the dominant GDGT in deeper lakes. This is not surprising if aquatic Thaumarchaeota is the presumed dominant source and catchment (soil) inputs provide a minimal contribution to the total sediment GDGT pool. Fig. 4 shows that sites with higher GDGT-V indicative of methanogenic activity include a cluster of Ugandan lakes with elevated conductivities (up to $74,100 \mu\text{S cm}^{-1}$) and also Nar Golu (Turkey; $4000 \mu\text{S cm}^{-1}$). GDGT composition in Nar Golu differs substantially from other lakes. Tierney et al. (2010) also found unusual GDGT composition in sediments from saline lakes (where conductivity was as high as $>30,000 \mu\text{S cm}^{-1}$), and suggested that some of the compounds present in these sites may be structurally distinct from known branched GDGTs.

In our dataset the BIT index ranged from 0.28 to 1.00 although in the majority of sites (84%) the index was greater

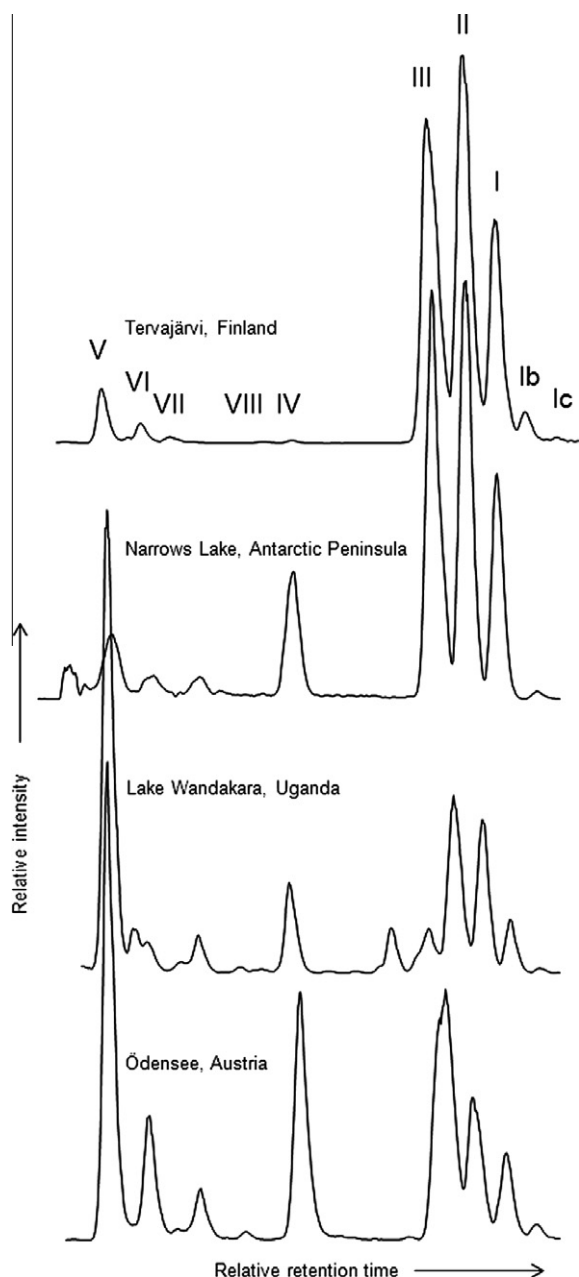


Fig. 3. LC-MS base peak chromatograms of GDGTs from four different lake environments examined in this study, illustrating examples of the different GDGT compositions encountered within our dataset. Roman numerals refer to the compound structures illustrated in Fig. 1.

than 0.9, reflecting the relatively large proportion of branched GDGTs. Our predominantly high BIT values are comparable to those found in soils (Hopmans et al., 2004; Weijers et al., 2007), with the lowest BIT values found in Lake Tana (Ethiopia) and two of the deepest lakes in our dataset, Grundlsee (64 m) and Vorderer Lahngangsee (78 m) which also had the largest proportions of aquatic crenarchaeol present. As found by Weijers et al. (2007) and Tierney et al. (2010), the BIT index in our study also predominantly reflects crenarchaeol concentration ($r = -0.75$) rather than branched GDGT concentration

($r = 0.2$). Two lakes (Nåitejauratj and Pallemjauratj, both from northern Sweden) had no crenarchaeol detected and in our dataset 79 out of our 90 lakes had a GDGT-V/crenarchaeol ratio of >2 . GDGT-V is a common membrane lipid of Archaea and in lake sediments methanogens and Group I Crenarchaeota (methanogenic Euryarchaeota) are thought to be the most likely sources (Koga et al., 1993; Sinninghe Damsté et al., 2000; Schouten et al., 2002; Wuchter et al., 2005; Blaga et al., 2009) although high ratios found in particulate organic matter from aerobic water columns does suggest that Archaea other than methanogens can also produce GDGT-V (see Blaga et al., 2009).

In order to examine environmental controls on GDGT composition we carried out redundancy analysis (RDA) and variance partitioning analysis on three different groups of GDGT compounds. Fig. 5 and Table 3 shows the results of RDA and variance partitioning analyses carried out on: (a) all GDGTs, (b) isoprenoid GDGTs as used in the TEX₈₆ index, and (c) all branched GDGTs. In all cases GDGT compounds are expressed as a percentage of the total GDGTs in that group.

In the RDA of all GDGTs (Fig. 5a) component 1 (which accounts for 38.3% of the variance in the GDGT composition) reflects the gradient from low conductivity, low pH lakes on the left which are dominated by branched GDGTs, to higher pH/conductivity lakes on the right, which are dominated by the isoprenoid GDGT-V, and clearly separates the Ugandan lakes within the dataset. Component 2 (which accounts for 11% of the variance in the GDGT composition) reflects, in part, the temperature gradient, with Antarctic and Siberian lakes characterised by high relative proportions of GDGT-III (bottom left) through to Ugandan lakes characterised by higher proportions of GDGT-Ib (top right). All four environmental variables account for statistically significant independent fractions of variance in the GDGT data (Table 3) although conductivity and temperature have the highest independent explanatory power. As a single explanatory variable pH accounts for almost 20% of the variation in GDGT composition but it has a very weak independent effect (1.5%) indicating that most of the pH signal is confounded with changes in conductivity and temperature.

RDA of isoprenoid GDGTs is shown in Fig. 5b. Components 1 and 2 account for only 13.3% and 4.9% of the variance in the GDGT data respectively, and essentially reflect the varying dominance of GDGT-V, with greater relative abundance of GDGT-V in higher conductivity sites displayed on the left of the diagram, suggesting that while methanogens are thought to be the most likely sources for GDGT-V (see above), this is also a more “universal” GDGT that can be produced by a broad array of Archaea (e.g. Powers et al., 2010) and here, may reflect a broad spectrum of source inputs. Water depth (and not temperature) is the only other significant environmental variable and appears related to minor variation on Component 2, with deeper lakes characterised by higher proportions of GDGT-IV’ and GDGT-IV reflecting higher proportions of aquatic crenarchaeol inputs and comparable to other findings of larger relative inputs or dominance of crenarchaeol in

Table 2

Minimum, maximum, mean and median proportions of GDGTs (expressed as a percentage of total GDGTs). GDGT compounds I, II, III and IV and V dominate. GDGT structures are shown in Fig. 1. IQR = inter-quartile range; n.d. = not detected in some lakes.

GDGT	Min	Max	Mean	Median	IQR
GDGT-I (m/z 1022)	1.33	61.9	19.9	18.5	18.3
GDGT-Ib (m/z 1020)	<0.1	6.2	2.2	2.1	1.6
GDGT-Ic (m/z 1018)	<0.1	8.1	0.7	0.6	0.5
GDGT-II (m/z 1036)	4.1	40.0	25.6	26.1	14.7
GDGT-IIb (m/z 1034)	<0.1	9.9	3.5	2.9	2.2
GDGT-IIc (m/z 1032)	<0.1	2.5	0.6	0.5	0.4
GDGT-III (m/z 1050)	1.6	56.0	18.4	19.0	14.3
GDGT-IIIb (m/z 1048)	<0.1	2.7	0.5	0.3	0.4
GDGT-IIIc (m/z 1046)	<0.1	6.1	0.4	0.1	0.2
GDGT-IV (m/z 1292)	<0.1	38.1	3.3	0.9	2.1
GDGT-IV' (m/z 1292 isomer)	<0.1	2.0	0.1	0.0	0.1
GDGT-V (m/z 1302)	1.9	77.0	21.1	11.9	26.8
GDGT-VI (m/z 1300)	0.2	11.1	2.0	1.3	1.5
GDGT-VII (m/z 1298)	n.d.	7.1	1.2	0.9	1.0
GDGT-VIII (m/z 1296)	n.d.	10.0	0.5	0.2	0.2

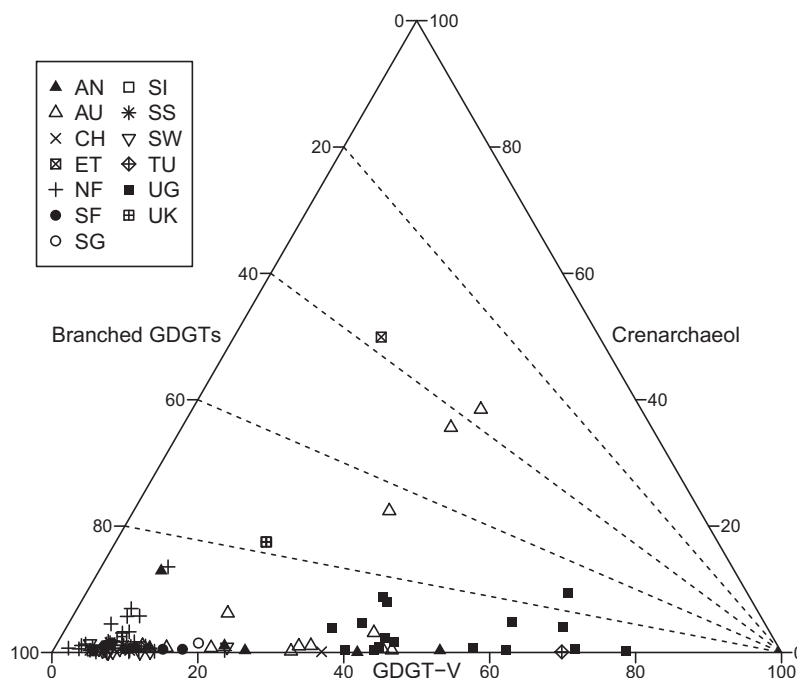


Fig. 4. Ternary diagram illustrating the relative proportions of branched GDGTs, Crenarchaeol and GDGT-V in the lakes studied. Lake dataset code: AN (Antarctic and Sub-Antarctic islands), AU (Austria), ET (Lake Tana, Ethiopia), NF (northern Finland), SF (southern Finland), SI (Siberia), SS (southern Sweden), SW (northern Sweden), TU (Nar Golu, Turkey), UG (Uganda), UK (United Kingdom).

deeper (and sometimes, but not always, larger) lakes (Blaga et al., 2009; Powers et al., 2010; Bechtel et al., 2010; Tierney et al., 2010). The negative joint effect for isoprenoid GDGTs arises because conductivity and depth are weakly positively correlated ($r = 0.17$) but have opposite effects on GDGT composition, leading to the counter-intuitive effect of suppression in the RDA (cf. Lewis and Escobar, 1986).

The RDA of branched GDGTs is shown in Fig. 5c. Component 1, which accounts for 38.8% of the variance, reflects the temperature gradient (see Table 3), with GDGTs, notably GDGT-Ic and GDGT-I, characteristic of higher temperature lakes (e.g. African, right) and GDGT-III

predominant in lower temperature lakes plotted on the left (e.g. Antarctic, Siberian). In their soil study Weijers et al. (2007) similarly found GDGT-I to be characteristic of warmer temperatures, being dominant in soils from warm, tropical areas, while GDGT-III was found to be more abundant in soils from colder regions and with dominance of GDGT-III (and also GDGT-II) in Arctic soils. More recently, Tierney et al. (2010) also found GDGT-III in East African lake sediments to be strongly correlated with temperature ($r = -0.96$; $r = -0.76$ in our study). They argue that high proportions of GDGT-III in lake sediments compared to soils suggests that GDGT-III is unlikely to be soil-derived and that branched GDGTs with a different

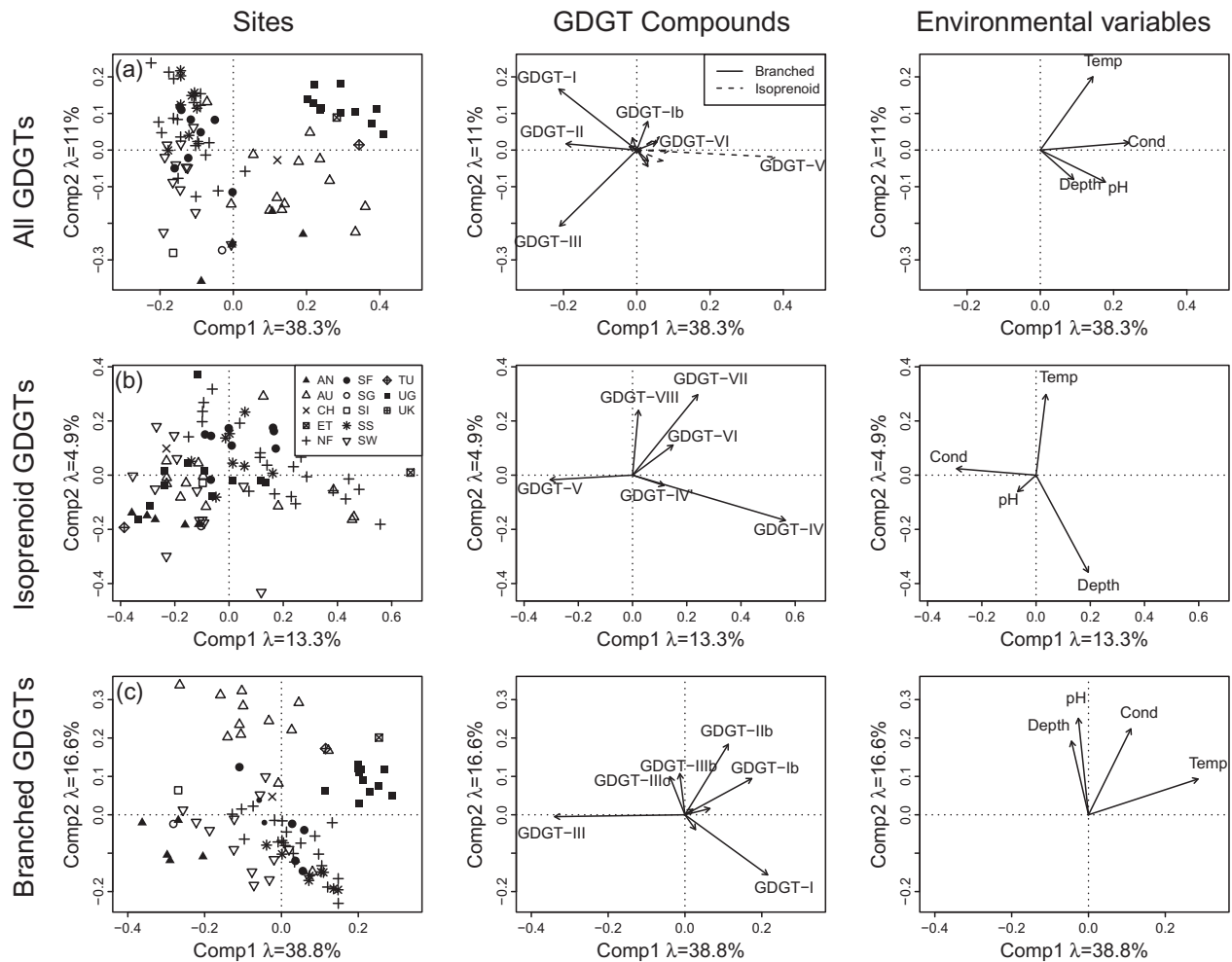


Fig. 5. Redundancy analysis (RDA) plots showing relationships between sites, GDGT composition and environmental variables using (a) all GDGTs, (b) isoprenoid GDGTs, and (c) branched GDGTs expressed as a proportion of the GDGTs examined within that group. Lake dataset codes as Fig. 4.

Table 3

Results of RDA and partial RDA, showing percentage variance in GDGT composition explained by each environmental variable. All components of variance are significant ($p \leq 0.01$) except those asterisked.

Variable	All GDGTs		Isoprenoid GDGTs		Branched GDGTs	
	Total	Unique	Total	Unique	Total	Unique
Temperature	18.7	7.9	0.7*	0.6*	35.9	27.2
pH	19.9	1.5	0.1*	0.1*	10.9	2.8
Conductivity	35.4	10.9	3.7	5.1	13.6	0.9
Water depth	6.5	3.1	3.4	4.9	6.7	4.4
All variables	49.9		8.5		53.8	
Joint effects		26.5		-1.5		18.5

composition from those in catchment soils are produced in lakes (Tierney and Russell, 2009; Tierney et al., 2010). As we did not analyse soil samples in our study we assume GDGT-III could originate from both *in situ* and soil-derived sources in our lakes.

Component 2 (Fig. 5c) reflects the pH/conductivity gradient with higher pH Austrian lakes and higher conductivity Ugandan lakes plotted top middle and right respectively, and which are characterised by cyclic GDGTs including

GDGT-Ic, GDGT-Ib and GDGT-IIb which have also been identified as driving relationships with pH by Weijers et al. (2007) and Tierney et al. (2010). More dilute, lower pH, lakes are plotted in the lower part of the diagram. Tierney et al. (2010) found (surface) water pH to account for a significant amount of variance in branched GDGT distributions in East African lakes, independent of other variables including temperature. Table 3 shows, however, that in our study although all four environmental variables are

significant, pH and conductivity have only small unique effects (2.8% and 0.9% respectively) making it difficult to identify their independent controls on GDGT composition. Temperature explains the largest fraction of variance and the difference between the total (35.9%) and unique (27.2%) fractions is small, indicating that temperature exerts a strong, statistically significant, and largely independent control on branched GDGT composition in these lakes.

3.2. Quantitative relationships between GDGTs, environment and temperature

The three sets of analyses shown in Fig. 5 suggest that, overall, the main influences on GDGT composition are temperature and conductivity but that temperature alone explains a much greater percentage of the variance in branched GDGT composition, conductivity (surrogate for

salinity) plays a greater role in explaining overall GDGT distributions and water depth is the only significant variable in explaining isoprenoid GDGT distributions. Our exploratory RDA analysis has shown temperature to be the most important variable influencing branched GDGT distributions in our dataset. Quantitative regression and modelling of GDGT-temperature relationships and further analyses will focus on this group of GDGT compounds (Section 3.2.3). First, however, we examine existing GDGT indices (TEX_{86} and MBT/CBT).

3.2.1. TEX_{86} -temperature relationships

While a significant relationship between TEX_{86} and temperature does exist for our dataset ($p = 0.0013$) this relationship is extremely weak ($r = 0.257$). The Ugandan sites show the widest scatter of TEX_{86} values (0.07–0.65) while all sites generally display a wide range of TEX_{86} values within each discrete geographical region and similar

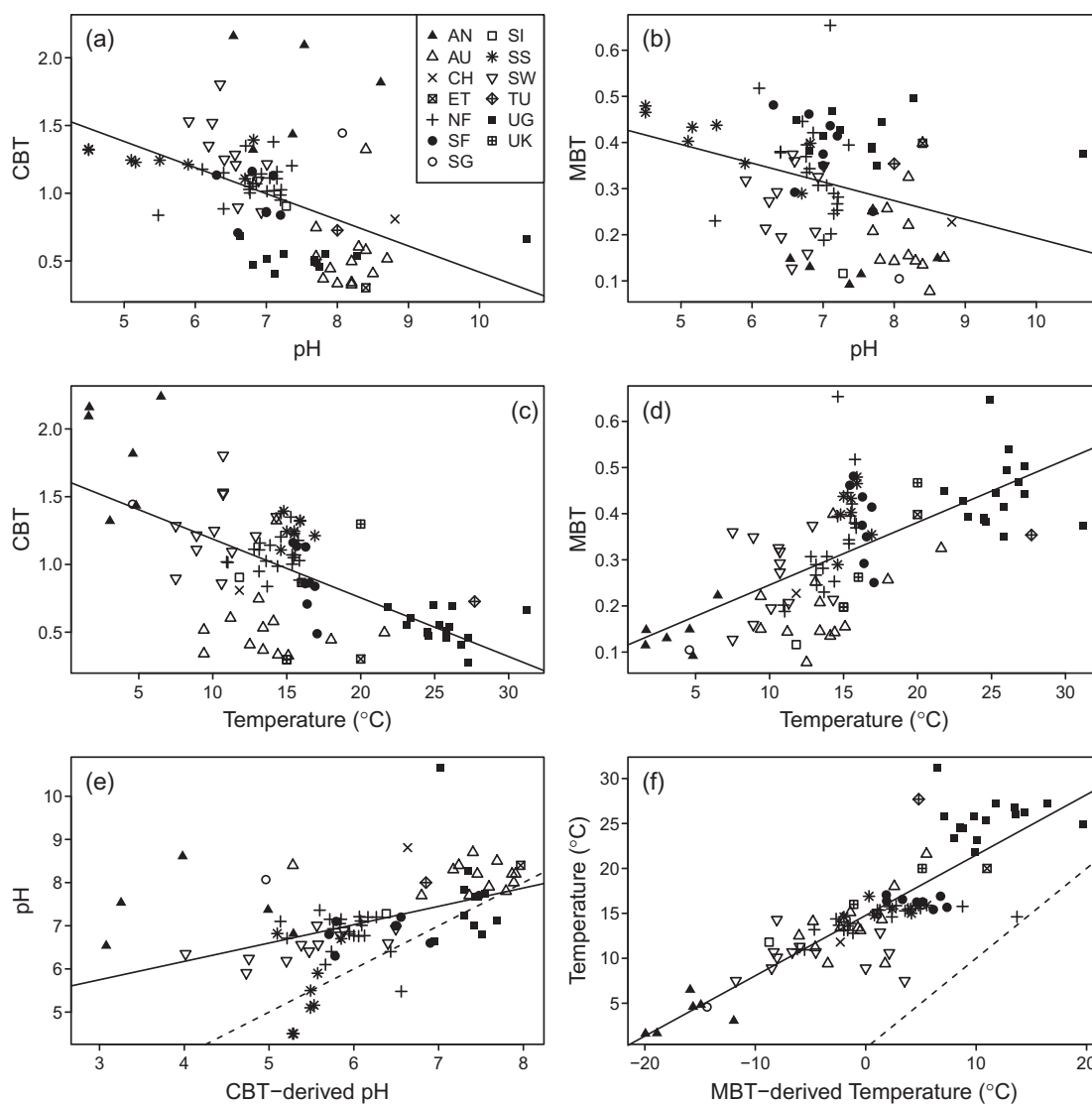


Fig. 6. Regression plots of relationships between lake water pH and temperature data with published CBT, MBT and MBT/CBT indices of Weijers et al. (2007). Lake dataset codes as Fig. 4.

temperature range (e.g. Swedish: range 0.29–0.76; Finnish: range 0.26–0.59; Austrian: range 0.36–0.58). As described above (Section 3.1, Fig. 5), the largest variation in both total and isoprenoid GDGTs is influenced by conductivity (surrogate for salinity) rather than temperature. Little has been previously reported regarding the influence of salinity on lacustrine GDGTs although Tierney et al. (2010) noted how branched GDGT distributions in highly saline ($>30,000 \mu\text{S cm}^{-1}$) East African lakes differed substantially from fresh to slightly saline lakes (up to $5900 \mu\text{S cm}^{-1}$) which suggests, as in this study, that salinity does play a significant role in influencing GDGT distributions in some lakes. The generally high BIT and GDGT-V/crenarchaeol values and the lack of a significant relationship between temperature and isoprenoid GDGT composition means it is no surprise that we observe a weak relationship between TEX_{86} and temperature in our 90-lake dataset. It further emphasizes the caution required before applying any version of this index to lacustrine sediment archives.

3.2.2. MBT/CBT-temperature and environment relationships

In addition to exploring TEX_{86} , recent studies have also examined the applicability of the soil-derived MBT/CBT (methylation ratio/cyclisation ratio of branched tetraethers) temperature index (Weijers et al., 2007; Eqs. 3, 4 and 5) to lacustrine environments, either using the soil calibration of Weijers et al. (2007) or direct regression models (e.g. Tierney and Russell, 2009; Bechtel et al., 2010; Blaga et al., 2010; Tierney et al., 2010; Zink et al., 2010; Sun et al., 2011).

The MBT/CBT index was originally based on a non-lacustrine (soil) calibration dataset and results exhibit an offset and large under-prediction of measured temperatures when applied to lake sediments (e.g. Blaga et al., 2010; Tierney and Russell, 2009; Tierney et al., 2010). However, since the MBT index comprises branched GDGTs and, given that our RDA results suggest that temperature is an important factor in determining distributions of branched GDGTs in our dataset, this suggests there could be some potential for the application of this index to our lakes and is worthy of investigation.

Regression plots of relationships between lake water pH and temperature data with published CBT, MBT and MBT/CBT indices of Weijers et al. (2007) are shown in Fig. 6. These plots and regressions demonstrate that, although significant ($p < 0.001$), the relationships between MBT and CBT ratios and temperature and pH are weak ($R^2 = 0.1\text{--}0.43$; Fig. 6a–e). The correlation between measured and MBT-derived temperature using Eq. 5 from Weijers et al. (2007) (Fig. 6f) is strong ($r = 0.85$, $n = 90$) but the relationship exhibits considerable bias, with temperatures under-predicted by c. 20°C (comparable with the findings of Tierney and Russell, 2009). Interestingly, Zink et al. (2010) found that calculations of mean annual temperature from MBT and CBT indices alone (rather than the combined MBT/CBT index) gave more realistic predicted temperatures with similar overall correlations ($R^2 = 0.74$ and $R^2 = 0.73$ for MBT and CBT respectively, compared to $R^2 = 0.78$ for MBT/CBT) though their study used a much smaller dataset ($n=10$). Other studies, like ours, have

found that, despite there being a significant correlation between measured and MBT/CBT-inferred temperatures, the latter are considerably lower than measured values (e.g. Blaga et al., 2010: $R^2 = 0.47$, $n = 82$, predicted temperatures underestimated by up to $\sim 30^\circ\text{C}$; Zink et al., 2010: $R^2 = 0.78$, $n = 9$, predicted temperatures underestimated by up to $\sim 15^\circ\text{C}$; Sun et al., 2011: $R^2 = 0.62$, $n = 139$, predicted temperatures underestimated by up to $\sim 9^\circ\text{C}$). Since the MBT index was derived from a soil calibration dataset it is not surprising that it is not directly applicable to lakes where contributions from *in situ* production of branched GDGTs may confound the relationship with temperature (see Tierney and Russell, 2009; Sinninghe Damsté et al., 2009). Indeed, Blaga et al. (2010) found that the relationship between reconstructed and measured mean annual air temperature indicated that temperature played only a partial role in setting the MBT/CBT values and that high residual variability in the GDGT composition makes it important to establish source and origin of the branched GDGTs. As with the TEX_{86} index, the potential application of the MBT/CBT index to lakes must also be exercised with extreme caution.

3.2.3. GDGT-temperature regression models

Although existing GDGT-temperature calibrations (TEX_{86} and MBT/CBT) are not appropriate for use with our lake dataset our exploratory analysis (Section 3.1) demonstrated that temperature is a major and statistically significant determinant of branched GDGT compositions. In this section we therefore explore the use of branched GDGT compounds for predicting lake-water temperature using regressions based on individual GDGT compounds. We first evaluate a model based on compounds used by Tierney et al. (2010) in East African lakes. We then develop our own model using best subsets regression to identify the most parsimonious predictive model: that is the subset of compounds that produce a model with minimum prediction error. In both cases we use leave-one-out cross-validation to estimate the true prediction error of the models and remove any outliers that have standardised residuals greater than 2.0.

Tierney et al. (2010) use the three major branched GDGTs (GDGT-I, GDGT-II and GDGT-III) and calibrate their model for mean annual lake temperature. However, our temperature data comprise estimates of mean summer temperature. We therefore re-calibrate the regression model using our temperature data (Eq. 7):

$$\begin{aligned} \text{Temperature}(^\circ\text{C}) = & 47.4 - (20.9 \cdot \text{GDGT-I}) \\ & - (37.1 \cdot \text{GDGT-II}) \\ & - (53.5 \cdot \text{GDGT-III}) \end{aligned} \quad (7)$$

Eq. 7 describes an accurate and precise model that has a low prediction error ($R^2 = 0.84$, $\text{RMSE} = 2.4^\circ\text{C}$, $\text{RMSEP} = 2.6^\circ\text{C}$, $n = 85$) and exhibits only slight bias in under-prediction at high temperatures (Fig. 7a). Prediction error is comparable to the Tierney et al. (2010) original model ($\text{RMSE} = 2.2^\circ\text{C}$), indicating that GDGT-temperature relationships found in East Africa are robust and apply across a wide range of lake types and regions.

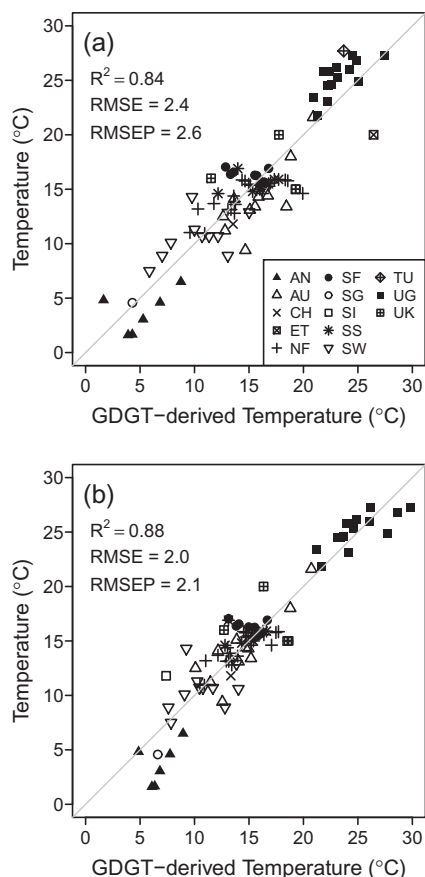


Fig. 7. Relationships between measured and GDGT-inferred temperature for regression models based on (a) compounds used in Tierney et al. (2010) (Eq. 7), and (b) best subsets regression (Eq. 8). See text for details. Lake dataset code as Fig. 4.

Our GDGT-temperature model derived using best subsets regression is described in Eq. 8.

$$\begin{aligned} \text{Temperature (}^{\circ}\text{C)} = & 20.9 + (98.1 \cdot \text{GDGT-Ib}) \\ & - (12.0 \cdot \text{GDGT-II}) \\ & - (20.5 \cdot \text{GDGT-III}) \end{aligned} \quad (8)$$

This model is similar to that expressed in Eq. 7 except that GDGT-Ib is selected instead of GDGT-I. The new model (Eq. 8) exhibits a lower overall prediction error ($R^2 = 0.88$; $\text{RMSE} = 2.0$ °C; $\text{RMSEP} = 2.1$ °C, $n = 85$) (Fig. 7b). Tierney et al. (2010) exclude cyclic GDGTs from their model as their relative abundances may be related to pH as well as temperature (Weijers et al., 2007). Tierney et al. (2010) also found that cyclic GDGTs, especially GDGT-Ic and GDGT-IIc, were influenced by depth and thus reflect a different source from the other GDGTs and so excluded them. In our dataset the relative abundance of both GDGT-I and GDGT-Ib exhibit significant correlation with pH although the correlation is weaker for GDGT-Ib (GDGT-I: $r = -0.44$, $p < 0.001$; GDGT-Ib: $r = 0.29$, $p = 0.008$). However, residuals for the models show no significant correlation with pH, suggesting that neither model is confounded by lake water pH. However, while residuals

from our new model (Eq. 8) show no significant correlation with either water depth or conductivity, the residuals from Eq. 7 are, in fact, weakly correlated to the latter ($r = 0.25$, $p = 0.02$), suggesting that predictions using the model in Eq. 7 may be influenced by conductivity in addition to temperature changes. Therefore, based on our dataset, our new temperature model using GDGT-Ib, GDGT-II, and GDGT-III has lower prediction errors and also appears to be more robust across a wide range of lake types of differing pH and conductivity.

4. CONCLUSIONS

Our study provides a rigorous analysis of the relationships between GDGT distributions and temperature that will be of use in studies of palaeolimnology and applications of organic geochemical techniques to reconstruct past continental temperatures using lake sediments. We have provided new information on distributions of GDGTs in a diverse range of lakes from varied geographical locations latitudinally ranging from Arctic Scandinavia to Antarctica and covering a wide temperature range (~ 1 – 31 °C).

We derive a new model for predicting temperature using 3 branched GDGT compounds (GDGT-Ib, GDGT-II and GDGT-III). This model has high accuracy and precision ($R^2 = 0.88$, $\text{RMSE} = 2.0$ °C $\text{RMSEP} = 2.1$ °C) using a total of 85 out of our 90 lakes, and appears to be free from confounding effects of pH, conductivity or water depth.

The accuracy of such predictive models depends, in part, on the accuracy or the original data used to calibrate the model. The maximum standard error in the temperature estimate of our model is ± 0.24 °C. This is small in comparison with the RMSEP value (2.1 °C), suggesting that experimental errors are a relatively small component of the overall error. An undoubtedly greater source of error in our study is the uncertainty in the estimates of mean summer lake-water temperature. These errors are largely unquantified for our dataset but are likely to be in the order of 1 °C or more for some sites.

Despite these uncertainties, the fact that we obtain a model with $\text{RMSE} = 2.0$ °C ($R^2 = 0.88$, $n = 85$) for a suite of lakes which covers such a large geographical and temperature range are extremely promising and our GDGT-temperature model therefore shows huge potential for application to sediment cores to reconstruct past continental temperatures across a wide global area.

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