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Applicability and calibration of the TEX_{86} paleothermometer in lakes

Lindsay Powers [a,*], Josef P. Werne [a,b], Andrea J. Vanderwoude [a,1], Jaap S. Sinninghe Damsté [c,d], Ellen C. Hopmans [c], Stefan Schouten [c]

[a] Large Lakes Observatory, University of Minnesota Duluth, 2205 E. 5th St., Duluth, Minnesota 55812, USA
[b] Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, USA
[c] NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, P.O. Box 59, 1790 AB Den Burg, The Netherlands
[d] Department of Earth Sciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands

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ABSTRACT

We have conducted a global survey of archaeal glycerol dialkyl glycerol tetraether (GDGT) lipids in lake sediments in order to develop the TEX_{86} paleotemperature proxy for application in continental systems. Surface sediments of 46 globally distributed lakes were analyzed for GDGT, but isoprenoid GDGT derived from aquatic Crenarchaeota, were only unambiguously detected in 20 of the 46 lakes analyzed. Aquatic crenarchaeotal GDGT were detected mainly in sediments from large lakes (>4000 km^2) and hydrothermal or volcanic lakes, suggesting that in some (mostly smaller) lakes either aquatic Crenarchaeota are present at low abundance resulting in sedimentary lipids below levels of detection, or they are absent. Branched GDGT, thought to be derived primarily from soil bacteria, were identified in all lake sediments analyzed. Correlation of the TEX_{86} in those lakes with sufficient amounts of putative crenarchaeotal GDGT with annual mean lake temperature is reasonably good ($r^2 = 0.68$, $N = 20$). In order to reduce the influence of soil derived isoprenoid GDGT on the TEX_{86} lake temperatures, we have applied a filter based on relative soil derived inputs (as determined by the BIT [Branched and Isoprenoid Tetraether] index) which results in a calibration relationship with $r^2 = 0.86$ ($N = 12$) and an estimated temperature error of 3.6 °C. Our results suggest that the TEX_{86} should be applied only in lakes with sufficient production of GDGT by aquatic Crenarchaeota relative to isoprenoid GDGT derived from soil in the watershed or other aquatic sources.

1. Introduction

In the quest for an increased understanding of continental climate dynamics, the need for a hydrologically independent high resolution paleothermometer has emerged. Lakes respond to climate integrated over the broad expanse of their drainage basins, and their sediments archive long, often continuous, high resolution records of past climate change (Cohen, 2003). Most of the biological or carbonate based paleotemperature proxies previously applied to continental climate archives are potentially confounded by changes in the hydrologic cycle (Ito, 2001); clumped isotope paleotemperatures (Ghosh et al., 2006) are only possible in systems that preserve carbonate, and noble gas temperature records are severely limited by their low temporal resolution (Farerra et al., 1999).

We proposed the use of the TEX_{86} paleotemperature tool (TetraEther indeX of tetraethers consisting of 86 carbon atoms; Schouten et al., 2002) in lake systems (Powers et al., 2004). This proxy is based upon membrane lipids produced by widely occurring aquatic Crenarchaeota preserved in marine and lacustrine sediments (Schouten et al., 2000; Powers et al., 2004; Blaga et al., 2009). Crenarchaeota are a widespread component of many diverse environments as evidenced by the presence of crenarchaeotal ribosomal DNA (rDNA) in marine (DeLong, 1992; Fuhrman et al., 1992) and lacustrine waters (Coolen et al., 2004; Keough et al., 2003), hydrothermal systems (Barns et al., 1996), terrestrial soils (Bintrim et al., 1997) and freshwater sediments (MacGregor et al., 1997; Schleper et al., 1997). Crenarchaeota may have the capability for both autotrophic and heterotrophic metabolism (Ouvernay and Fuhrman, 2000; Wuchter et al., 2003; Könneke et al., 2005; Hallam et al., 2006). Some studies indicate unequivocally that at least some aquatic and soil Crenarchaeota are capable of nitrification (Könneke et al., 2005; Wuchter et al., 2006a; Leininger et al., 2006), suggesting they may be important for N-cycling globally. Sinninghe Damsté et al. (2002a) found maximum concentrations of crenarchaeotal GDGT in the Arabian Sea at 500 m water depth, well within the oxygen minimum zone, suggesting that they may be facultative anaerobes.

Ether linked GDGT produced by the Archaea typically contain 0–4 cyclopentane moieties with two glycerol head groups. The proposed biomarker for Group I Crenarchaeota is crenarchaeol

* Corresponding author. Tel.: +1 218 343 3978; fax: +1 218 726 6979.
E-mail address: powe0285@umu.edu (L. Powers).
[1] Present address: College of Ocean and Atmospheric Sciences, Oregon State University.

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(Sinninghe Damsté et al., 2002b), and its regio-isomer, which contains four cyclopentane and one cyclohexane moieties (Fig. 1). Although crenarchaeol is considered to be the primary biomarker for mesophilic aquatic Crenarchaeota (Schouten et al., 2000), it has recently also been detected in a culture of thermophilic nitrifying Crenarchaeota (de la Torre et al., 2008), as well as soils (Weijers et al., 2006b, 2007) and hot springs (Pearson et al., 2004; Zhang et al., 2006; Schouten et al., 2007b; Pitcher et al., 2009). Several studies have also identified crenarchaeotal GDGT in lake sediments (Powers et al., 2004, 2005; Escala et al., 2007; Tierney et al., 2007; Tierney and Russell, 2009; Blaga et al., 2009; Sinninghe Damsté et al., 2009).

In the present study, we applied the TEX_{86} paleothermometer, which is based on the relative abundance of cyclopentane containing isoprenoid glycerol dialkyl glycerol tetraethers (GDGT, see Fig. 1 for structures), to lacustrine systems to reconstruct continental paleotemperatures (Powers et al., 2004). The original development of the TEX_{86} paleothermometer was based on the relationship between mean annual sea surface temperature (SST) and TEX_{86} values in 41 samples from 15 globally distributed marine locations (Schouten et al., 2002), resulting in a linear relationship (Eq. (1)).

$$TEX_{86} = 0.015 * SST + 0.28, r^2 = 0.92 \quad (1)$$

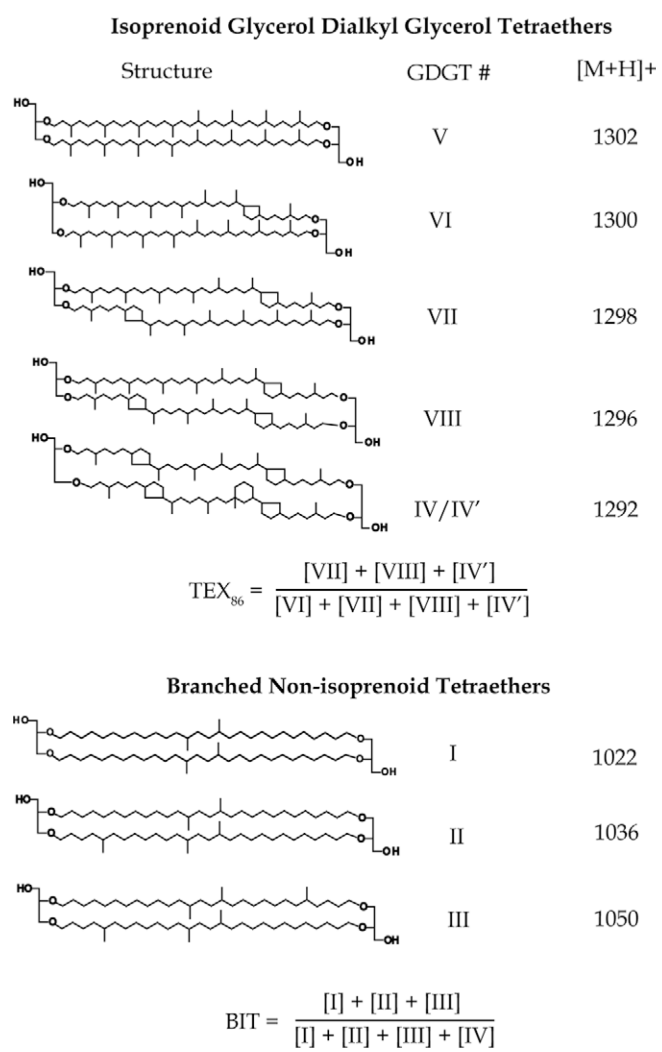

Fig. 1. The glycerol dialkyl glycerol tetraether (GDGT) structures, numbers from text, and molecular weights with formulas for TEX_{86} and BIT calculations.

The marine calibration has since been expanded to include 223 data points, resulting in a slight modification of the linear relationship shown in Eq. (1) (Kim et al., 2008).

$$T = -10.78 + 56.2 * TEX_{86}, r^2 = 0.935, n = 223 \quad (2)$$

Liu et al. (2009) have recently amended this by applying a non-linear equation to the complete data set of Kim et al. (2008).

The first lacustrine calibration of TEX_{86} (Powers et al., 2004) was based on sediments from four large lakes and resulted in a linear relationship nearly identical to the original marine calibration relationship of Schouten et al. (2002). The similarity of the marine and preliminary lacustrine calibrations suggests that the paleothermometer could also work in lacustrine systems. The first application of TEX_{86} to sediment cores from Lake Malawi and Lake Tanganyika provided high resolution continental paleotemperature records reflecting well documented global climate changes in East Africa (Powers et al., 2005; Tierney et al., 2007).

One major concern for the validity of the TEX_{86} paleothermometer in lacustrine and nearshore marine systems is the influence of external inputs of isoprenoid GDGT into the aquatic environment (Weijers et al., 2006b). Isoprenoid GDGT are produced in small quantities by soil Archaea (Weijers et al., 2006b), while alkyl branched GDGT (non-isoprenoid, e.g. compounds I–III in Fig. 1) are thought to be produced by anaerobic terrestrial bacteria (Sinninghe Damsté et al., 2000; Weijers et al., 2006a,b, 2009). Hopmans et al. (2004) developed an index to assess the input of soil organic matter in aquatic sediments based on the relative abundance of branched GDGT derived from soil environments. This index, known as the BIT (Branched and Isoprenoid Tetraether) index, is a measure of the abundance of the primarily soil derived branched GDGT (I–III, Fig. 1) to crenarchaeol (GDGT IV). The BIT index ranges in value from close to 0, indicating predominantly aquatic organic matter to 1, indicating mostly soil derived organic matter. Soils may contain minor amounts of isoprenoid GDGT produced by Archaea (Weijers et al., 2006b) that can interfere with the TEX_{86} temperature signal, therefore the BIT index can be used to assess whether GDGT used in the TEX_{86} calculations are potentially affected by input of isoprenoid GDGT derived from soil Archaea.

Recent studies have shown that crenarchaeotal GDGT are found in the water column (Blaga et al., 2009; Sinninghe Damsté et al., 2009) and sediments (Escala et al., 2007; Blaga et al., 2009; Sinninghe Damsté et al., 2009) of lakes of diverse size and character. In order to further constrain the applicability of TEX_{86} in lakes and improve its calibration in lacustrine systems as has been done in the marine realm (Kim et al., 2008), we have analyzed GDGT in core top sediments from 46 globally distributed lakes of varying size from climatically diverse regions (Fig. 2, Table 1). Here we present the results of this global calibration of TEX_{86} and constrain its applicability in lacustrine systems.

2. Methods

2.1. Sediments

Sediment samples (1–5 g dry mass) were collected from core tops from 46 globally distributed lakes (Fig. 2).

2.2. Temperature data

The temperature data for five of the lakes comes from the International Lake Environment Committee database (http://www.ilec.or.jp/database/index/idx-lakes.html) (Table 1). The temperature data from this website varies in its temporal resolution and in some cases the original source of the data is not provided. The remaining data have been obtained from the primary literature

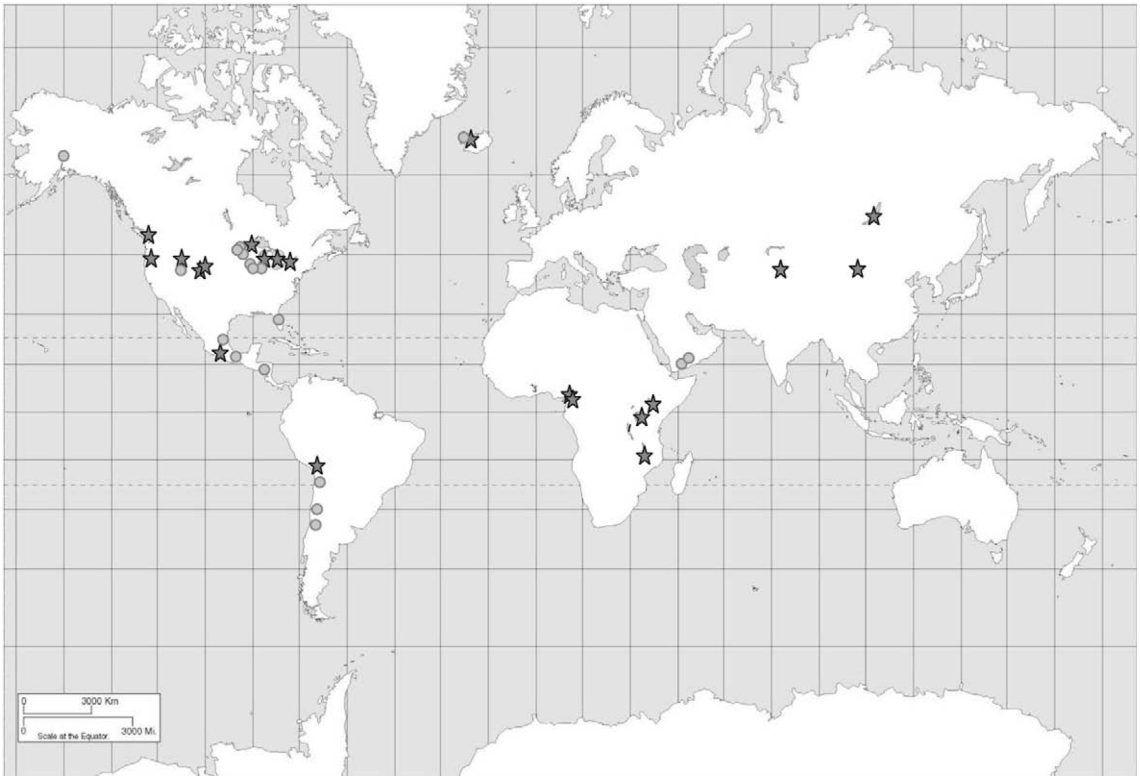

Fig. 2. Distribution of lakes surveyed for TEX_{86}. Stars indicate the 20 lakes that produce a TEX_{86} temperature signal. Dots indicate lakes that are not successful TEX_{86} lakes. Dots in the central US may represent more than one lake.

(see Table 1), individual scientists, and in the case of Lake Washington, from a regional water board monitoring station. There is not a complete mean monthly temperature data set (only an annual mean temperature) available from Hvitarvatn Lake, therefore this lake has been excluded from the seasonal temperature relationships. We attempted to use satellite derived estimated lake surface temperature data (Moderate Resolution Imaging Spectroradiometer [MODIS] Aqua) for the calibration of TEX_{86} in lakes. However, these data were only available for a few of the largest lakes and the estimated satellite temperature data for these specific lakes were significantly warmer than the measured data taken from the literature and World Lakes Database website. We have therefore relied on the literature and the ILEC World Lakes Database for all temperature data.

2.3. GDGT analysis

Samples were freeze dried and homogenized by mortar and pestle. Sediments were extracted with dichloromethane (DCM)/methanol (2/1, v/v) using Soxhlet or Dionex™ accelerated solvent extraction (ASE) techniques, to acquire the total lipid extract (TLE). The TLE were separated by Al_2O_3 column chromatography using hexane/DCM (9/1, v/v) and DCM/methanol (1/1, v/v) as subsequent eluents. The polar fraction (DCM/methanol) was condensed by rotary evaporation, dissolved in hexane/isopropanol (99/1, v/v), and filtered using a PTFE 0.4 μm filter prior to injection. Analyses were performed using an HP (Palo-Alto, CA, USA) 1100 series LC–MS equipped with an auto-injector and Chemstation chromatography manager software. Separation was achieved on a Prevail Cyano column (2.1 × 150 mm, 3 μm; Alltech, Deerfield, IL, USA), maintained at 30 °C. Injection volumes varied from 1 to 5 μl. GDGT were eluted isocratically with 99% *A* and 1% *B* for 5 min, followed by a linear gradient to 1.8% *B* in 45 min, where *A* = hexane and *B* = propanol. Flow rate was 0.2 ml/min. After each analysis the column was cleaned by back-flushing hexane/propanol (90/10, v/v) at 0.2 ml/min for 10 min. Detection was achieved using atmospheric pressure positive ion chemical ionization mass spectrometry (APCI-MS) of the eluent. Conditions for APCI-MS were as follows: nebulizer pressure 60 psi, vaporizer temperature 400 °C, drying gas (N_2) flow 6 l/min and temperature 200 °C, capillary voltage −3 kV, corona 5 μA (∼3.2 kV). GDGT were initially analyzed by full scan analysis (*m*/*z* 950–1450) and quantified by integration of the peak areas of the $[M+H]^+$. All lake sediments in which crenarchaeol was detected were then re-analyzed by selected ion monitoring (SIM) of the $[M+H]^+$ ions (dwell time = 234 ms) of the GDGT, as this gives a much higher sensitivity and reproducibility (Schouten et al., 2007a). TEX_{86} and BIT index values were calculated according to the equations in Fig. 1. Recent studies have demonstrated that the analyses of BIT indices are variable among different laboratories and/or equipment and care must be taken in interpreting absolute BIT values (Escala et al., 2009; Schouten et al., 2009).

2.4. Statistical analysis

Multiple regression analyses were performed to characterize the seasonal influence on the TEX_{86} signal and determine the best fit calibration curve (Sall et al., 2001). Linear regression analysis (Sall et al., 2001) was performed to establish the relationship between TEX_{86} values and lake surface temperatures. The error for the calibration relationship was determined by dividing the root mean square error by the slope of the calibration curve when analyzed with TEX_{86} as the dependent variable, which results in the error in degrees Celsius due to the variance around the mean of the linear fit. Here we have written the equations with temperature as the dependent variable following Kim et al. (2008).

Table 1
Morphometric, physical and chemical data for all 46 lakes surveyed. Lakes in italics were analyzed using the SIM method.

Lake	Country	Lat/long	Surface area (km^2)	Catchment area (km^2)	BIT	TEX_{86}	GDGT V/ crenarchaeol	Published ALST (°C)	Published WLST (°C)
Issyk Kul	Kyrgyzstan	42°N/77°E	6236	15,844	0.01	0.35	0.97	11.2[a]	6.8
Lake Titicaca	Bolivia/Peru	16°S/69°W	8372	58,000	0.12	0.48	0.83	13[a]	11.5
Lake Qinghai	China	37°N/100°E	5694		0.14	0.43	1.02	5[c]	3
Lake Victoria	Kenya/TZ/UG	1°S/32°E	68,800	184,000	0.19	0.63	0.20	24.5[a]	24
Lake Turkana	Kenya	3°N/36°E	6750	130,860	0.20	0.70	0.08	28[d]	26
Lake Malawi	MW/TZ/MO	9°S/34°E	6400	6593	0.21	0.73	0.14	25.5[e]	23.5
Jackson Lake	USA	43°N/110°W	110	810	0.26	0.51	0.97	10[f]	3
Lake Superior	US/Canada	47°N/90°W	82,367	127,700	0.26	0.35	0.80	5.3[a]	3.8
Crater Lake	USA	43°N/122°W	53	60	0.39	0.46	0.83	7.9[g]	4.4
Lake Baikal	Russia	53°N/108°E	31,500	560,000	0.41	0.33	0.59	4[h]	2.5
Lake Washington	USA	48°N/122°W	88	1274	0.41	0.47	1.56	13.5[i]	9.7
Lake Ontario	USA/Canada	43°N/78°W	19,009	64,030	0.42	0.34	0.73	9[a]	3.2
Lago Zirahuen	Mexico	19°N/101°W	10.5	260	0.53	0.56	0.89	16.1[j]	16
Lake Oku	Cameroon	6°N/10°E	2.19		0.53	0.41	0.58	24[k]	23
Yellowstone Lake	USA	44°N/110°W	352		0.59	0.42	0.82	11.6[b]	3.7
Lake Michigan	USA	45°N/86°W	58,016	118,000	0.60	0.32	0.82	8.5[a]	2.4
Hvítárvatn	Iceland	64°N/19°W	30		0.72	0.32	1.21	4[l]	–
Lake Huron	USA/Canada	45°N/82°W	59,570	134,100	0.72	0.31	0.76	8.4[a]	2.4
Bear Lake	USA	42°N/111°W	282	23,726	0.82	0.49	3.93	10.2[m]	3.9
Lake Nyos	Cameroon	6°N/10°E	1.58		0.89	0.52	2.45	24[k]	23
Lagos Verde	Mexico	18°N/96°W	0.11	0.45	0.95				
Lake Tulane	USA	28°N/81°W	0.33	1.39	0.97				
Great Salt Lake	USA	42°N/113°W	5000	34,601	0.98				
Ghayal wa Bazir	Yemen	13°N/46°E			1.00				
Jebel al Shouhran	Yemen	13°N/46°E			1.00				
Lago Miscanti	Chile	23°S/67°W			1.00				
Lago Negro Francisco	Chile	27°S/69°W			1.00				
Laguna Seca	Chile	18°S/69°W			1.00				
Lago Chungara	Chile	18° S/69°W	22	22	1.00				
Efstadalsvatn	Iceland	66°N/22°W			1.00				
Iceberg Lake	USA	61°N/154°W	4.4	74	1.00				
Lake McCarrons	USA	45°N/93°W			1.00				
Deep Lake	USA	46°N/94°W			1.00				
Pine Lake	USA	46°N/94°W	0.80		1.00				
Benjamin Lake	USA	47°N/94°W			1.00				
Hoot Owl	USA	46°N/94°W			1.00				
Elk Lake	USA	47°N/95°W	1.6		1.00				
Green Lake	USA	45°N/95°W			1.00				
Otter Lake	USA	43°N/85°W	0.27	92.5	1.00				
Silver Lake	USA	45°N/84°W	0.27	1.55	1.00				
Big Lake	USA	43°N/85°W			1.00				
Derby Lake	USA	43°N/85°W			1.00				
Gull Lake	USA	43°N/85°W			1.00				
Half Moon Lake	USA	42°N/84°W			1.00				
Union Lake	USA	46°N/83°W			1.00				
Miner Lake	USA	42°N/85°W	1.33	92.5	1.00				

[a] http://www.ilec.or.jp/database/index/idx-lakes.html (1999).
[b] http://nwis.waterdata.usgs.gov/wy (2005).
[c] Tigbao and Xianghua (2001).
[d] Halfman (1987).
[e] Vollmer et al. (2005).
[f] Interlandi et al. (1999).
[g] Collier (2005).
[h] Gurulev (1994).
[i] Blomquist (2004).
[j] Bradbury (2000) and Tavera and Martinez-Almeida (2005).
[k] Kantha and Freeth (1996).
[l] Miller (2004).
[m] Dean (2004).

3. Results

Core top sediments from 46 lakes on five continents spanning 63°N–27°S (Fig. 2) were analyzed by HPLC–MS in full scan mode to determine the presence and abundance of isoprenoid and non-isoprenoid GDGT, and to calculate TEX_{86} and BIT indices. We have classified the isoprenoid GDGT into three groups, those known to be produced primarily by mesophilic Crenarchaeota, i.e. crenarchaeol and its regio-isomer, referred to as ‘‘aquatic GDGT" (GDGT IV and IV′; Fig. 1), ‘‘universal" GDGT that can be produced by a broad array of Archaea, including methanogens, methane oxidizers, and halophiles (GDGT V, VI, VII, VIII), and ‘‘soil derived" GDGT, which are non-isoprenoidal GDGT thought to be primarily derived from soil bacteria (GDGT I, II and III). All of the 48 lakes contained substantial relative amounts (5–88% of total GDGT) of soil derived GDGT (Fig. 3). BIT indices range from 0.01 in Issyk Kul to 1 in most of the small lakes (Table 1). Only 20 of the 46 lake sediments had substantial relative amounts (i.e. >8% of total GDGT) of crenarchaeol, the proposed diagnostic biomarker for mesophilic Crenarchaeota, and the full complement of isoprenoid GDGT

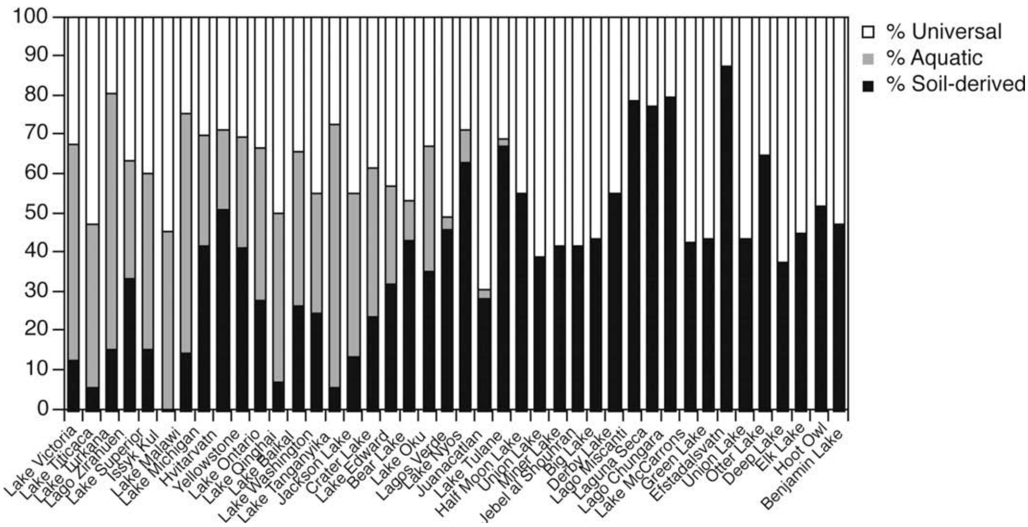

Fig. 3. Relative abundance of isoprenoid GDGT derived from both Euryarchaeota (GDGT V, VI, VII, VIII) and Crenarchaeota (labeled universal), GDGT derived from Crenarchaeota only (GDGT IV and IV') (labeled aquatic) and non-isoprenoid soil derived GDGT (GDGT I, II, III) (labeled soil-derived).

required for the TEX_{86} analysis (Fig. 3). These 20 lake sediments were then re-analyzed by HPLC–MS in SIM mode as this has improved sensitivity and reproducibility (Table 1). However, the TEX_{86} and BIT values were quite similar between those obtained in full scan mode and with SIM.

4. Discussion

4.1. Absence of crenarchaeotal GDGT in lake sediments

Crenarchaeol, the key biomarker for Crenarchaeota, was below detection limit in 24 of the 46 lakes analyzed. However, the full scan method used to identify GDGT in the initial survey has a much lower sensitivity than the SIM method (Schouten et al., 2007a) and thus it is likely that minor amounts of crenarchaeol were present but not detected using the full scan method. Nevertheless, our results suggest that aquatic Crenarchaeota are either present at low concentrations or are absent in most small lakes. In contrast, Blaga et al. (2009) found crenarchaeol in the sediments of all of the 47 European lakes that they surveyed using HPLC–MS in SIM mode, though in most lakes it was present in relatively minor amounts. Escala et al. (2007) also found crenarchaeol in the water column and sediments of several Spanish lakes. It should be noted that while crenarchaeol was found in the sediments of Lagos Verde, Lake Tulane and Great Salt Lake, the regio-isomer GDGT IV′ was absent and therefore TEX_{86} values could not be calculated for these lakes.

Our results thus suggest that Crenarchaeota are either not present in sufficient abundance in many small lakes to produce detectable quantities of crenarchaeol in the sediments or that the signal from aquatic Crenarchaeota is overwhelmed by input of allochthonous isoprenoidal GDGT (cf. Blaga et al., 2009). In contrast, aquatic isoprenoid GDGT appear to be sufficiently abundant in large to medium sized lakes to produce viable TEX_{86} values. It is noted that other studies have found crenarchaeotal GDGT in sufficient abundance to calculate TEX_{86} in some small and medium sized lakes (Escala et al., 2007; Blaga et al., 2009).

4.2. TEX_{86} calibration with annual mean lake surface temperatures

The linear relationship between mean annual lake surface temperature (ALST) and TEX_{86} of the 20 lakes, analyzed in SIM mode, containing the full complement of GDGT used in the TEX_{86} is described by the equation:

$$ALST = -10.4 + 50.8 * (TEX_{86}), r^2 = 0.68, n = 20 \qquad (3)$$

with a mean error of the estimate of ±5.6 °C (Fig. 4a). This equation does not statistically differ from the marine calibration (Kim et al., 2008) over the same range of temperatures. Possible environmental factors that may be influencing the temperature estimates derived from the TEX_{86} are discussed below.

4.3. Factors affecting the TEX_{86} signal in aquatic systems

4.3.1. Crenarchaeotal depth distribution

The depth distribution of aquatic Crenarchaeota is highly variable within marine and lacustrine water columns and in many cases Crenarchaeota are numerically dominant at greater depth (Urbach et al., 2001; Keough et al., 2003; Herndl et al., 2005; Varela et al., 2008). Very little is known of the ecology of Crenarchaeota in lacustrine systems. A recent study in Lake Challa suggests a seasonal aspect to crenarchaeotal productivity as well as predominance in the surface waters (Sinninghe Damsté et al., 2009). Sinninghe Damsté et al. (2009) found that suspended particulate matter from 35 m water depth in Lake Challa analyzed for TEX_{86} reflect ambient water temperatures above the oxycline, but surface sediments do not, suggesting an additional source of isoprenoid GDGT other than surface dwelling Crenarchaeota. Blaga et al. (2009) also showed a high similarity in crenarchaeol relative abundance between surface and bottom water particulate organic matter, suggesting a surface water source of crenarchaeol. The most likely explanation for the reflection of surface water temperatures in sediments and sediment trap materials is that sinking organic matter is dominated by fast sinking particles produced in surface waters by zooplankton grazing and fecal pelletization and other mechanisms of aggregation (McCave, 1984; Wakeham et al., 2003). The current, albeit limited, evidence suggests that Crenarchaeota are predominantly productive in the upper part of the water column in lacustrine systems, and that this surface signal is exported to the sediments.

The physical and chemical limnology of lakes may affect the diversity and distribution of Archaea within the water column and sediments. For example, methanogenic Archaea may be more abundant in the hypolimnion and/or sediments of lakes that are

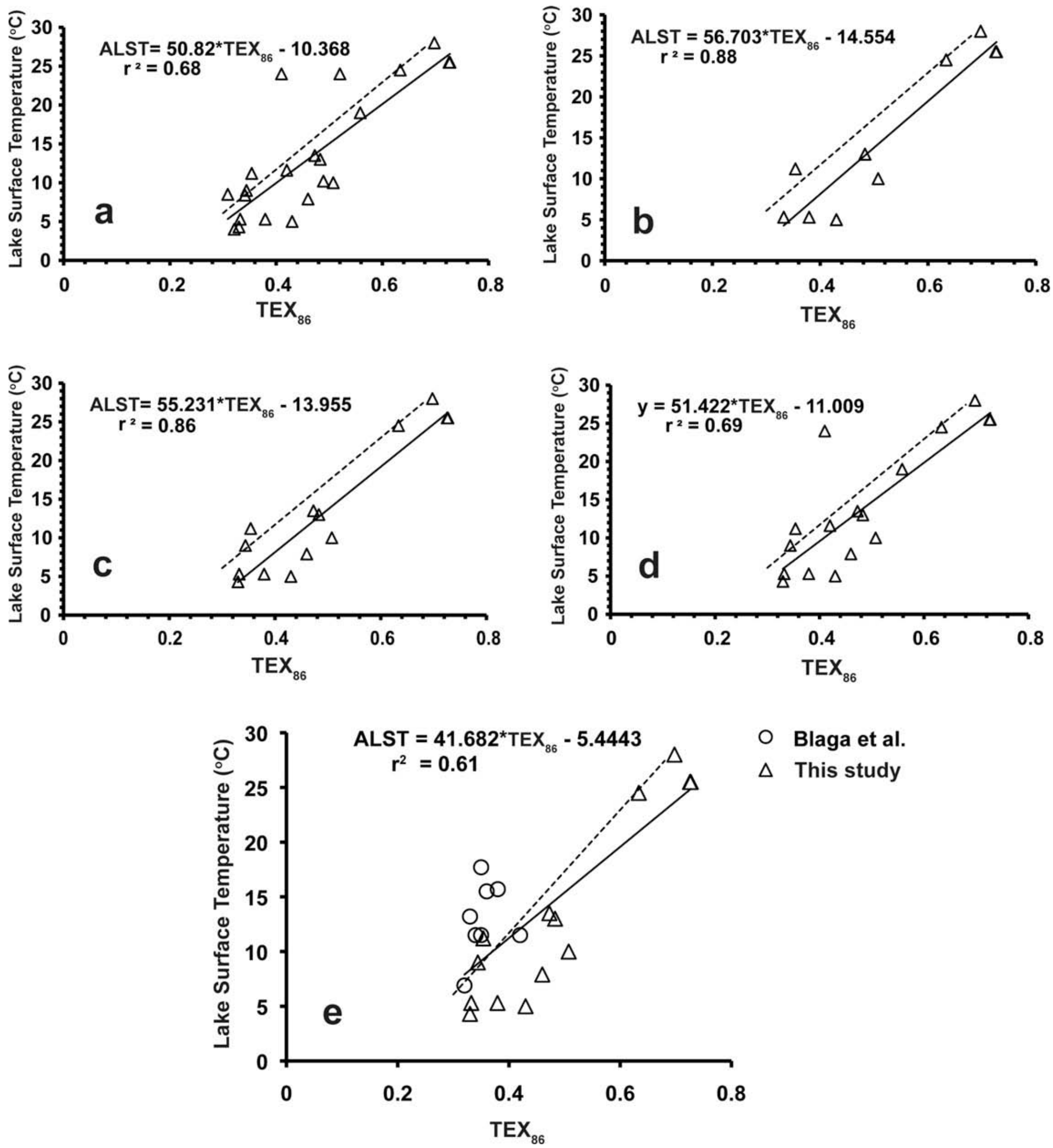

Fig. 4. Calibration relationships for the suite of lakes as described in the text. (a) All lakes containing the full complement of GDGT for TEX_{86} analysis, n = 20 lakes, calibration error = 5.59 °C. (b) TEX_{86} plotted for all lakes with BIT <0.3, n = 8 lakes, calibration error = 3.87 °C. (c) TEX_{86} plotted for all lakes with BIT <0.5, n = 12 lakes, calibration error = 3.62 °C. (d) TEX_{86} plotted for all lakes with BIT <0.6, n = 15 lakes, calibration error = 5.78 °C. (e) TEX_{86} calibration curve including all lakes with BIT <0.5 and lake data from Blaga et al. (2009), calibration error = 5.73 °C. BIT <0.5 and 0.6 also include two samples for Crater Lake. Only Crater Lake had BIT values between 0.3 and 0.4 therefore this category was excluded. All plots include two samples for lakes Malawi and Superior, and the marine calibration line of Kim et al. (2008) (dashed line), SST = $56.2*TEX_{86}$-10.78.

eutrophic or undergo a substantial period of anoxia. In temperate regions most lakes undergo complete mixing twice a year preventing permanently anoxic conditions in the hypolimnion. In some deep tropical lakes there is never complete mixing due to the stable stratification of the warmer water column as well as the lack of seasonality, resulting in an anoxic hypolimnion. In addition, tropical lakes generally have little difference between epilimnetic and hypolimnetic temperatures, however temperate lakes can have a large difference. Regardless of where the Crenarchaeota are residing in the water column, it is apparent that they require a transport mechanism (e.g. fecal pellets) to be efficiently transported to the sediment (Wuchter et al., 2006b; Huguet et al., 2007), and the sedimentary record is therefore likely to reflect the depth from which the crenarchaeal lipids are exported – assuming that there is little addition from sedimentary Archaea.

4.3.2. Influence of soil derived GDGT

Some of the isoprenoid GDGT used to calculate TEX_{86} are also produced in small amounts by soil Crenarchaeota and perhaps other soil Archaea (Weijers et al., 2006b) and can be transported into lakes. In soils, BIT index values typically range from 0.8 to 1.0, indicating that a significant proportion of crenarchaeal lipids could derive from soils (Weijers et al., 2006b). In this study, lake sediment BIT index values range from 0.01 to 1.0, indicating a wide range of soil organic matter inputs (Table 1) and thus, of potential biases in the TEX_{86} signal due to input of soil derived crenarchaeotal GDGT (Weijers et al., 2006b). Of the 20 lakes containing substantial amounts (>8%) of crenarchaeol, BIT values range from 0.01 in Issyk Kul to 0.72 in Lake Huron and Lake Hvitarvatn (Table 1). In order to examine the influence of soil derived archaeal GDGT on the TEX_{86} calibration relationship, we compared the calibration obtained using lakes with BIT values <0.3, <0.5 and <0.6. (only Crater Lake had BIT values between 0.3 and 0.4), similar to Blaga et al. (2009). The TEX_{86} – ALST relationship was essentially the same for BIT cutoff values of 0.3 and 0.5, however, the relationship changes significantly when the lakes with BIT values between 0.5 and 0.6 are included (Fig. 4d). To rigorously exclude potential biases of soil derived isoprenoid GDGT input we only used TEX_{86} values of lake sediments where BIT values were <0.5 and thus contain substantial amounts of aquatic GDGT relative to those derived from soils. The removal of lakes with BIT >0.5 resulted in the removal of eight lakes and the following calibration equation.

$$ALST = -14.0 + 55.2 * (TEX_{86}), r^2 = 0.86, n = 12 \quad (4)$$

Eq. (4) has a root mean square error of 0.058, resulting in a mean error of +3.6 °C (Fig. 4d).

The correlation is thus substantially improved compared to Eq. (3), strongly suggesting that soil derived GDGT input into lakes may bias TEX_{86} temperature reconstructions (Fig. 4a–c). The equation has a higher intercept and a steeper slope than that in Eq. (3), suggesting that in this case soil input tends to bias TEX_{86} values towards lower temperatures. When compared to the marine calibration of Kim et al. (2008) the equations have nearly identical slopes but the intercept differs by approximately 4 °C.

We have included TEX_{86} data from six lakes with BIT indices below 0.4 from Blaga et al. (2009) in Fig. 4e expanding the number of lakes to 18. The addition of these lakes does not improve the calibration relationship as there is high variability in TEX_{86} values within a small range of lake surface temperatures. It should be noted that three of the points from Blaga et al. (2009) are from Lake Lucerne and each had differing TEX_{86} and BIT indices. The addition of these data changes the slope of the calibration resulting in cooler predicted temperatures.

BIT indices for most lakes in this study are well above 0.5 (Table 1), indicating substantial amounts of branched compared to isoprenoid GDGT. Of the 20 lakes that contained crenarchaeotal GDGT, 11 are large lakes (>4000 km^2; Table 1) five are medium sized lakes (50–352 km^2) and four are small lakes. In contrast, most small lakes, especially those that are small relative to their watershed size (Table 1), do not contain detectable amounts of crenarchaeol in the sediments, at least when analyzed in full scan mode. Of the 12 lakes with BIT values <0.5, 9 are large lakes and 3 are medium lakes. The smallest of these lakes is Crater Lake, which is very deep (>550 m) and has a small catchment to surface area ratio (1.13, see Table 1). It should be noted, however, that Blaga et al. (2009) found high variability in BIT values from Lake Lucerne (a medium sized lake of 113 km^2) ranging from 0.11 in a central basin to 0.83 in the basin with the primary inflowing river, resulting also in variability in TEX_{86} values among basins. Thus, although large lakes should generally be less influenced by soil organic matter inputs than smaller lakes, care must be taken in selecting coring sites for TEX_{86} analysis so that any influences of soil derived GDGT on the temperature reconstruction are minimized.

4.3.3. Influence of methanogens and methane oxidizers on TEX_{86}

The sediments of most lakes contain substantial amounts of methane because methanogenesis is the dominant anaerobic metabolism in freshwater systems. Much of this methane is formed within the sediments and is likely produced by methanogenic Archaea. For example, piston cores from Lake Malawi contain abundant methane, which is generally true of cores from the East African rift lakes (based on visual observation of degassing in recovered cores, Tom Johnson, pers. comm.). The presence of methanogenic Archaea is difficult to identify, because they produce biomarkers that are similar to those of other Eury- and Crenarchaeota, and their biomarkers are not necessarily isotopically distinct from those of other Archaea. For example, the acyclic biphytane (derived from GDGT V) identified in Holocene sediments from Lake Challa (Sinninghe Damsté et al., 2009) was slightly ^{13}C depleted relative to bi- and tricyclic biphytanes (derived from crenarchaeol), clearly indicating a difference in the source of these two GDGT, but not unambiguously indicating methanogens (Sinninghe Damsté et al., 2009). Blaga et al. (2009) found an increase in the GDGT V to crenarchaeol ratio down-core in a shallow sediment core from Sempachersee, which they attributed to in situ methanogenesis by Euryarchaeota. Thus, the presence of methanogenic Euryarchaeota could potentially influence the TEX_{86} values in lakes where methane production is abundant, but remains to be demonstrated.

In an effort to constrain the influence of methanogenic Archaea on the TEX_{86} signal we have examined the ratio of GDGT V, which is the GDGT predominantly produced by methanogenic Euryarchaeota, to crenarchaeol. Following Blaga et al. (2009), we consider a ratio of more than two to be an indicator of methanogen influence. Using this indicator, Lake Malawi and other African rift lakes do not indicate a strong methanogen influence, and in fact none of the lakes included in the final calibration relationship have values greater than 1.3. However, two of the lakes already excluded due to high BIT indices have values well above two (Bear Lake and Lake Nyos, Table 1). In any case, for the lakes surveyed in this study that have the requisite compounds to calculate TEX_{86}, methanogenic inputs seem to play a minor role in influencing TEX_{86} values, though methanogenesis should be considered in future studies given the high inputs to Bear Lake and Lake Nyos.

Archaea involved in the anaerobic oxidation of methane (AOM) contain relatively high amounts of GDGT with 1–2 cyclopentane rings compared to GDGT with no cyclopentane rings (Pancost et al., 2001; Wakeham et al., 2003; Blumenberg et al., 2004), clearly demonstrating that if they are present, they will impact the TEX_{86} values observed in lake sediments. Schubert et al. (2007) have shown that anaerobic oxidation of methane (AOM) mediated by ANME-2 Archaea can be an important process in lake sediments, and Eller et al. (2005) found active AOM Archaea in the water column of a eutrophic lake in Germany. Given the widespread occurrence of methanogenesis in lakes, AOM may prove to be an important process impacting TEX_{86} values in some eutrophic lacustrine systems containing sulfate; however, GDGT derived from methanotrophic Euryarchaeota can be identified because they are depleted in ^{13}C relative to those of Crenarchaeota due to the use of ^{13}C depleted methane to build up biomass (Pancost et al., 2001; Wakeham et al., 2003). In contrast, crenarchaeol, or biphytanes derived therefrom, typically have $\delta^{13}C$ values from -18 to -22‰ (Hoefs et al., 1997; Schouten et al., 1998; Werne and Sinninghe Damsté, 2005; Sinninghe Damsté et al., 2009). Thus, while AOM may be an important confounding influence on TEX_{86} in some systems, it should be easily recognizable.

4.3.4. Seasonal effects on TEX_{86}

It is likely that seasonal productivity of Crenarchaeota varies across latitudinal and environmental gradients, which will increase the uncertainty in the calibration relationship. For example, seasonal studies in the North Sea indicate highest GDGT concentrations during winter months when ammonium levels are high but primary productivity is low (Wuchter et al., 2005). Consistent with the work of Wuchter et al. (2006a) and Herfort et al. (2006) found that TEX_{86} values in surface sediments from the North Sea reflect winter temperatures better than mean annual temperatures. In a sediment trap study from Lake Challa, Sinninghe Damsté et al. (2009) found water column isoprenoidal GDGT to be most abundant just after peak phytoplankton productivity following the heavy rain period, with TEX_{86} values from these samples corresponding well with in situ surface temperatures.

Despite the clear temporal (and spatial) variability in crenarchaeotal distribution, the TEX_{86} temperatures, at least in some settings, appear to reflect mean annual surface temperature. The empirical linear relationship between TEX_{86} and mean annual sea and lake surface temperatures does not necessarily mean that the TEX_{86} is *directly* representing an annual surface temperature signal (e.g. because of equal growth throughout the year). In fact, biologically it is unlikely that Crenarchaeota are constantly productive only in the surface water throughout the year, which is what might be expected to obtain an integrated mean annual surface temperature. For example, in high latitude lakes, crenarchaeotal production at depth or integrated over a broad depth could provide a signal that appears to reflect a mean annual surface temperature because of the buffered meta/hypolimnetic temperature. High latitude lakes spend much of the year much closer to their winter temperature and therefore have relatively low mean annual temperatures, thus, growth predominantly during spring and/or fall could result in a temperature signal close to the mean annual temperature in many systems. In contrast, low latitude lakes have relatively stable surface temperatures year round (approximate range of less than 5 °C). Additionally, a seasonal signal may represent the season during which GDGT are most efficiently transported to the sediments, such as during periods of abundant zooplankton productivity.

In order to investigate potential seasonal influences in the TEX_{86} calibration relationship, we compared TEX_{86} values ($N = 12$, whereby the Blaga et al., 2009 data is not included as there was no seasonal surface temperature data available and only sediment samples with BIT <0.5 were used) with winter and summer mean surface temperatures (Fig. 5). There is a statistically significant difference in the relationship between winter lake surface temperatures and summer lake surface temperatures, with a better fit observed for the winter calibration relationship than for the summer calibration relationship ($r^2 = 0.84$ compared to $r^2 = 0.71$, $n = 12$), suggesting that peak productivity of the aquatic Crenarchaeota may occur during the winter (or possibly spring, when waters are still cooler). In agreement with this data, Wuchter et al. (2005, 2006a) found the highest GDGT and 16S rDNA concentrations in the North Sea during the winter months. However, the mean annual lake surface temperature calibration still has a slightly better overall fit ($r^2 = 0.86$, Fig. 4b) than either seasonal calibration, which suggests that there is not a strong seasonal bias.

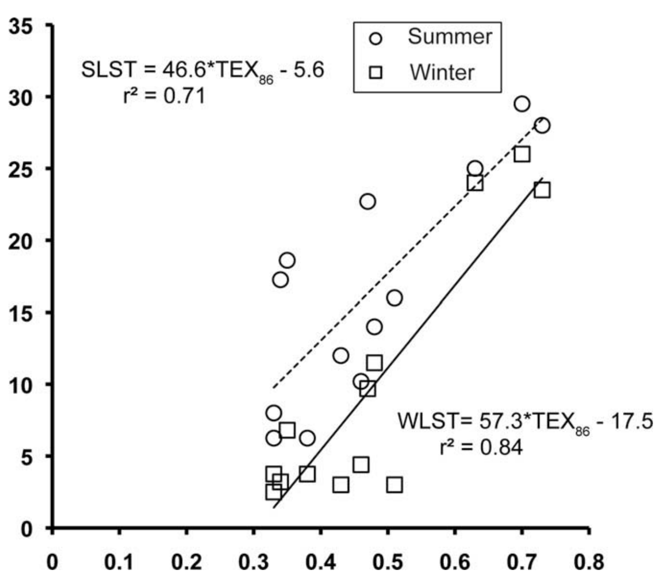

Fig. 5. Comparison of summer and winter lake surface temperatures with TEX_{86} ($n = 12$).

5. Conclusions

The TEX_{86} paleothermometer shows promise as a valuable tool to determine past lake surface temperatures in continental settings, providing high resolution paleotemperature records from primarily large lakes. We have developed a calibration for the TEX_{86} paleotemperature proxy from a suite of globally distributed lacustrine systems in climatically diverse settings. The results of this calibration show a strong linear relationship between TEX_{86} values and published mean annual lake surface temperatures with an estimated calibration error of ±3.7 °C. Our data suggest that the TEX_{86} index appears to work primarily in large lakes, whereas in smaller lakes the GDGT required for the TEX_{86} are typically not abundant enough to perform TEX_{86} palaeothermometry. It should be noted that other studies have also found that the TEX_{86} may sometimes be applicable in some small lakes (Escala et al., 2007; Blaga et al., 2009).

Biases in TEX_{86} derived temperatures occur if a large amount of soil derived organic matter is supplied to the lakes (e.g. as determined by the BIT index), and if there is substantial euryarchaeotal productivity in the water column or sediments compared to autochthonous crenarchaeotal production. Care should be taken in selecting coring sites in order to reduce the influence of allochthonous material, and the BIT index should always be analyzed in concert with TEX_{86} to assess the degree of any potential interference from soil derived GDGT. Furthermore, the TEX_{86} paleothermometer should be applied with caution in systems with known methanogenic activity.

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References

Barns, S.M., Delwiche, C.F., Palmer, J.D., Pace, N.R., 1996. Perspectives on archaeal diversity, thermophily and monophily from environmental rRNA sequences. Proceedings of the National Academy of Sciences USA 93, 9188–9193.

Bintrim, S.B., Donohue, T.J., Handelsman, J., Roberts, G.P., Goodman, R.M., 1997. Molecular phylogeny of Archaea from soil. Proceedings of the National Academy of Sciences USA 94, 277–282.

Blaga, C.I., Reichart, 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. Journal of Paleolimnology 41, 523–540.

Blomquist, R., 2004. Lake Washington Surface Temperatures. Metro King County Water Board, Seattle, WA.

Blumenberg, M., Seifert, R., Reitner, J., Pape, T., Michaelis, W., 2004. Membrane lipid patterns typify distinct anaerobic methanotrophic consortia. Proceedings of the National Academy of Sciences USA 101, 11111–11116.

Bradbury, J.P., 2000. Limnologic history of Lago Patzcuaro, Michoacan, Mexico for the past 48,000 years: impacts of climate and man. Palaeogeography, Palaeoclimatology, Palaeoecology 163, 69–95.

Cohen, A.S., 2003. Paleolimnology: The History and Evolution of Lake Systems. Oxford University Press, New York.

Collier, R.J., 2005. Crater Lake Surface Temperatures. Unpublished data

Coolen, M.J.L., Hopmans, E.C., Rijpstra, W.I.C., Muyzer, G., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2004. Evolution of the methane cycle in Ace Lake

(Antarctica) during the Holocene: Response of methanogens and methanotrophs to environmental change. Organic Geochemistry 35, 1151–1167.

de la Torre, J.R., Walker, C.B., Ingalls, A.E., Konneke, M., Stahl, D.A., 2008. Cultivation of a thermophilic ammonia oxidizing archaeon synthesizing crenarchaeol. Environmental Microbiology 10, 810–818.

Dean, W.E., 2004. Bear Lake Temperature Data. USGS, Denver, CO.

DeLong, E.F., 1992. Archaea in coastal marine environments. Proceedings of the National Academy of Sciences USA 89, 5685.

Eller, G., Känel, L., Krüger, M., 2005. Cooccurrence of aerobic and anaerobic methane oxidation in the water column of Lake Plußsee. Applied and Environmental Microbiology 71, 8925–8928.

Escala, M., Rosell-Mele, A., Masque, P., 2007. Rapid screening of glycerol dialkyl glycerol tetraethers in continental Eurasia samples using HPLC/APCI-ion trap mass spectrometry. Organic Geochemistry 38, 161–164.

Escala, M., Fietz, S., Rueda, G., Rosell-Mele, A., 2009. Analytical considerations for the use of the paleothermometer tetraether index$_{86}$ and the branched vs isoprenoid tetraether index regarding the choice of cleanup and instrumental conditions. Analytical Chemistry 81, 2701–2707.

Farerra, I., Harrison, S.P., Prentice, I.C., Ramstein, G., Guiot, J., Bartlein, P.J., Bonnefille, R., Bush, M., Cramer, W., von Grafenstein, U., Holmgren, K., Hooghiemstra, H., Hope, G., Jolly, D., Lauritzen, S.-E., Ono, Y., Pinot, S., Stute, M., Yu, G., 1999. Tropical climates at the last glacial maximum: a new synthesis of terrestrial paleoclimatic data. I. Vegetation, lake levels and geochemistry. Climate Dynamics 15, 823–856.

Fuhrman, J.A., McCallum, K., Davis, A.A., 1992. Novel marine archaebacterial group from marine plankton. Nature 356, 695–697.

Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W.F., Schauble, E.A., Schrag, D., Eiler, J.M., 2006. ^{13}C–^{18}O bonds in carbonate minerals: a new kind of paleothermometer. Geochimica et Cosmochimica Acta 70, 1439–1456.

Gurulev, S.A., 1994. The Face of Baikal II. Water. Irkutsk (In Russian).

Halfman, J.D., 1987. High-resolution sedimentology and paleoclimatology of Lake Turkana, Kenya. Ph.D., Duke University.

Hallam, S.J., Mincer, T.J., Schleper, C., Preston, C.M., Roberts, K., Richardson, P.M., DeLong, E.F., 2006. Pathways of carbon assimilation and ammonia oxidation suggested by environmental genomic analyses of marine Crenarchaeota. PLOS Biology 4, 520–536.

Herfort, L., Schouten, S., Boon, J.P., Sinninghe Damsté, J.S., 2006. Application of the TEX$_{86}$ temperature proxy in the southern North Sea. Organic Geochemistry 37, 1715–1726.

Herndl, G.J., Reinthaler, T., Teira, E., van Aken, H., Veth, C., Pernthaler, A., Pernthaler, J., 2005. Contribution of Archaea to total production in the deep Atlantic Ocean. Applied and Environmental Microbiology 71, 2303–2309.

Hoefs, M.J.L., Schouten, S., De Leeuw, J.W., King, L.L., Wakeham, S.G., Sinninghe Damsté, J.S., 1997. Ether lipids of planktonic Archaea in the marine water column. Applied and Environmental Microbiology 63, 3090–3095.

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 and Planetary Science Letters 224, 107–116.

Huguet, C., Schimmelmann, A., Thunell, R., Lourens, L.J., Sinninghe Damsté, J.S., Schouten, S., 2007. A study of the TEX$_{86}$ paleothermometer in the water column and sediments of the Santa Barbara Basin, California. Paleoceanography 22, PA3203. doi:10.1029/2006PA001310.

Interlandi, S.J., Kilham, S.S., Theriot, E.C., 1999. Responses of phytoplankton to varied resource availability in large lakes of the greater Yellowstone ecosystem. Limnology and Oceanography 44, 668–682.

Ito, E., 2001. Application of stable isotope techniques to inorganic and biogenic carbonates. In: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change Using Lake Sediments: Physical and Geochemical Methods. Kluwer, Dordrecht.

Kantha, L.H., Freeth, S.J., 1996. A numerical simulation of temperature and CO_2 stratification in Lake Nyos since the 1986 disaster. Journal of Geophysical Research 101, 8187–8203.

Keough, B.P., Schmidt, T.M., Hicks, R.E., 2003. Archaeal nucleic acids in picoplankton from great lakes on three continents. Microbial Ecology 46, 238–248.

Kim, J.-H., Schouten, S., Hopmans, E.C., Donner, B., Sinninghe Damsté, J.S., 2008. Global sediment core-top calibration of the TEX$_{86}$ paleothermometer in the ocean. Geochimica et Cosmochimica Acta 72, 1154–1173.

Könneke, M., Bernhard, A.E., De La Torre, J.R., Walker, C.B., Waterbury, J.B., Stahl, D., 2005. Isolation of an autotrophic ammonia-oxidizing marine archaeon. Nature 437, 543–546.

Leininger, S., Urich, T., Schloter, M., Schwark, L., Qi, J., Nicol, G., Prosser, J.I., Schuster, S.C., Schleper, C., 2006. Archaea predominate among ammonia-oxidizing prokaryotes in soils. Nature 442, 806–809.

Liu, Z.H., Pagani, M., Zinniker, D., DeConto, R., Huber, M., Brinkhuis, H., Shah, S.R., Leckie, R.M., Pearson, A., 2009. Global cooling during the Eocene–Oligocene climate transition. Science 323, 1187–1190.

MacGregor, B., Moser, D.P., Wheeler, A.E., Nealson, K.H., Stahl, D.A., 1997. Crenarchaeota in Lake Michigan sediment. Applied and Environmental Microbiology 63, 1178–1181.

McCave, I.N., 1984. Size spectra and aggregation of suspended particles in the deep ocean. Deep Sea Research 31, 329–352.

Miller, G., 2004. Lake Hvitarvatn Surface Temperature. Unpublished data.

Ouvernay, C.C., Fuhrman, J.A., 2000. Marine planktonic Archaea take up amino acids. Applied and Environmental Microbiology 66, 4829–4833.

Pancost, R.D., Hopmans, E.C., Sinninghe Damsté, J.S., 2001. Archaeal lipids in Mediterranean cold seeps: molecular proxies for anaerobic methane oxidation. Geochimica et Cosmochimica Acta 65, 1611–1627.

Pearson, A., Huang, Z., Ingalls, A.E., Romanek, C.S., Wiegel, J., Freeman, K.H., Smittenberg, R.H., Zhang, C.L., 2004. Non-marine crenarchaeol in Nevada hot springs. Applied and Environmental Microbiology 70, 5229–5237.

Pitcher, A., Schouten, S., Sinninghe Damsté, J.S., 2009. In situ production of crenarchaeol in two California hot springs. Applied and Environmental Microbiology 75, 4443–4451.

Powers, L.A., Werne, J.P., Johnson, T.C., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2004. Crenarchaeotal membrane lipids in lake sediments: a new paleotemperature proxy for continental paleoclimate reconstruction? Geology 32, 613–616.

Powers, L.A., Johnson, T.C., Werne, J.P., Castaneda, I.S., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2005. Large temperature variability in the southern African tropics since the last glacial maximum. Geophysical Research Letters 32, L08706.

Sall, J., Lehman, A., Creighton, L., 2001. JMP Start Statistics. Duxbury, Pacific Grove.

Schleper, C., Holben, W., Klenk, H.-P., 1997. Recovery of crenarchaeotal ribosomal DNA sequences from freshwater lake sediments. Applied and Environmental Microbiology 63, 321–323.

Schouten, S., Hoefs, M.J.L., Koopmans, M.P., Bosch, H.-K., Sinninghe Damsté, J.S., 1998. Structural characterization, occurrence and fate of archaeal ether-bound acyclic and cyclic biphytanes and corresponding diols in sediments. Organic Geochemistry 29, 1305–1319.

Schouten, S., Hopmans, E.C., Pancost, R.D., Sinninghe Damsté, J.S., 2000. Widespread occurrence of structurally diverse tetraether membrane lipids: Evidence for the ubiquitous presence of low-temperature relatives of hyperthermophiles. Proceedings of the National Academy of Sciences USA 97, 14421–14426.

Schouten, S., Hopmans, E.C., Schefuss, E., Sinninghe Damsté, J.S., 2002. Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures? Earth and Planetary Science Letters 204, 265–274.

Schouten, S., Huguet, C., Hopmans, E.C., Kienhuis, M.V.M., Sinninghe Damsté, J.S., 2007a. Analytical methodology for TEX$_{86}$ paleothermometry by high-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry. Analytical Chemistry 79, 2940–2944.

Schouten, S., van der Meer, M.T.J., Hopmans, E.C., Rijpstra, W.I.C., Reysenbach, A.L., Ward, D.M., Sinninghe Damsté, J.S., 2007b. Archaeal and bacterial glycerol dialkyl glycerol tetraether lipids in hot springs of Yellowstone National Park (USA). Applied and Environmental Microbiology 73, 6181–6191.

Schouten, S., Hopmans, E.C., van der Meer, J., Mets, A., Bard, E., Bianchi, T.S., Diefendorf, A., Escala, M., Freeman, K.H., Furukawa, Y., Huguet, C., Ingalls, A., Menot-Combes, G., Nederbragt, A.J., Oba, M., Pearson, A., Pearson, E.J., Rosell-Mele, A., Schaeffer, P., Shah, S.R., Shanahan, T.M., Smith, R.W., Smittenberg, R., Talbot, H.M., Uchida, M., Van Mooy, B.A.S., Yamamoto, M., Zhang, Z.H., Sinninghe Damsté, J.S., 2009. An interlaboratory study of TEX$_{86}$ and BIT analysis using high-performance liquid chromatography–mass spectrometry. Geochemistry Geophysics Geosystems 10. doi:10.1029/2008GC002221.

Schubert, C.J., Loesekann, T., Knittel, K., Boetius, A., 2007. Anaerobic oxidation of methane in sediments of a high alpine lake. Geophysical Research Abstracts 9, 10229.

Sinninghe Damsté, J.S., Hopmans, E.C., Pancost, R.D., Schouten, S., Geenevasen, J., 2000. Newly discovered non-isoprenoid dialkyl diglycerol tetraether lipids in sediments. Journal of the Chemical Society-Series Chemical Communications, 1683–1684.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopmans, E.C., Prahl, F.G., Wakeham, S.G., Schouten, S., 2002a. Distribution of membrane lipids of planktonic Crenarchaeota in the Arabian Sea. Applied and Environmental Microbiology 68, 2997–3002.

Sinninghe Damsté, J.S., Schouten, S., Hopmans, E.C., van Duin, A.C.T., Geenevasen, J.A.J., 2002b. Crenarchaeol: the characteristic core glycerol dibiphytanyl glycerol tetraether membrane lipid of cosmopolitan pelagic Crenarchaeota. Journal of Lipid Research 43, 1641–1651.

Sinninghe Damsté, J.S., Ossebaar, 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 TEX$_{86}$ paleothermometer and BIT index in lacustrine settings. Geochimica et Cosmochimica Acta 73, 4232–4249.

Tavera, R., Martinez-Almeida, V., 2005. Atelomixis as a possible driving force in the phytoplankton composition of Zirahuen, a warm monomictic tropical lake. Hydrobiologia 533, 199–208.

Tierney, J.E., Russell, J.M., 2009. Distributions of branched GDGT in a tropical lake system: Implications for lacustrine application of the MBT/CBT paleoproxy. Organic Geochemistry 40, 1032–1036.

Tierney, J.E., Russell, J.M., Huang, Y., Sinninghe Damsté, J.S., Hopmans, E.C., Cohen, A.S., 2007. Northern Hemisphere controls on tropical Southeast African climate during the past 60,000 years. Science 322, 252–255.

Tigbao, Y., Xianghua, L., 2001. Seasonal population dynamics of Neoechinorhynchus qinghaiensis in the carp, Gymnocypris przewalskii przewalskii, from Qinghai Lake, China. Journal of Helminthology 75, 93–98.

Urbach, E., Vergin, K.L., Young, L., Morse, A., Larson, G., Giovannoni, S.J., 2001. Unusual bacterioplankton community structure in ultra-oligotrophic Crater Lake. Limnology and Oceanography 46, 557–572.

Varela, M.M., van Aken, H.M., Sintes, E., Herndl, G.J., 2008. Latitudinal trends of Crenarchaeota and Bacteria in the meso- and bathypelagic water masses of the Eastern North Atlantic. Environmental Microbiology 10, 110–124.

Vollmer, M.K., Bootsma, H.A., Hecky, R.E., Patterson, G., Halfman, J.D., Edmond, J.M., Eccles, D.H., Weiss, R.F., 2005. Deep-water warming trend in Lake Malawi, East Africa. Limnology and Oceanography 50, 727–732.

Wakeham, S.G., Lewis, C.M., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2003. Archaea mediate anaerobic oxidation of methane in deep euxinic waters of the Black Sea. Geochimica et Cosmochimica Acta 67, 1359–1374.

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., 2006a. Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits. Environmental Microbiology 8, 648–657.

Weijers, J.W.H., Schouten, S., Spaargaren, O.C., Sinninghe Damsté, J.S., 2006b. Occurrence and distribution of tetraether membrane lipids in soils: Implications for the use of the TEX_{86} proxy and the BIT index. Organic Geochemistry 37, 1680–1693.

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. Geochimica et Cosmochimica Acta 71, 703–713.

Weijers, J.W.H., Panoto, E., van Bleijswijk, J., Schouten, S., Balk, M., Stams, A.J.M., Rijpstra, W.I.C., Sinninghe Damsté, J.S., 2009. Constraints on the biological source(s) of the orphan branched tetraether membrane lipids. Geomicrobiology Journal 26, 402–414.

Werne, J.P., Sinninghe Damsté, J.S., 2005. Mixed sources contribute to the molecular isotopic signature of methane-rich mud breccia sediments of Kazan mud volcano (Eastern Mediterranean). Organic Geochemistry 36, 13–27.

Wuchter, C., Schouten, S., Boschker, H.T.S., Sinninghe Damsté, J.S., 2003. Bicarbonate uptake by marine Crenarchaeota. FEMS Microbiology Letters 219, 203–207.

Wuchter, C., Schouten, S., Wakeham, S., Sinninghe Damsté, J.S., 2005. Temporal and spatial variation in tetraether membrane lipids of marine Crenarchaeota in particulate organic matter: Implications for TEX_{86} paleothermometry. Paleoceanography 20. doi:10.1029/2004PA001110.

Wuchter, C., Abbas, B., Coolen, M.J.L., Herfort, L., Van Bleijswijk, J., Timmers, P., Strous, M., Teira, E., Herndl, G.J., Middelburg, J.J., Schouten, S., Sinninghe Damsté, J.S., 2006a. Archaeal nitrification in the ocean. Proceedings of the National Academy of Sciences USA 103, 12317–12322.

Wuchter, C., Schouten, S., Wakeham, S.G., Sinninghe Damsté, J.S., 2006b. Archaeal tetraether membrane lipid fluxes in the northeastern Pacific and the Arabian Sea: Implications for TEX_{86} paleothermometry. Paleoceanography 21, PA4208.

Zhang, C.L., Pearson, A., Li, Y.-L., Mills, G., Wiegel, J., 2006. Thermophilic temperature optimum for crenarchaeol synthesis and its implication for archaeal evolution. Applied and Environmental Microbiology 72, 4419–4422.