

Crenarchaeotal membrane lipids in lake sediments: A new paleotemperature proxy for continental paleoclimate reconstruction?

Lindsay A. Powers
Josef P. Werne
Thomas C. Johnson
Ellen C. Hopmans
Jaap S. Sinninghe Damsté*
Stefan Schouten

Large Lakes Observatory, University of Minnesota Duluth, 10 University Drive, Duluth, Minnesota 55812, USA

Netherlands Institute for Sea Research, Department of Marine Biogeochemistry and Toxicology, P.O. Box 59, 1790 AB Den Burg, Netherlands

ABSTRACT

Paleoclimate studies of continental environments have been hampered by the lack of an independent paleotemperature proxy. A novel sea-surface temperature proxy has been proposed for marine systems based on membrane lipids of marine crenarchaeota (the TEX₈₆—tetraether index of tetraethers with 86 carbon atoms). Analysis of archaeal membrane lipids in core-top sediments from a diverse suite of lacustrine systems suggests the ubiquitous occurrence of low-temperature crenarchaeota in lake systems as well. Application of the TEX₈₆ proxy in these lacustrine systems indicates that it is valid in lake environments, and the calibration of TEX₈₆ in lacustrine systems is similar to that in the marine environment. This proxy will provide an independent continental paleotemperature tool that will allow paleoclimatologists to address fundamental questions about temperature variability in continental environments and its relationship to climate change.

Keywords: paleothermometer, lacustrine sediments, climate change, continental climate, biomarkers.

INTRODUCTION

Understanding past climate variability is imperative to the development of predictive climate models. One essential ingredient in the development of such models is knowledge of past temperatures. The study of continental paleoclimates is currently limited by our ability to determine accurately temperature variability. In order to understand global climate patterns and processes we must be able to quantify past continental temperature variability. Many of the important questions regarding paleoclimatology are directly related to temperature. For example, estimates of temperatures in the African tropics during the Last Glacial Maximum are highly variable and range from 2 to 8 °C cooler than those of today, according to climate models (CLIMAP Project Members, 1981), oxygen isotope analyses from speleothems (Talma et al., 1974), and pollen (Bonnefille et al., 1992; Chalié, 1992). Unfortunately, none of these proxies are independent measures of temperature. These temperature proxies can be dependent upon precipitation rate, evaporation rate, and changes in source composition, as well as temperature.

The development of independent or less dependent proxies of past temperature has been much more successful in marine than in lacustrine systems. Foraminiferal assemblage reconstruction is used to infer sea-surface temperature (SST) on the basis of the specific temperature requirements of species and their relative abundance in sediments (CLIMAP Project Members, 1981; Chapman et al., 1986). The $\delta^{18}\text{O}$ values of corals (Cole et al., 2000) and foraminifera (Billups and

Schrag, 2002) in marine systems, and ostracodes (von Grafenstein et al., 1999) and diatoms (Hu and Shemesh, 2003) in lacustrine systems, have also been used for paleotemperature reconstruction. In marine systems the $\delta^{18}\text{O}$ signature is a function of the $\delta^{18}\text{O}$ value of the source water, ice volume, organism preservation, and carbonate concentration during organism growth, but is much less dependent upon hydrologic balance on short time scales, which can be a major issue in lacustrine systems. Biological effects on isotope fractionation and organism depth preference must be known when using biogenic $\delta^{18}\text{O}$ as a temperature proxy in order to separate biological and environmental effects. Huang et al. (2002) developed a paleothermometer based on hydrogen isotope ratios of specific organic compounds. To date, all stable isotopes used for paleothermometers in lacustrine systems are potentially confounded by changes in source isotopic composition, variable biological effects, and changes in the regional hydrologic cycle. The Mg/Ca ratios in biogenic carbonates, primarily from foraminifera in marine systems (Lea et al., 2003) and ostracodes in lacustrine systems (Holmes, 1996), have also been used to reconstruct paleotemperatures. As with isotopes, there are biological effects on Mg/Ca ratios, and the effects vary among species. Potential temperature proxies like $\delta^{18}\text{O}$ values and Mg/Ca ratios of carbonates are often impossible to measure in lacustrine systems owing to the lack of carbonates in the system. Temperature reconstructions based on chironomid assemblage composition show promise, but are primarily limited to use in shallow, oxic, and typically short-lived systems (Walker, 2001).

Biomarkers such as long-chain alkenones (Brassell et al., 1986; Prah and Wakeham, 1987) and, more recently, glycerol dialkyl glycerol tetraethers (GDGTs) (Schouten et al., 2002, 2003b), have been used successfully to reconstruct SSTs in many marine environments. The alkenone index, U_{37}^K , is based on the number of carbon double bonds in C_{37} long-chain unsaturated ketones (alkenones) produced by certain haptophyte algae; the production rate appears to be primarily dependent upon growth temperature (Brassell et al., 1986; Prah and Wakeham, 1987). Alkenones have been found in some lake sediments (Zink et al., 2001; Thiel et al., 1997; Cranwell, 1985), but their occurrence is highly scattered, and reliable temperature calibrations for alkenones in lake sediments do not exist, because the well-known alkenone-producing haptophytes (*Emiliani huxleyii*, *Geophyrocapsa oceanica*) only grow at elevated salinities. It is therefore unlikely that alkenones will prove to be a useful tool in lakes.

Schouten et al. (2002, 2003b) proposed a molecular paleotemperature proxy, TEX₈₆ (tetraether index of tetraethers with 86 carbon atoms), for the marine environment based on the distribution of GDGTs, membrane lipids derived from pelagic crenarchaeota. Culture studies of thermophilic archaea have shown a strong positive relationship between the average number of cyclopentane rings in the GDGTs and growth temperature (Gliozzi et al., 1983; Uda et al., 2001), where the

*Also at Faculty of Geosciences, Utrecht University, P.O. Box 80.021, Utrecht, Netherlands.

incorporation of cyclopentane rings in the lipid structure of GDGTs allows for adjustment of fluidity of the membrane under different temperature conditions. Nonthermophilic crenarchaeota are phylogenetically closely related to the thermophilic archaea and also have membrane structures composed of GDGTs (Sinninghe Damsté et al., 2002b). Schouten et al. (2002, 2003a) showed that the fine tuning of the physical properties of the membranes of marine crenarchaeota is also performed by adjusting the number of cyclopentane rings in the GDGT membrane lipids, and used this to reconstruct SSTs back into the middle Cretaceous.

Crenarchaeota, a subgroup of the archaea, were previously thought to be primarily extremophiles living under conditions of extreme temperature, salinity, pH, or anoxia (DeLong, 1998). Subsequent studies have shown that nonthermophilic crenarchaeota are an abundant component of the marine planktonic community (Karner et al., 2001; Hoefs et al., 1997; Sinninghe Damsté et al., 2002a) and may compose 20% of the picoplankton in the open ocean (Karner et al., 2001). Molecular ecological methods have established that these crenarchaeota also exist in lake systems (Keough et al., 2003; Macgregor et al., 1997; Urbach et al., 2001; Jurgens et al., 2000; Pernthaler et al., 1998; Schleper et al., 1997), hinting at the possibility that their fossilized membrane lipids may also be used as a paleothermometer in continental systems. Unfortunately, molecular ecological techniques do not provide information about organism abundance: they amplify the genetic signature, which allows detection at much lower concentrations than necessary for lipid analysis. Although it is becoming clear that nonthermophilic crenarchaeota are not restricted to marine environments, but also live in lakes, GDGTs have not previously been reported in nonsaline lakes (Schouten et al., 2000). Here we present evidence for the presence of nonthermophilic crenarchaeotal biomarkers (GDGTs) in four large lakes, representing a wide range of climatic conditions, and we present the first results from the application of the TEX₈₆ technique that suggest that fossilized GDGT membrane lipids may also be used as a paleothermometer in continental systems.

METHODS

Large lakes representing different climatic and physical settings were chosen for this study. Lake Superior and Lake Michigan are of glacial origin, are ~10,000 yr old, and are centrally located on the North American continent. Lake Malawi is a tectonically formed lake in the East African rift system and is older than 5 Ma (Cohen et al., 1993). Issyk Kul (northeast Kyrgyzstan) is a tectonically formed lake in the Tien Shan rift system of central Asia, and is older than 5 Ma (Grosswald et al., 1994). The variety of the climatic settings, coupled with the ages and location of the lakes, makes them excellent candidates for continental paleoclimate studies.

Surface sediments (5–10 g dry mass from the upper 2 cm) from multicores were freeze-dried and homogenized by mortar and pestle. Sediments were then extracted with dichloromethane (DCM)/methanol (2:1) by using Soxhlet extraction techniques to acquire the total lipid fraction. The extracts were purified and separated by Al₂O₃ column chromatography using hexane/DCM (9:1), DCM/methanol (1:1), and methanol as subsequent eluents to separate the lipid fractions by polarity. The first polar fraction (DCM/methanol) was condensed by rotary evaporation and further purified as described by Schouten et al. (2002). Separation, identification, and quantification of the GDGTs by high-performance liquid chromatography–atmospheric-pressure positive-ion chemical ionization–mass spectrometry (HPLC-APCI-MS) were conducted as described by Hopmans et al. (2000). Samples were analyzed in duplicate; typical errors in TEX₈₆ values were ±0.02.

GDGTs IN LAKES

We identified GDGTs in the core-top sediments of all four lakes analyzed thus far. Three nonisoprenoidal GDGTs (I–III; Fig. 1) of un-

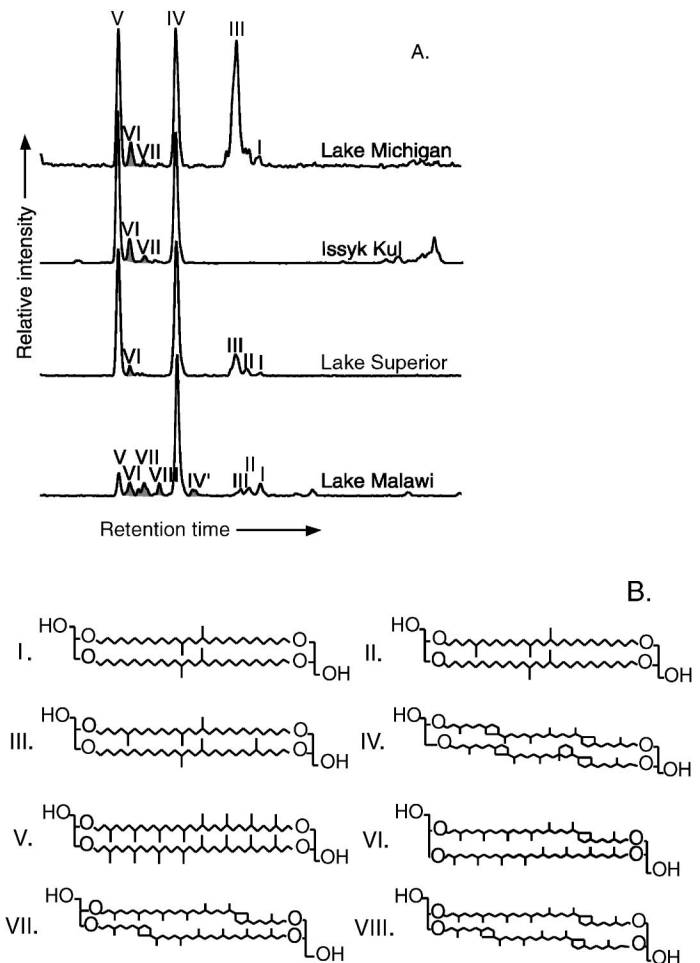


Figure 1. A: High-performance liquid chromatography–mass spectrometry base-peak chromatograms of glycerol dialkyl glycerol tetraether (GDGT) compounds from Lake Michigan, Issyk Kul, Lake Superior, and Lake Malawi. Some compounds are not visible on base-peak chromatogram but were determined via partial ion chromatograms. Peaks relevant to TEX₈₆ (see text) calculation are shaded. **B:** GDGT structures. GDGT IV' is stereoisomer of crenarchaeol (GDGT IV).

certain origin and six isoprenoidal GDGTs (IV–VIII, Fig. 1), derived from crenarchaeota, were detected. The nonisoprenoidal GDGTs I–III (Sinninghe Damsté et al., 2000) are likely derived from bacteria or archaea thriving in terrestrial soils and peats (Schouten et al., 2000) and were probably transported into the lakes by erosion. Their absence in Issyk Kul sediments is likely due to the high-altitude arid environment of the lake.

The isoprenoid, archaea-derived GDGTs (IV–VIII) in the lake sediments are exactly the same as those found in marine sediments, marine particulate matter, and the only available cultures from the group of nonthermophilic crenarchaeota, *Cenarchaeum symbiosum* (Schouten et al., 2000; Sinninghe Damsté et al., 2002a, 2002b). Crenarchaeol (GDGT IV), typically the most abundant GDGT in aquatic systems, is thought to be solely produced by “cold” crenarchaeota (i.e., nonthermophilic) and is unique in its possession of a single cyclohexane ring (Sinninghe Damsté et al., 2002b). The presence of the cyclohexane ring in crenarchaeol is thought to be an adaptation to the relatively cold environments (i.e., compared to those of the hyperthermophiles) and prevents dense packing of the biphytanyl chains in the GDGT membrane, resulting in a lower thermal transition point of the membrane (Sinninghe Damsté et al., 2002b). In addition to crenarchaeol,

the isoprenoidal GDGT with no cyclopentane ring (V) is also abundant. It can be derived from (hyper)thermophilic and nonthermophilic crenarchaeota, and from euryarchaeota (including methanogens). Cyclopentane-containing GDGTs (VI–VIII) occur in smaller relative amounts (Fig. 1). Overall, the distribution of isoprenoidal GDGTs is strikingly similar to those of nonthermophilic crenarchaeota (Sinninghe Damsté et al., 2002b). The presence of the isoprenoidal GDGTs in surface lake sediments therefore confirms the existence of nonthermophilic crenarchaeota in lakes and suggests that they are derived from the water column of the lake.

The GDGT distribution varies among the lakes, which could be due either to the crenarchaeotal community structure or to a physiological response to temperature of the crenarchaeota. In a study of great lakes on three continents, Keough et al. (2003) demonstrated that there is a surprisingly small phylogenetic diversity of freshwater crenarchaeota, suggesting that a physiological response is a more likely explanation. The abundance of GDGT V relative to crenarchaeol is high in the three “cold” lakes, but low in the Lake Malawi sediments (Fig. 1). It is well known from the marine environment studies that this difference is a physiological response to adjust the membrane of the crenarchaeota to higher temperatures (Schouten et al., 2002, 2003b), and suggests that a similar response applies to nonthermophilic freshwater crenarchaeota. In line with this possibility, we also find higher relative abundances of the cyclopentane-containing GDGTs (VI–VIII) in the Lake Malawi sediments (Fig. 1), also a characteristic of GDGT distributions of populations of marine crenarchaeota adjusted to higher SSTs (Schouten et al., 2002).

APPLICATION OF TEX_{86} TO LAKE GDGT DATA

Analyses of core-top sediments from globally distributed marine locations led Schouten et al. (2002, 2003b) to propose a paleotemperature proxy based on the relative distribution of the cyclopentane-containing GDGTs called TEX_{86} (Fig. 1B). TEX_{86} is a weighted average index based on the observation that the number of cyclopentane rings in the GDGTs increases with increasing growth temperature. It is a ratio of the abundance of cyclopentane-containing GDGTs (including the relatively small isomer of crenarchaeol IV') defined by the following equation:

$$TEX_{86} = \frac{([IV'] + [VII] + [VIII])}{([IV'] + [VI] + [VII] + [VIII])} \quad (1)$$

This index has shown a high correlation ($R^2 = 0.92$) with mean annual SST at several marine locations in both surface-sediment and water-column samples (Fig. 2) (Schouten et al., 2002, 2003b). The TEX_{86} is linearly related to mean annual SST (T) according to the equation $TEX_{86} = 0.015T + 0.29$. GDGTs can be well preserved in sediments and have been used to infer paleotemperatures in sediments as old as 120 Ma (Schouten et al., 2003a).

We have plotted the results of the TEX_{86} index for the isoprenoidal GDGT distributions of the four lake sediments in this study against published mean annual lake-surface temperatures from the International Lake Environment Committee Foundation database (<http://www.ilec.or.jp/database/index/idx-lakes.html>, accessed December 2003) in combination with updated marine TEX_{86} data from Schouten et al. (2002, 2003b) (Fig. 2). The relationship between the TEX_{86} for the lake samples and mean annual surface temperature fits well with the marine data. There is a strong positive relationship between the TEX_{86} for lakes and the mean annual surface temperature. Our results are well within the error of the marine TEX_{86} relationship, with the exception of the Lake Michigan sample, which had a concentration of GDGTs at the limit of detection. These results suggest that the lacustrine

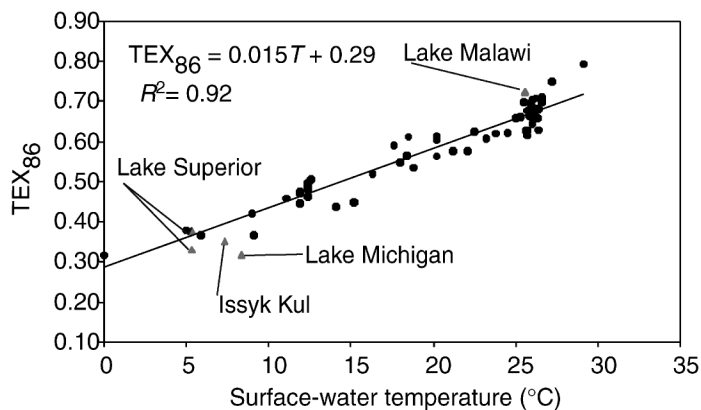


Figure 2. Correlation of TEX_{86} with mean annual sea-surface temperatures (SSTs) in marine samples (solid dots) and mean annual lake-surface temperatures for lacustrine samples (gray triangles). There are two identical points for Lake Malawi.

crenarchaeota have a biological mechanism to adapt their membrane to environmental conditions that is similar to that of their marine counterparts. This suggestion is in agreement with molecular biological data of Keough et al. (2003), who found that the crenarchaeota species living in large lakes, including Lake Superior, are phylogenetically very similar to marine crenarchaeota. Our preliminary results thus strongly suggest that the TEX_{86} index is a promising tool for lake paleotemperature reconstruction.

It is unknown why TEX_{86} reflects mean annual SST, as marine crenarchaeota are known to thrive in great abundance at depths >100 m, where temperatures are substantially lower than those at the surface (Schouten et al., 2002, 2003b; Wakeham et al., 2003; Sinninghe Damsté et al., 2002; Urbach et al., 2001). Lacustrine crenarchaeota have been identified from near surface to 500 m water depth (Keough et al., 2003; Urbach et al., 2001), though their depth preference is unknown. In order to better understand the sedimentary signature provided by TEX_{86} , it is necessary to know where in the water column the crenarchaeota are living, whether there is seasonal variability in their abundance, and whether the sediments accurately preserve these signatures. Further work is also needed to characterize the habits of these organisms, which may allow a more specific temperature relationship to be developed. Many more lakes also need to be added to this data set in order to develop a stringent calibration set for TEX_{86} in lakes.

CONCLUSIONS

Archaeal GDGTs have been found in all lakes surveyed to date, supporting the molecular biological studies suggesting the ubiquity of crenarchaeota in lacustrine systems. GDGTs are sufficiently abundant in lake sediments to apply the TEX_{86} temperature proxy. Preliminary application of the TEX_{86} temperature proxy to lakes results in excellent temperature prediction. Development of the TEX_{86} tool for use in lakes will provide an independent temperature proxy for continental paleotemperature reconstruction. This tool will allow paleoclimatologists to address questions about temperature variability over many spatial and temporal scales, which are currently unanswered. For example, just how cold were the tropics during the Last Glacial Maximum, and do the tropics lead or lag warming at the poles? Determination of continental temperatures over long time scales may provide insight into the driving mechanisms of climate variability, e.g., solar forcing versus volcanic activity. Further, being able to constrain continental temperature will allow better interpretation of changes in hydrologic cycles and budgets. Future work should focus on characterizing the depth, seasonality, and temperature habitats of nonthermophilic crenarchaeota in lakes, as well as increasing the number of lakes in the database.

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