Glycerol dialkyl glycerol tetraether membrane lipids in lacustrine environments and their application as proxies for palaeoclimate reconstructions

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Glycerol dialkyl glycerol tetraether membraanlipiden in meersedimenten en hun toepassing in palaeoklimaat reconstructies

(met een samenvatting in het Nederlands)

Glicerol tetra-eteri din sedimentele lacurilor şi utilizarea lor în reconstituirea paleoclimatului

(cu un rezumat în limba română)

Proefschrift

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Chapter 1

General introduction

1.1 Lakes as recorders of climate change

Palaeoclimatic reconstructions offer the possibility to test hypotheses and numerical models for future anthropogenic forcing of climatic change. Whereas the marine realm has been extensively and intensely studied over the last decades, much less is known about palaeoclimatic changes in terrestrial systems. Investigating terrestrial systems is crucial since societal and economic impacts of climate change are most important on the continent.

Lakes are considered to be particularly sensitive reflectors of environmental variability, including climate change (Batarbee, 2000). Their limited size, compared to seas and oceans, and delicate physiology makes them susceptible to regional, subtle changes. The sediments accumulating at the lake bottom provide a natural archive that integrates information from the water column, catchment area, and the atmosphere and consequently represent a valuable recorder of present and past environmental change. Lake sediments accumulate quite rapidly, often >1 mm per year, and after retrieval, sediment cores can be sub-sampled finely to provide data with decadal or sub-decadal resolution. Annually-laminated (varved) lake sediments allow even higher resolution climate reconstructions in combination with an inherent annual chronology. Some lake records go back in time to the last glacial termination, the sediments allowing detailed reconstruction of the associated climatic and environmental changes in the lake catchment area.

Based on a range of numerical models, it is likely, future climatic changes will be more intense, and continents will experience larger peak wind speeds and more heavy precipitation associated with ongoing increases of temperatures (Dalton et al., 2005). These can be linked to a catchment response in terms of hydrology, snow cover, soil, and vegetation development with consequent physical, chemical, and biological lake responses (Dalton et al., 2005). However, these climate models used, to predict future climate changes, are tested with instrumental climate data, that for temperature go back only a few hundred years, and data inferred from past climates. In the past years progress has been made in understanding how climate is changing in time and space, but to understand these changes we need knowledge about past conditions in as many different regions of the world as possible. Climate reconstructions strongly rely on relationships between measurable variables from the sedimentary record, processes in the water column and climate. Reading the sedimentary archives, thus, requires the use of so-called proxy climate indicators, relating these variables to physical and chemical conditions in the past. Proxies are crucial for developing a long-term perspective on past environmental conditions and thus natural climate forcing mechanisms. This approach also allows extending reconstructions of past climate change to the time before widespread instrumental temperature recordings. Such records are needed in order to capture the full range of natural climate variability. Most proxies are currently based on empirical calibrations only, whereas a process-based understanding is required to reliably apply proxy relations to potentially dissimilar settings further back in time.

In contrast to the marine realm the development of proxies for lacustrine environments has been relatively limited. Stable isotopes (e.g. Stuiver, 1970; Talbot, 1990), minerogenic clastic components of lake sediments (e.g. Noon, 1997) and varve thickness (e.g. Itkonen and Salonen, 1994; Zolitschka and Negendank, 1998; Hughen et al., 1999) have been used as climate indicators, complementary to biological approaches based on transfer functions (e.g. Birks et al., 1990; Battarbee, 1991). Most studies currently apply a so-called multi-proxy approach for the reconstruction of past climate change from lake sediments. Using multiple proxies next to each other not only makes the reconstruction itself more reliable, but also has the potential to generate additional information. Still, a robust reconstruction of past (climate) change cannot be guaranteed by combining proxies only. Not all sedimentary records are suitable for a multi proxy approach since they might not contain all signal carriers, whereas combining records from different locations in the lake adds the problem of inter calibration (Battarbee, 2000).

Palaeolimnological proxy methods are used to reconstruct changes in precipitation–evaporation regimes and temperature (Hastenrath and Kutzbach, 1983) but also wind regimes (e.g. Bradbury et al., 1993), moisture sources, atmospheric circulation patterns (e.g. McKenzie and Hollander, 1993) and atmospheric pCO_2 (Street-Perrott et al., 1997) have been reconstructed. Temperature reconstructions from lake sediment records are usually based on stable oxygen isotopes (Stuiver, 1970) and biological transfer functions using chironomids, diatoms, chrysophytes or cladocera (Walker et al., 1991; Lotter et al., 1997). Using biological data inherently adds to the uncertainty of reconstructions, as observed from the comparative output of inference models with different training sets or different proxies (Birks et al., 1999). Biochemical compounds like membrane lipids from lake sedimentary records have become only recently available as a tool for reconstructing past climatic conditions (Powers et al., 2004). An additional, independent temperature proxy would not only be useful in a multi proxy approach, but when based on a mechanistic understanding, could help to evaluate existing biological-proxies and extend their interpretation.

1.2. Sedimentary organic carbon in lakes: composition and potential application

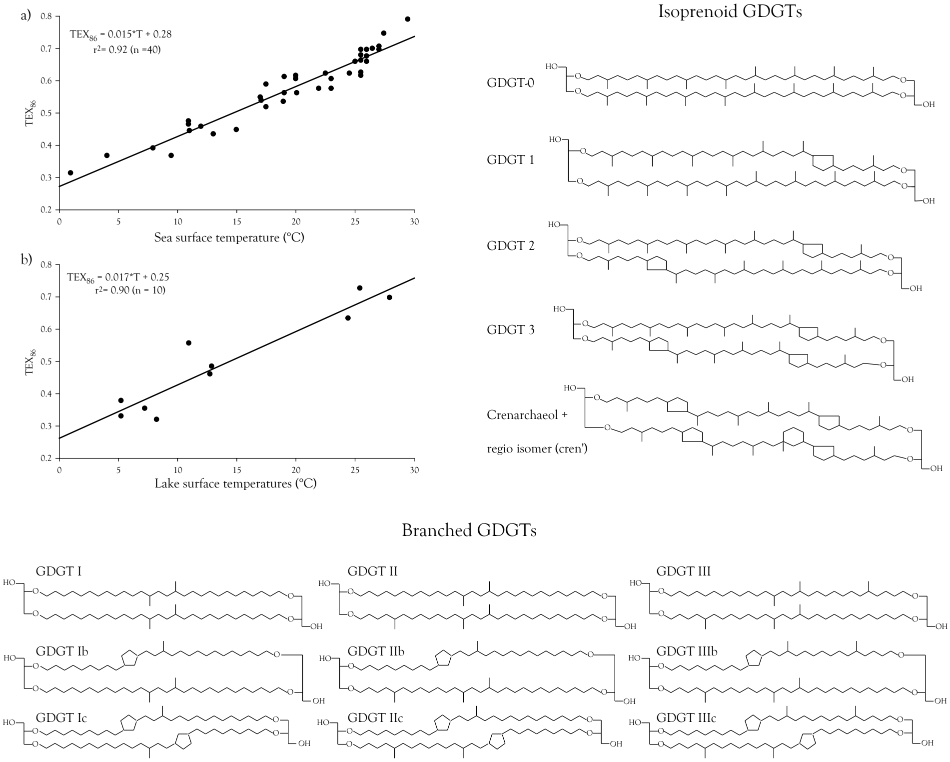
Organic matter in lacustrine sediments also provides an important signal carrier of past environmental change. Lacustrine sediments often contain relatively high amounts of organic matter because of bottom water anoxia and relatively high sedimentation rates. The complex mixture of lipids, carbohydrates, proteins and other organic components in lake sediments (Meyers, 2003) derived from organisms that once lived in and near the lake holds information for reconstructing changes in both local and regional environments. When the source information is retained, they become important parts of palaeolimnological and palaeoclimatological records. Bulk parameters, such as elemental and isotopic composition ($\delta^{13}C$, $\delta^{15}N$) (e.g. Talbot and Johannssen, 1992, Peterson and Horwath, 1987), Rock-Eval pyrolysis data (e.g. Espitalié et al., 1977, Talbot and Livingstone, 1989), and lignin oxidation products (e.g. Hedges and Mann, 1979) may provide basic information on changes in organic matter sources. The carbon to nitrogen ratios of the bulk organic matter potentially reflects the relative contribution of aquatic versus land-derived material (e.g. Meyers, 1994). Changes in carbon, nitrogen and hydrogen isotopic compositions of lake-derived organic matter reflect changes in productivity, watershed vegetation, biogeochemical cycling and hydrologic balance of the catchment (Meyers, 2003).

Specific molecules characteristic to a group of organisms, so-called biomarkers, carry information about their source organisms. When found in sedimentary records of lakes, the relative abundance and isotopic composition of these molecules provide information on the environmental conditions during their life cycle and, therefore, can be used as proxies for paleoenvironmental reconstructions (see Meyers and Ishiwatari, 1993; Meyers, 1997, 2003; Meyers and Lallier-Vergés, 1999 for reviews). Due to the relatively easy analysis, n-alkane distributions have been widely investigated in various types of possible source organisms as well as in lake sedimentary settings. The distribution of n-alkanes in lake sediments has been used to determine the dominant vegetation in and around the lake (e.g. Parrish et al., 1992; Ficken et al., 2000). The compound-specific carbon ($\delta^{13}C$) and hydrogen (δD) isotope composition of sedimentary n-alkanes is increasingly used as a palaeoclimate proxy (Meyers et al., 1994, Sauer et al., 2001). Long-chain alkenones (LCA) are key biomarkers for haptophytes in marine environments where they are ubiquitous and are well known for their use in marine palaeotemperature reconstructions via the $U_{37}^{k}$and $U_{37}^{k'}$ indices (Brassell et al., 1986; Brassell, 1993). A limiting aspect of alkenone based palaeothermometry is the restricted habitat of *Emiliania huxleyi*, the species producing these compounds, to marine systems. The occurrence of LCAs has been documented in a limited number of different lake types from a range of geographical regions (e.g. Li et al., 1996; Thiel et al., 1997). Some attempts to use LCAs to determine past lake temperatures have been undertaken (e.g. Zink et al., 2001; Pearson et al., 2008) but the scattered occurrence of LCAs in lakes hampers the wide application of LCA palaeothermometry in lakes. Furthermore, the biological origin of the LCAs is often not clear and it has been demonstrated that different haptophytes possess different LCA unsaturation – temperature calibrations. Coolen et al. (2004) showed that by using a combined stratigraphic analysis of lipid biomarkers and 16S rRNA genes haptophyte species can be identified for LCAs in Holocene lake sediments that are excellently preserved. Eutrophication of lacustrine systems, changes in watershed vegetation, and intensive land use in the catchment area for agriculture are other (palaeo)environmental aspects that can be inferred from specific biomarkers in lake sediments (Meyers, 2003).

1.3. Tetraether membrane lipids and their application as potential organic proxies in lake sediments

Molecular ecological analyses revealed that Archaea, one of the three domains of life, are not restricted to extreme environments like volcanic hot springs, brines or anoxic conditions, but are also present in more temperate environments such as oceans, soils and lakes (DeLong, 1998). Formerly thought to consist only of hyperthermophilic organisms living at temperatures >60 °C, phylogenetically related Crenarchaeota are also present in oceans and lakes with environmental temperatures ranging from 0 to 30 °C.

Hyperthermophilic Archaea are known to biosynthesize specific membrane lipids composed of isoprenoid alkyl chains linked by ether bonds to the glycerol backbone to form glycerol dialkyl diether and glycerol dialkyl glycerol tetraethers (GDGTs; Fig. 1), which can contain up to 8 cyclopentane rings (DeRosa and Gambacorta, 1988). Crenarchaeota, one of the two major lineages of Archaea (Woese et al., 1990), present in the marine water column make similar GDGTs as those encountered in cultured hyperthermophilic organisms (Schouten et al., 2000) with the exception of "crenarchaeol", which is only produced by non-thermophilic Crenarchaeota and is uniquely characterized by the presence of a cyclohexane moiety. Crenarchaeol is thus a specific marker for mesophilic ("cold" loving) Crenarchaeota (Schouten et al., 2000; Sinninghe Damsté et al., 2002a, b). The change in the distribution of GDGTs, in marine environments, was shown to vary with temperature and this variation was expressed in the new proxy TEX_{86} (<u>T</u>etra<u>E</u>ther inde<u>X</u> of tetraethers with <u>86</u> carbon atoms) (Fig. 1a). Schouten et al. (2002) proposed this palaeotemperature proxy based on an index of the cyclopentane-containing GDGTs. TEX_{86} as a novel paleotemperature proxy has shown great potential in marine systems (Schouten et al., 2002) back into the Cretaceous (Schouten et al., 2003 - Cretaceous sediments from low latitudes; Jenkyns et al., 2004 - Late Cretaceous Arctic Ocean; Sluijs et al., 2006 - Eocene high latitudes; Huguet et al., 2006 - glacial to Holocene sediments from the Arabian Sea).



$$TEX_{86} = \frac{[2]+[3]+[CREN']}{[1]+[2]+[3]+[CREN']}$$

$$BIT = \frac{[I]+[II]+[III]}{[I]+[II]+[III]+[CREN]} \qquad MBT = \frac{[I+Ib+Ic]}{[I+Ib+Ic]+[II+IIb+IIc]+[III+IIIb+IIIc]} \qquad CBT = -LOG\frac{[Ib]+[IIb]}{[I]+[II]}$$

Fig. 1 Structures of different isoprenoid and branched GDGTs used for calculating TEX_{86}, BIT, MBT and CBT. In panel a) and b) the empirical correlation between TEX_{86} values of marine (Schouten et al., 2002) and lacustrine (Powers et al., 2004) surface sediments and temperature is presented.

Various molecular ecological studies (e.g. Keough et al., 2003 and references therein) have detected non-thermophilic Crenarchaeota in lake water and sediments. Using recent sediments from a number of climatologically diverse lakes (Lake Michigan, U.S.A., Lake Superior, U.S.A., Lake Issyk Kul, Kyrgyzstan, and Lake Malawi, Malawi) Powers et al. (2004) showed that all lake sediments contained substantial amounts of crenarchaeotal GDGTs allowing the calculation of TEX_{86} values. The linear correlation between the calculated TEX_{86} values and measured temperatures was similar to the one based on marine core tops (Fig. 1b), suggesting that this palaeotemperature proxy is applicable in diverse environments, including lakes. The first application of the TEX_{86} palaeotemperature proxy in a lake setting by Powers et al. (2005) reconstructed mean annual lake surface temperatures (LST) through the Last Glacial Maximum (LGM) in Lake Malawi. The results revealed that the TEX_{86} can be applied in lake sediments to decipher past changes in LSTs (Fig. 2). For continental climate reconstruction this is a very promising tool since proxies for the determination of LST in lacustrine systems are rare and generally rely on stable oxygen isotope ratios measured on carbonates, which depend not only on temperature but also on the isotopic composition of the lake water, which can vary much more rapidly in lakes than in marine systems. The palaeothermometer potential of TEX_{86} was further explored by Tierney et al. (2008) reconstructing lake temperature variations using sediment cores from Lake Tanganyika. Inferred temperatures revealed climatic changes at the millennial scale over the past 60.000 years, encouraging palaeo-lake surface temperature reconstructions.

In a study of peat bogs, Sinninghe Damsté et al. (2000) identified another group of GDGTs containing branched instead of isoprenoid alkyl chains with a variable number of methyl groups attached on the alkyl chains and cyclopentyl moieties in the alkyl chain (Fig. 1). It is still uncertain whether they are produced by Archaea or Bacteria, but based on the stereochemistry of the glycerol moieties a bacterial origin has been suggested (Weijers et al., 2006a). Isoprenoid and branched GDGTs were ubiquitously detected in terrestrial, lacustrine and marine environments (Schouten et al., 2000, Powers et al., 2004). Later on, soils were deemed to be the most likely origin for branched GDGTs (Weijers et al., 2006b). Based on the observed difference in relative abundances of branched and isoprenoid GDGTs, the BIT index was developed in order to rapidly assess the relative input of soil-derived organic matter to sediments (Hopmans et al., 2004) (Fig. 1). Weijers et al. (2006b) indicated that the fluvial transport of terrestrial derived isoprenoid GDGTs to lacustrine environments could potentially bias the application of TEX_{86} as a proxy for reconstructing LST and suggested that the BIT index should be used in a first step to quantify the relative input of terrestrial organic matter.

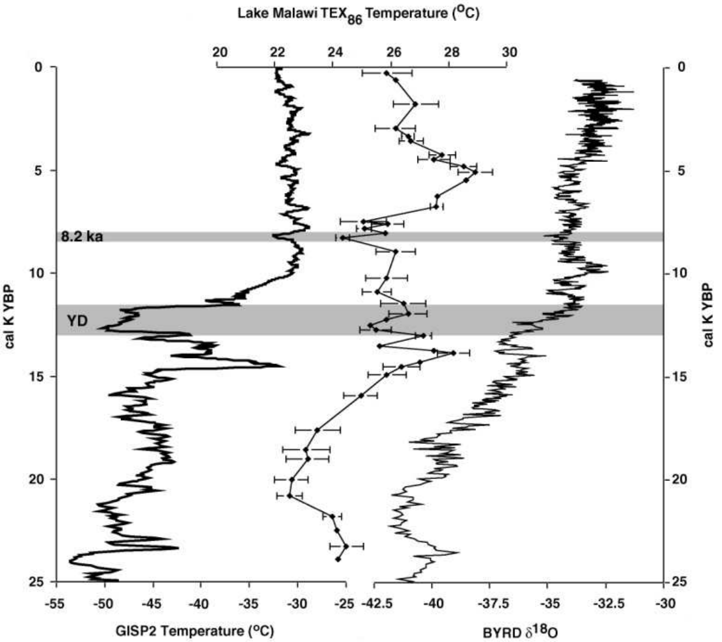


Fig. 2 Lake Malawi TEX_{86} temperature curve plotted with a reconstructed air temperature curve based on the GISP2 ice core and the Byrd oxygen isotope record (on the GISP2 timescale). Two major events are highlighted, the Younger Dryas (YD), and the cooling at 8.2 ka (Powers et al., 2005).

In a study on the occurrence of branched GDGTs in a set of globally distributed soils, Weijers et al. (2007a) revealed that the large variation in relative abundance of these compounds is correlated to variations in temperature and soil pH. Following this observation the methylation ratio/cyclization ratio of branched tetraethers (MBT/CBT) proxy for air temperature and soil pH was introduced (Fig. 1). The newly developed proxy was subsequently applied to reconstruct an integrated temperature and soil pH record over the last deglaciation (Weijers et al., 2007b) and one covering the Paleocene-Eocene Thermal Maximum (Weijers et al., 2007c). Owing to their abundant and ubiquitous presence in lake sediments (Powers et al., 2004), soil derived branched GDGTs potentially allow for an application of the MBT/CBT proxy also in lakes.

Despite, the large potential of GDGTs in lake sediments as climatic proxies very little is known about the ecology of the Archaea or Bacteria from which the GDGTs are derived, especially in lake systems. It is not known, for example, at what depth they thrive in the water column, whether they are "bloom type" organisms, when during the annual cycle they have their major production period, or even the most fundamental aspects of their metabolism (autotrophic vs. heterotrophic; chemo- vs. photoautotrophs).

The potential for the membrane lipids of Crenarchaeota as palaeotemperature proxy is based exclusively on core-top calibrations from a diverse series of marine environments (Schouten et al., 2002) and just a few lake sediments (Powers et al., 2004). The apparent success of the pilot studies of the application of TEX_{86} palaeothermometry to lacustrine environments raised, however, a series of questions. Does the isoprenoid GDGT distribution provide a realistic temperature estimate in a wide variety of lakes differing in area, climatic regimes or geographical location? Is the isoprenoid GDGT signal reflecting a physiological response of freshwater Crenarchaeota to changes in temperature or are there other environmental factors that might influence the response? In marine settings it is established that Crenarchaeota occur at all depths but how does the GDGT abundance vary with depth and when is the temperature signal produced during the seasonal cycle in lakes? As in other environments some GDGTs are produced by other archaeal or bacterial groups as well so how does this interfere with TEX_{86} palaeothermometry? Are branched GDGTs found in lake sediments good recorders of temperature and soil pH? What is their potential as recorders of climate change using the MBT/CBT proxy?

1.4. Objective and framework of this thesis

The objective of this thesis is to further develop and validate GDGT-based lacustrine proxies. By analyzing the distribution and abundance of GDGT membrane lipids in surface lake sediments, particulate organic matter in the water column and down core in lacustrine sedimentary records we determined the applicability of the TEX_{86} proxy to reconstruct temperatures. The potential of the MBT/CBT proxy was also tested using lake surface sediments.

In **Chapter 2** the distributions of GDGTs in particulate matter and the top 5 cm of the sediment from 47 lakes, along a latitudinal transect from southern Italy to the northern part of Scandinavia is addressed (Fig. 3). This study was conducted in order to trace the biological sources and potential palaeoenvironmental applications of GDGTs in lacustrine sediments. Archaea-derived isoprenoid and bacteria-derived branched GDGTs were detected in all lake sediments but substantial differences in their distribution were apparent. The results show that the applicability of TEX_{86} as a palaeothermometer in lakes could be hindered by in situ production of GDGTs by other Archaea (e.g. methanogenic Euryarchaeota) or the allochthonous input of soil-derived isoprenoid GDGTs. When compared with annual lake surface temperature, winter temperatures correlate better with TEX_{86}, indicating the probable season in which these organisms have their peak abundances.

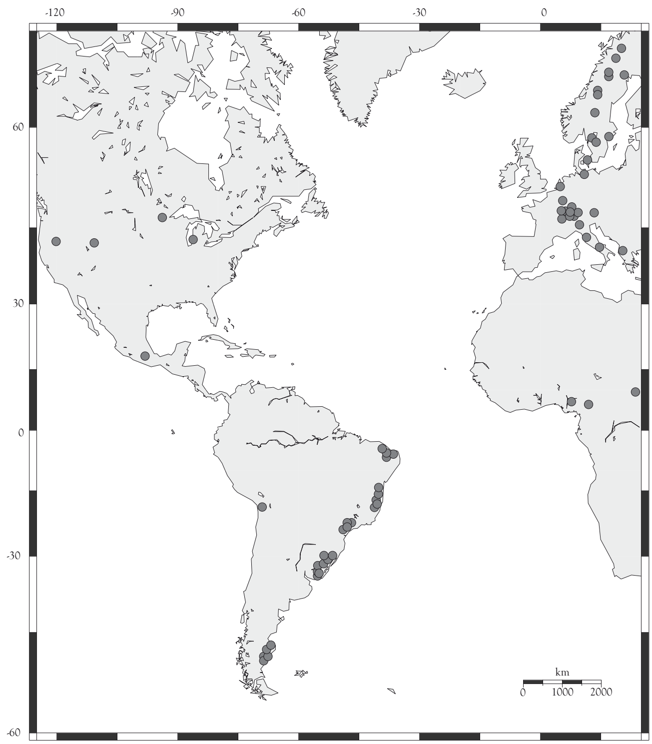


Fig. 3 Map with a general overview of different lake locations from where the sediment samples used in this thesis were obtained.

The potential of the MBT/CBT as a continental palaeothermometer in lacustrine environments was investigated in **Chapter 3**. Branched GDGTs were detected in high abundance also in lake sediments where their source is assumed to be largely soil-derived. The strong correlation between the branched GDGT compositions in soils and air temperature and soil pH served as the ground for the MBT/CBT proxy (Weijers et al., 2007a). Lacustrine sediments integrate organic remains of organisms living in the lake and its drainage basin thus offering a unique opportunity for calibrating MBT and CBT, as small scale variability is averaged out. Branched GDGTs dominated in most of the lake sediments as indicated by the high BIT values. The values for both MBT and CBT varied substantially among the lake sediments. The mean annual air temperatures (MAAT) reconstructed based on the branched GDGT distribution and using the existing global soil based calibration were considerably lower than the in situ measured values, while the pH values were similar to soil pH values of soils in the drainage basin. Since the source of the branched GDGTs in lake sediments remains unknown it is not clear yet whether only temperature and pH in the catchment area are the only factors driving the distribution of branched GDGTs in lake sediments.

Chapter 4 describes the seasonal dynamics of GDGTs in Lake Lucerne over a full annual cycle. Using material from different sources and different extraction methods shows that the concentrations and fluxes of isoprenoid GDGTs vary over the seasonal cycle with highest values shortly after the maximum lake surface productivity. Fluxes of GDGTs and concentrations in the water column vary according to a seasonal pattern, showing a similar trend in the SPM and sediment traps. Fluxes and concentrations of isoprenoid GDGTs increase with depth, maximum values being observed in the deeper part of the water column, indicating production of isoprenoid GDGTs by Group 1 Crenarchaeota in the deep (~50 m), aphotic zone of Lake Lucerne. A sediment core from the same location showed that in the first few centimeters of the core TEX_{86} and BIT values are similar to those recorded for descending particles and SPM, indicating that the sedimentary TEX_{86} records the annual mean temperature of deeper waters in Lake Lucerne. The offset in indices values between the upper and lower part of the core is apparently caused by the different trophic periods the lake has gone through, which most probably resulted in a change in crenarchaeotal community. Branched GDGTs represent only a minor fraction of the total GDGTs in the lake and it remains unclear if they also have an allochtonous origin.

The last chapter (**Chapter 5**) describes the application of the TEX_{86} temperature proxy in a sediment core recovered from Lake Lucerne from the same location as the seasonal study (**Chapter 4**). The obtained GDGT-based record provides, with an almost decadal resolution, an integrated temperature signal over the Younger Dryas and Early Holocene (ca. 14,600 to 10,600 cal. BP). The TEX_{86} proxy indicates a sequence of temperature shifts during the late glacial period that strongly resembles the shifts in $\delta^{18}O$ values from the Greenland ice core record (Rasmussen et al., 2005). The rapid changes in temperature associated with the last deglaciation are reflected in the highest possible detail in the TEX_{86} record. It is thus clear that lacustrine TEX_{86} records capture rapid, decadal to century scale, environmental change comparable with the Greenland ice cores.

Chapter 2

Tetraether membrane lipid distributions in water-column particulate matter and sediments: a study of 47 European lakes along a north-south transect

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We studied the distribution of glycerol dialkyl glycerol tetraethers (GDGTs) in particulate matter and the top 5 cm of sediment from 47 lakes along a transect from southern Italy to the northern part of Scandinavia. Our objective was to investigate the biological sources and potential palaeoenvironmental applications of GDGTs in lacustrine sediments. Both archaea-derived isoprenoid and bacteria-derived branched GDGTs, produced by yet unknown soil bacteria, were identified in all lake sediments. GDGT distributions varied substantially. Crenarchaeotal GDGTs, including the characteristic GDGT crenarchaeol, were found in varying relative concentrations, and were more dominant in lakes from the Alps and some of the lakes from the more southern part of the latitudinal transect. In some lakes, we observed high amounts of the GDGT with no cyclopentane moieties relative to crenarchaeol. As methanogenic Euryarchaeota are known to biosynthesise this GDGT predominantly, these Archaea, rather than Crenarchaeota, may be its dominant biological source. In most of the lakes, high amounts of soil-bacteria-derived, branched GDGTs (>40 % of total GDGTs) indicated a substantial contribution from soil erosion. Branched GDGTs dominated, especially in the northern lakes, possibly related to high soil erosion rates. In many of the lakes, soil input affects the distribution of isoprenoidal GDGTs and prevents the reliable application of the TEX_{86} temperature proxy for lake water temperature, which is based on in situ crenarchaeotal GDGTs production. In 9 out of the 47 lakes studied, the TEX_{86} temperature proxy could be used reliably. When we compared the TEX_{86} correlation with annual and winter lake surface temperature, respectively, the relationship between TEX_{86} and winter temperature was slightly stronger. This may indicate the season in which these GDGT-producing organisms have their peak production.

2.1. Introduction

Our knowledge of how climate varied in the past is based mostly on proxy indicators in environmental archives, such as the fossil remains found in marine and lacustrine sediments. Lake sediments are potentially detailed, accurate, and high-resolution recorders of continental climate, in part due to their rapid accumulation rates. Because of high biological productivity in inland water bodies and good preservation conditions, lake sediments typically contain more organic matter than marine sediments. The complex mixture of lipids, carbohydrates, proteins and other organic components (Meyers, 2003; Rullkötter, 2000) derived from organisms that lived in and near the lake holds information for reconstructing changes in both local and regional environments. However, to date, most organic geochemical methods used for environmental reconstruction were developed almost exclusively for the marine environment. In most cases, climate proxies established in the marine environment cannot be applied in lacustrine settings. For example, in contrast to marine sediments (Brassell et al., 1987; Schouten et al., 2003), organic geochemical proxies for reconstructing lake water temperature were, until recently, scarce (Liu et al., 2006; Hou et al., 2007). Recent investigations indicate that membrane lipids of Crenarchaeota, a sub-group of the Archaea, also hold promise as recorders of past lake surface temperature (Powers et al., 2004).

Archaea, one of the three domains of life, comprises three phyla: Crenarchaeota, Euryarchaeota and Korarchaeota. The first two occur ubiquitously in the environment. One characteristic by which Archaea can be distinguish from Bacteria and Eucarya is their core membrane lipid composition. This manifests predominantly in the isoprenoidal versus n-alkyl chain architecture, the sn-2,3 versus sn-1,2 stereochemistry of the glycerol moieties, and to a lesser degree, in the presence of ether instead of ester linkages (Koga et al., 1998a,b). In mesophilic environments such as marine and lacustrine water and sediments, an important group of Archaea that produce glycerol dialkyl glycerol tetraethers (GDGTs) are the non-thermophilic, pelagic Crenarchaeota, an abundant group of the marine and lacustrine picoplankton (Karner et al., 2001; Keough et al., 2003). The core membrane lipids, known to occur in the mesophilic Crenarchaeota, consist of GDGTs, which contain two glycerol head groups linked by two biphytanyl moieties with 0 to 3 cyclopentane moieties. The number of cyclopentane moieties in the GDGT structure is considered to be a key factor in the adaptation to temperature change. Crenarchaeol, the tetraether membrane lipid with one cyclohexane moiety and four cyclopentane moieties (Sinninghe Damsté et al., 2002) and its regio-isomer form, together with GDGT-0, are characteristic mesophilic crenarchaeal GDGTs. Crenarchaeol is considered to be a specific marker for “cold” Crenarchaeota because it has been found primarily in the membrane composition of non-thermophilic Crenarchaeota from aquatic environments (Schouten et al., 2008), although it has also been reported recently in a thermophilic nitrifier (de la Torre et al., 2008). Crenarchaeol was also found in terrestrial environments in relatively small amounts (Weijers et al., 2006a). GDGTs with 0-3 cyclopentane moieties have been shown to derive also from mesophilic Euryarchaeota capable of anaerobic oxidation of methane (Pancost et al., 2001; Aloisi et al., 2002).

The membrane lipid composition of marine Crenarchaeota is strongly correlated with sea surface temperature (Schouten et al., 2002; Kim et al., 2008). The strong control of sea surface temperature on crenarchaeotal lipid composition probably reflects a biological adaptation to the environment in which the microorganisms thrive. Based on this compositional difference related to temperature, the TEX_{86} (TetraEther indeX of tetraethers consisting of 86 carbon atoms) temperature proxy was developed and has been used to reconstruct seawater temperatures from different settings and time periods (e.g. Schouten et al., 2003; Sluijs et al., 2006; Huguet et al., 2006). The linear relationship between SST and TEX_{86} values in marine sediments is expressed by:

$$TEX_{86} = 0.015*SST + 0.28 \ (r^2 = 0.92, n = 41) \quad (1).$$

Powers et al. (2004) studied four large lakes from different climatic and geographic settings to test the applicability of the TEX_{86} proxy in freshwater environments and suggested that the TEX_{86} palaeothermometer can be used in lakes as well. In a follow-up study, this observation was extended to encompass 11 lakes (Powers, 2005); the linear relationship between the mean annual lake surface temperature (LST) and the TEX_{86} values was almost identical to the one from the marine environments:

$$TEX_{86} = 0.015*LST + 0.29 \ (r^2 = 0.92, n = 10) \quad (2).$$

The TEX_{86}-surface temperature relationship in marine and freshwater systems is in good agreement with mesocosm studies by Wuchter et al. (2004), who noted that salinity had no significant effect on TEX_{86}. In the study by Powers (2005) the TEX_{86} palaeotemperature proxy was tested for 48 globally-distributed lakes and it was noted that TEX_{86} can be applied successfully only in large lake systems, while in small-sized lakes its applicability is limited by several factors that affect the GDGT distribution. First, in aquatic systems, other Archaea, not necessarily limited to the water column (e.g. non-extremophilic Euryarchaeota like methanogens), can thrive and biosynthesize some GDGTs that are identical to the ones produced by the aquatic Crenarchaeota. This may affect the distribution of sedimentary GDGTs and thus potentially bias TEX_{86} values and the reconstructed temperatures (cf. Weijers et al., 2006b). Second, allochthonous input of archaeal membrane lipids may influence the GDGT distribution in lake sediments. To estimate the input of allochthonous terrestrial isoprenoid GDGTs, Weijers et al. (2006b) suggested using the Branched and Isoprenoid Tetraether index (BIT; Hopmans et al., 2004) before calculating temperatures by means of TEX_{86} analysis. This index is based on the relative abundance of crenarchaeol and the three main, branched GDGTs produced by anaerobic soil bacteria. Values of this index range from 0, implying no input of soil organic matter, to 1, indicating a dominant soil organic matter input. Although the branched GDGTs by themselves do not pose a problem for calculating TEX_{86} values, high concentrations of these components indicate a high likelihood that crenarchaeol and other isoprenoidal GDGTs are partly soil derived (Weijers et al., 2006b).

For a broader application of the TEX_{86} temperature proxy to lake sediments, greater insight is needed into the overall distribution of crenarchaeotal lipids and possible confounding of TEX_{86} values, and thus temperature reconstructions. The aim of the present study is to: i) investigate whether GDGTs in general are present along a north-south transect in European lakes, ii) establish the relative distribution of the GDGTs in relation to ambient temperatures, and iii) test for the different relative contribution of GDGTs produced by non-thermophilic Crenarchaeota, other archaea and anaerobic soil bacteria.

2.2. Methods

2.2.1. Study sites

Two field campaigns were carried out in January and July 2006, sampling 31 lakes along a south-north transect from Italy (Lago Grande di Monticchio 40°55'N, 15°36'E) to the northern part of Scandinavia (Torneträsk 68°21'N, 18°48'E) (Fig. 1). Water samples were taken from near the lake surface (ca. 1 m), at mid depth in the water column (which varied depending on the maximum depth of the lake), and at the lake bottom (to a maximum depth of 110 m). One to five litres of water were filtered through 0.7μm glass fibre filters until the capacity of the filter was reached. Lake sediments were collected using a gravity corer. In addition to this sample set, 16 sediment core tops, collected previously from lakes in the Swiss Alps and from Lake Ohrid (Albanian - Macedonian border), were analysed. The surface area, trophic conditions, convective turnover, surface water temperature, pH and other environmental variables of the lake water all vary greatly among lakes because of the large latitudinal gradient, the different soils, diverse vegetation communities, and different land uses in their catchments.

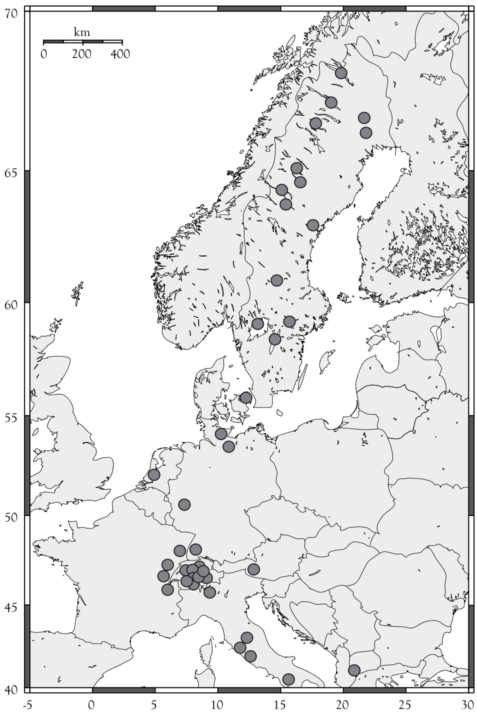


Fig. 1 Location of the 47 lakes studied. Some of the dots plotted in Switzerland represent more than one lake.

2.2.2. Extraction, fractionation and high performance liquid chromatography (HPLC)

Water filtrates and sediment core tops (5 cm) that were extruded in the field were stored at -20 °C. After freeze-drying and, if necessary, homogenization with a mortar and pestle, lipids were extracted from filters and from 1.5 to 2 g dry sediment. Filters were ultrasonically extracted with methanol, dichloromethane (DCM)/methanol (1:1, vol/vol) and DCM, each three times. Sediments were extracted using an Accelerated Solvent Extractor (DIONEX ASE

200). A mixture of DCM/methanol (9:1; vol/vol) was flushed through at a temperature of 120 °C and a pressure of $7.6*10^6$ Pa three times, with 5 min intervals between flushings. Extracts were condensed by rotary evaporation, and after drying over a Na_2SO_4 column using DCM as an eluent, they were separated by column chromatography for analyses. By using an activated Al_2O_3 column, the apolar and polar fractions were obtained with hexane:DCM 9:1 (vol/vol) and DCM:MeOH 1:1 (vol/vol), respectively, as an eluent. The polar fraction was dried under a nitrogen flow, dissolved in hexane:isopropanol 99:1 by sonication, and prior to injection, filtered through a 0.45 µm PTFE filter. GDGTs were measured (injection volume 10 µl) using HPLC/atmospheric pressure positive ion chemical ionization (APCI)/MS according to Schouten et al. (2007). To enable detection of low concentrations of GDGTs, a modification in the scanning procedure was made, as the single ion monitoring (SIM) mode was used to increase sensitivity and reproducibility (m/z 1302, 1300, 1298, 1296, 1292, 1050, 1036 and 1022 for the different GDGT isomers) (Schouten et al. 2007a). Samples used for TEX_{86} analyses were used also for BIT index analyses (Hopmans et al. 2004). After analyzing the mass chromatograms, peaks that were at least one order of magnitude greater than the background noise were integrated and used for TEX_{86} and BIT calculation. TEX_{86} values were determined according to the equation given by Schouten et al. (2002):

$$TEX_{86} = \text{GDGT-I+GDGT-III+GDGT-IV'}/\text{GDGT-I+GDGT-II+GDGT-III+GDGT-IV'} \quad (3),$$

where I – IV' refer to GDGT structures presented in Fig. 2.

BIT index values were calculated following the equation given by Hopmans et al. (2004) as follows:

$$BIT = \text{GDGT-V+GDGT-VI+GDGT-VII}/\text{GDGT-IV+GDGT-V+GDGT-VI+GDGT-VII} \quad (4).$$

2.3. Results

Figure 2 shows HPLC/MS base peak chromatograms revealing the distributions of GDGTs in the surface sediments of three lakes. The distribution of membrane lipids varies greatly among the studied lakes. Isoprenoid and branched GDGTs are found in most of the samples, but there is considerable variation in the distributions. Whereas some distributions are dominated by branched GDGTs, in others GDGT-0 is the major component, and still another group of sediments shows relatively high amounts of crenarchaeol and the other isoprenoid GDGTs produced by Crenarchaeota (Fig. 2). This is also clear from the ternary diagram (Fig. 3a) showing the relative abundance of the major GDGTs (i.e. GDGT-0, crenarchaeol, and the branched GDGTs). In the investigated lacustrine sediments, crenarchaeol is present in concentrations that vary between 0.2 - 49% of total GDGTs, 29% on average (Table 1). Overall, crenarchaeol (IV) is the dominant individual isoprenoid GDGT, however, in a substantial number of lake sediments crenarchaeol is present only in low amounts, whereas it is found in relatively high amounts (26 - 49% of total GDGTs) in only 13 of the 47 studied lake sediments (Table 1). In ten of the investigated lake sediments, some GDGTs were below the detection limit (Table 1). The regio-isomer of crenarchaeol (IV') was detected only in trace amounts in most lake sediments (0.02 - 0.9% of total GDGTs), with the exception of Lake St. Moritz, Laachersee, Grosser Plöner See, Maarseveenseplassen, Pfäffikersee, Arendsee and Lago Grande di Monticchio, in which GDGT IV' was below the detection limit. In the sediments of these lakes, crenarchaeol was also found in relatively small amounts. GDGT-0 was present in all sediments in substantial amounts (4 - 72% of total GDGTs, 28% on average). GDGT-I, -II and -III were detected, but in smaller amounts and in some lake sediments they are absent (Table 1). Finally, the branched GDGTs (V - VII), produced by an unknown group of anaerobic soil bacteria (Weijers et al., 2006a), dominate the GDGTs in the northern European lake sediments (Fig. 4) and in a few relatively small and shallow lakes from the south.

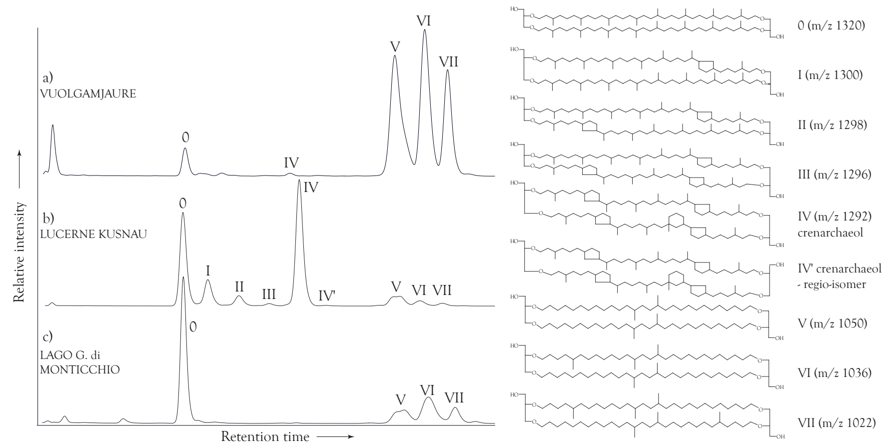
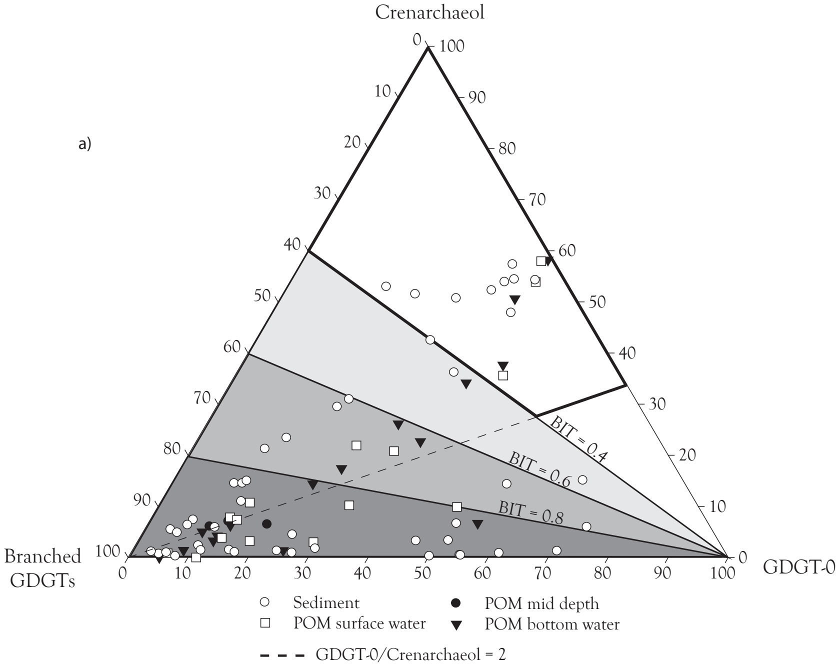


Fig. 2 HPLC/MS base peak chromatograms showing relative distribution of GDGTs in (a) Lake Vuolgamjaure (Sweden), (b) Lake Lucerne (Küssnachterbecken) (Switzerland), and (c) Lago Grande di Monticchio (Italy). Roman numbers refer to structures of GDGTs indicated in the right panel. The three base peak chromatograms provide examples of the three end-member GDGT distributions observed in this study: i.e. dominated by soil-derived GDGTs (a), dominated by aquatic crenarchaeotal GDGTs (b), and dominated by a GDGT presumed to derive from methanogens (c).

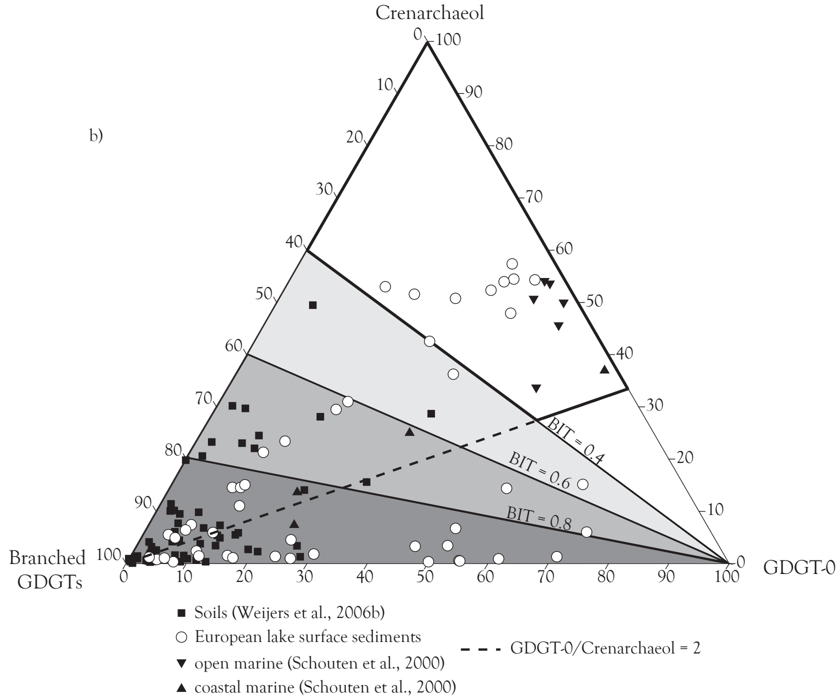
Particulate organic matter (POM) from the water column of 31 lakes was sampled by filtration of 1-5 litres of lake water. GDGTs were analysed in these samples, but the amount of material was sometimes not sufficient to obtain reliable distributions of GDGTs. In 24 lakes, however, it was possible to quantify all the major GDGTs (GDGT-0, crenarchaeol and the branched GDGTs) (Table 2). As in the sediments, a large variation in distributions of GDGTs was observed (Fig. 3a). GDGT distributions of POM in some lakes is dominated by crenarchaeol (Lago Maggiore, Lac du Bourget), in other lakes by GDGT-0 (Lac du Joux), but in most lakes by the branched GDGTs.

Fig. 3 (following page) (a) Ternary diagram showing the composition of the major GDGTs in the sediments and particulate organic matter from different depths from the 47 lakes of our North-South transect. (b) Ternary diagram showing the composition of the major GDGTs in the sediments from the European lakes in comparison with the composition of the major GDGTs in soils (data from Weijers et al., 2006b), open marine sediments and costal marine sediments as reported by Schouten et al., (2000). The increasing dark grey areas represent the increase in BIT values showing that the lake sediments with high BIT values have a GDGT composition similar to the one observed in soils. Also shown is the line corresponding to a GDGT-0 vs crenarchaeol ratio of 2 in order to indicate that in the lakes where this ratio is higher than 2, GDGT-0 originates from other Archaea than aquatic Crenarchaeota as well (i.e. predominantly methanogens, see text). Lakes plotting in the area of the ternary diagram defined by BIT<0.4 and GDGT-0/crenarchaeol <2 (indicated by a bold line) have a potential for TEX_{86} palaeothermometry. This plot indicates that only 9 of the 47 investigated European lakes fall in this area.

a)


Crenarchaeol
BIT = 0.4
BIT = 0.6
BIT = 0.8
Branched GDGTs
GDGT-0
Sediment
POM surface water
POM mid depth
POM bottom water
GDGT-0/Crenarchaeol = 2

b)


Crenarchaeol
BIT = 0.4
BIT = 0.6
BIT = 0.8
Branched GDGTs
GDGT-0
Soils (Weijers et al., 2006b)
European lake surface sediments
open marine (Schouten et al., 2000)
coastal marine (Schouten et al., 2000)
GDGT-0/Crenarchaeol = 2

2.4. Discussion

2.4.1. Potential biological sources for GDGTs

Surface (top 5 cm) sediments and POM from the water column of 47 lakes along a south-north transect in Europe show variable distributions of GDGTs. Since GDGTs are membrane lipids produced by both Archaea and Bacteria, sources of GDGTs in lake sediments can be diverse, as in marine environments, soils, peat bogs and hot water springs (e.g. Schouten et al., 2000; Weijers et al., 2004, 2006b; Pearson et al., 2004).

Crenarchaeol was found in all sediments analysed, with highest concentrations (up to 49% of total GDGTs) in the Alpine lakes, Lake Ohrid and Lago di Albano, and was also often detected in POM in highly variable relative amounts (0-58% of total GDGTs) (Fig. 4). Crenarchaeol is considered to be a specific biomarker for the mesophilic Crenarchaeota Group I (Sinninghe Damsté et al., 2002) and has been detected in marine and lacustrine environments (e.g. Schouten et al., 2000; Powers et al., 2004), in peat bogs (Weijers et al., 2004), and, in relatively low concentrations, in soils (Weijers et al., 2006b; Leiniger et al., 2006), confirming the widespread environmental occurrence of species falling in the Group I Crenarchaeota. Crenarchaeol was also reported in hot springs (Pearson et al., 2004; Zhang et al., 2006), suggesting that crenarchaeol can also originate from thermophilic archaea, as was recently confirmed using an enrichment culture (de la Torre et al., 2008). Schouten et al. (2007b) showed, however, that crenarchaeol in hot springs >50 °C most likely derives from erosion of soil. In any case, thermophilic Archaea are an unlikely source for crenarchaeol in the lakes studied. Mesophilic, Group I Crenarchaeota also produce small amounts of the regio-isomer of crenarchaeol (GDGT IV') (Sinninghe Damsté et al., 2002). GDGT-IV' was detected in almost all the sediments, but only in small amounts. In POM it was usually below the limit of detection. The crenarchaeol regio-isomer is known to be abundant in marine environments with temperatures higher than 25 °C (Wuchter et al., 2004). Considering that our lakes have annual mean water temperatures between 5 and 15 °C, the lack of substantial amounts of the regio-isomer is probably explained by these low temperatures.

GDGT-0 was found in all sediments studied, in relative abundances varying from 3 to 72% of total GDGTs. It was also detected in relatively high amounts in POM (up to 55% of total GDGTs) (Fig. 4). GDGT-0 is a rather common membrane lipid of Archaea. It has been reported to occur in both thermophilic Crenarchaeota and Euryarchaeota (Kates 1993), mesophilic Group I Crenarchaeota (Sinninghe Damsté et al., 2002), as well as in methanogens (Koga et al., 1993) and Euryarchaeota that mediate the anaerobic oxidation of methane (Pancost et al., 2001). In POM and sediments from lakes, methanogens and Group I Crenarchaeota are the most likely sources for GDGT-0. In Group I Crenarchaeota the GDGT-0/crenarchaeol ratio is temperature-dependent, but typically varies between 0.2 and 2 (Schouten et al., 2002). Thus we propose that if this ratio is >2, it indicates a substantial methanogenic origin for GDGT-0 (see below).

Isoprenoid GDGTs containing 1-3 cyclopentane moieties, together with GDGT-0 and crenarchaeol, are relatively abundant in the lakes from the southern part of the transect. GDGTs I-III have initially been described in cultures of hyperthermophilic Archaea (De Rosa and Gambacorta, 1988), but recent work has shown that GDGTs with cyclopentane moieties are present also in non-extreme environments (Schouten et al., 2000, 2002; Pancost et al., 2003 and references therein). In thermophiles, the biosynthesis of cyclopentane moieties is considered a temperature adaptation (Schouten et al., 2000). Group I Crenarchaeota also produce small amounts of these GDGTs (Sinninghe Damsté et al., 2002) and these

Table 1 Relative abundance (% of total) of GDGTs present in lake surface sediments, BIT-index, GDGT-0/GDGT-IV and TEX_{86} values. NA= Not applicable.

Lake	Latitude	Depth	Area	Relative abundance (%)								GDGT 0 /	
	(°N)	(m)	(km^2)	GDGT 0	GDGT I	GDGT II	GDGT III	GDGT IV	GDGT IV'	GDGTs V-VI	BIT	GDGT IV	TEX_{86}
Torneträsk	68.36	168	332	11.2	7	1.5	0.5	19.2	0.2	60.5	0.76	0.58	NA
Stora Lulevatten	67.13	28.5	155	4.3	1.9	0.8	0.2	5.2	0.1	87.4	0.94	0.82	NA
Hapsajaure	67.01	9.5	1.1	7.7	1	0.8	NQ[a]	0.2	NQ	90.4	1	38.3	NA[b]
Hornavan	66.18	228	283	10.3	1.3	0.3	0.1	14.2	0.1	73.7	0.84	0.73	NA
Vuolgamjaure	65.67	15	2	4.8	0.7	0.6	NQ	0.6	0	93.2	0.99	7.65	NA
Vojmsjon	64.94	145	70	20.5	2.7	0.7	1.1	29.4	0.2	45.4	0.61	0.7	NA
Malgomaj	64.77	148	101	7.1	1.2	0.5	0.3	7.1	0.1	83.6	0.92	1	NA
Mellan Rissjon	64.75	8.3	1.6	6.6	1.3	1	0.5	6.1	0.4	84.2	0.93	1.08	NA
Kallsjon	63.66	134	158	5.7	1.2	0.7	0.3	4.7	0.1	87.2	0.95	1.22	NA
Navarn	62.59	51.5	9.57	10.5	0.7	0.4	0.1	2.2	0	86.1	0.97	4.68	NA
Siljan	60.89	134	292	11.4	2.6	0.9	0.3	13.9	0.2	70.7	0.84	0.82	NA
Hjälmaren	59.15	22	483	5.9	0.8	0.3	0.1	0.9	0	92	0.99	6.68	NA
Vänern	58.96	106	5648	18.3	6.6	2.1	0.5	26.6	0.2	45.6	0.63	0.69	NA
Vättern	58.52	128	1893	13.4	7.1	1.7	0.5	21.1	0.2	56	0.73	0.64	NA
Furesø	55.8	37.7	7.39	26.3	1.5	0.6	NQ	0.8	0	70.7	0.99	31.8	NA
Grosser Plöner See	54.16	58	29.97	54.3	1	0.4	NQ	0.4	NQ	43.8	0.99	133	NA
Arendsee	52.89	48.7	5.2	49.3	1.2	0.6	NQ	0.2	NQ	48.7	1	252	NA
Maarseveense Plassen	52.14	30.8	0.7	15.8	0.9	0.9	0.5	1.4	NQ	80.5	0.98	11.5	NA
Laacher See	50.41	52	3.31	17.1	1.4	NQ	NQ	1	NQ	80.6	0.99	17.9	NA
Gerardmer	48.07	38.4	1.16	3.4	0.6	NQ	NQ	1.1	0	94.9	0.99	3.13	NA
Lac de Blanchemer	48.01	15		11.2	1.3	1.5	0.4	5.6	0.1	79.8	0.93	1.99	NA
Titisee	47.89	39.2	1.08	11.4	0.6	0.5	0.3	1.3	0	86	0.99	8.75	NA
Mondsee	47.82	68.3	14.2	45.8	0.7	0.4	0.2	3.1	0.1	49.7	0.94	14.7	NA
Pfäffikersee	47.35	36	3.3	70	0.9	0.3	0.1	1.2	NQ	27.5	0.96	60.1	NA
Tuerlersee	47.27	22	0.5	54	2	0.5	0.8	13.8	0.3	28.6	0.68	3.93	NA
Greifensee	47.21	32	160	71.6	1.1	1.1	0.3	5.7	0.2	20.1	0.78	12.5	NA
Baldeggersee	47.2	66	5.2	64.6	2.2	2.4	0.7	14.2	0.3	15.8	0.53	4.55	NA
Sempachersee	47.16	87	14.4	50.4	1.3	0.4	0.2	6.4	0.1	41	0.86	7.82	NA
Zugersee	47.14	198	38.2	35.4	7.9	3	0.6	42.3	0.2	10.7	0.2	0.84	0.32
Lucerne (Gersauerbecken)	46.99	214	113.6	30.2	9.8	4.2	0.7	48.7	0.2	6.1	0.11	0.83	0.34
Lucerne (Küssnachterbecken)	46.99	214	113.6	31.8	9.5	4	0.9	46.4	0.3	7.2	0.13	0.66	0.35
Lucerne (Horwerbecken)	46.99	214	113.6	29.2	8.9	5	1.1	44.2	0.3	11.2	0.2	0.69	0.42
Lucerne (Urisee)	46.99	214	113.6	11.5	3.7	2.4	0.7	13.9	0.2	67.6	0.83	0.62	NA
Hagelsee	46.67	18.5	0.03	27.5	6.8	3	0.5	30.7	0.2	31.3	0.51	0.43	NA
Lac du Joux	46.63	33	9	30.1	0.8	0.1	0.1	1.7	0	67.2	0.98	18.1	NA
Morat	46.56	45	22.8	61.2	0.5	NQ	NQ	0.8	0	37.5	0.98	80.3	NA
St. Moritz	46.49	44	0.078	23	1	8.1	NQ	4	NQ	64	0.94	5.74	NA
Hinterburgsee	46.43	11	1.62	50.7	0.9	0.9	0.2	3.2	0.1	43.9	0.93	15.8	NA
Silsersee	46.42	71	4.1	11.9	5.7	12.2	2.7	45.5	0.9	21	0.32	0.32	0.73
Lago di Poschiavo	46.28	85	1.98	32.4	8.1	2	0.6	32.2	0.2	24.6	0.43	1.01	NA
Lago Maggiore	45.9	370	212.5	25.7	8.2	3.2	0.6	37.2	0.2	24.8	0.4	0.69	0.33
Lac du Bourget	45.74	145	42	34.2	10.3	3.4	2.1	45.5	0.3	4.2	0.08	0.75	0.36
Lago Trasimeno	43.12	5.5	124.3	12.9	1.7	1.9	0.4	10.5	0.2	72.4	0.87	1.23	NA
Lago di Vico	42.31	48.5	12.1	23.6	1.6	0.8	0.1	1.2	0	72.7	0.98	19.6	NA
Lago di Albano	41.75	175.1	6	31.1	8.7	3.9	0.5	46.6	0.3	9	0.16	0.67	0.35
Lake Ohrid	41.03	286.7	358	24.8	9.6	5.2	0.6	42.7	0.2	16.9	0.28	0.58	0.38
Lago G. di Monticchio	40.93	36	0.405	54.3	1.4	0.3	NQ	0.3	NQ	43.5	0.99	157	NA

[a] NQ = not quantified, concentration too low, [b] NA = not applicable, GDGT composition not appropriate for calculation of TEX_{86} (see text)

components are used in fine-tuning the physical properties of their membrane as an adaptation to temperature (Schouten et al., 2002). Weijers et al. (2006b) found small amounts of GDGTs I-III in soils in a distribution not corresponding to the distribution pattern observed in Group I Crenarchaeota (i.e. dominated by GDGT-0 or crenarchaeol), suggesting an alternative mesophilic crenarchaeal and/or euryarchaeal, potentially methanogenic, source of these components, although they have not yet been reported in mesophilic methanogens (see Table 1 in Schouten et al., 2007b). Certain groups of Archaea involved in the anaerobic oxidation

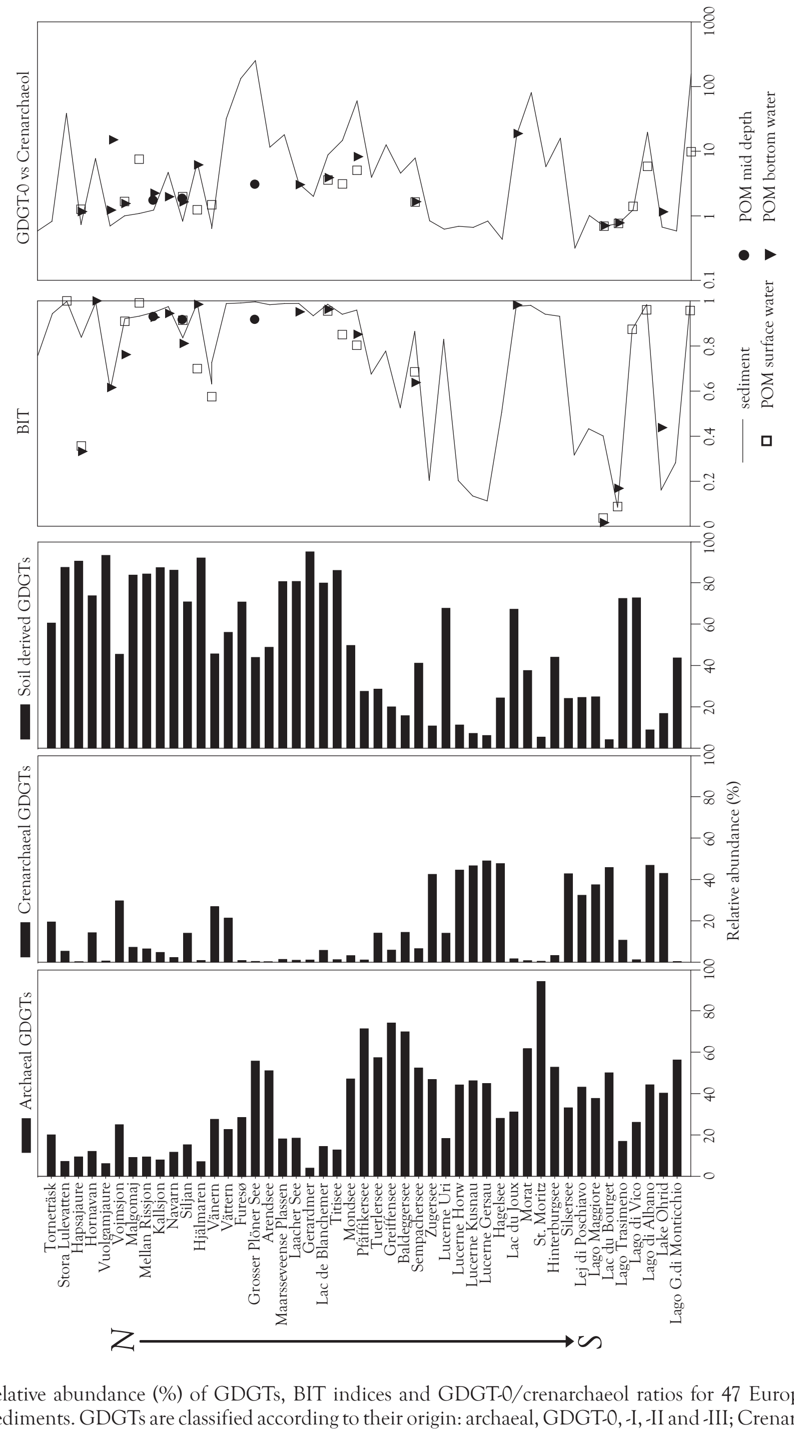


Fig. 4 Relative abundance (%) of GDGTs, BIT indices and GDGT-0/crenarchaeol ratios for 47 European lake surface sediments. GDGTs are classified according to their origin: archaeal, GDGT-0, -I, -II and -III; Crenarchaeotal, GDGTs IV and IV'; soil derived, GDGT V, VI, VII. BIT index and GDGT-0 vs crenarchaeol ratios from the particulate matter from the corresponding lakes are also shown. Note that the GDGT-0/crenarchaeol ratios are plotted on a logarithmic scale.

Table 2 Relative abundance (% of total) of GDGTs present in lake particulate matter, BIT and GDGT-0/ Crenarchaeol. Note that for these analyses only GDGT-0, crenarchaeol and the branched GDGTs could be quantified and therefore, these data are not directly comparable with those in Table 1. For a number of lakes, the amounts of GDGTs in particulate matter were below the level of quantification.

Lake	Latitude	Depth	Relative abundance (%)			BIT	GDGT-0/
	(°N)	of POM[a]	GDGT 0	crenarchaeol	Branched GDGTs		Crenarchaeol
Hapsajaure	67.01	s	11	0	89	1.00	NA[b]
Hornavan	66.18	s	45	36	20	0.36	1.3
		b	44	38	19	0.33	1.2
Vuolgamjaure	65.67	b	5	0	95	1.00	NA
Vojmsjon	64.94	b	32	26	42	0.62	1.2
Malgomaj	64.77	s	13	8	79	0.91	1.7
		b	27	17	56	0.76	1.5
Mellan Rissjon	64.75	s	6	1	93	0.99	7.5
Kallsjon	63.66	m	11	6	83	0.93	1.8
		b	14	6	80	0.93	2.2
Navarn	62.59	b	10	5	85	0.94	2.0
Siljan	60.89	s	14	7	78	0.91	2.0
		m	13	7	80	0.92	1.9
		b	24	14	62	0.81	1.6
Hjälmaren	59.15	s	27	22	51	0.70	1.2
		b	9	1	90	0.98	6.1
Vänern	58.96	s	39	26	35	0.58	1.5
Arendsee	52.89	m	20	6	74	0.92	3.1
Gerardmer	48.07	b	13	4	83	0.95	3.0
Titisee	47.89	s	14	4	82	0.96	3.6
		b	13	3	84	0.96	3.9
Mondsee	47.82	s	32	10	58	0.85	3.1
Pfäffikersee	47.35	s	50	10	40	0.80	5.0
		b	55	7	38	0.85	8.2
Sempachersee	47.16	s	34	21	45	0.69	1.6
		b	37	23	40	0.64	1.6
Lac du Joux	46.63	b	25	1	73	0.98	18.7
Lago Maggiore	45.9	s	40	58	2	0.04	0.7
		b	41	58	1	0.02	0.7
Lac du Bourget	45.74	s	41	54	5	0.09	0.8
		b	39	51	10	0.17	0.8
Lago Trasimeno	43.12	s	15	11	74	0.87	1.4
Lago di Vico	42.31	s	19	3	78	0.96	5.8
Lago di Albano	41.75	b	39	34	27	0.44	1.1
Lago G. di Monticchio	40.93	s	29	3	68	0.96	9.8
Hapsajaure	67.01	s	11	0	89	1.00	NA
Hornavan	66.18	s	45	36	20	0.36	1.3
		b	44	38	19	0.33	1.2
Vuolgamjaure	65.67	b	5	0	95	1.00	NA
Vojmsjon	64.94	b	32	26	42	0.62	1.2
Malgomaj	64.77	s	13	8	79	0.91	1.7
		b	27	17	56	0.76	1.5
Mellan Rissjon	64.75	s	6	1	93	0.99	7.5
Kallsjon	63.66	m	11	6	83	0.93	1.8
		b	14	6	80	0.93	2.2
Navarn	62.59	b	10	5	85	0.94	2.0
Siljan	60.89	s	14	7	78	0.91	2.0
		m	13	7	80	0.92	1.9
		b	24	14	62	0.81	1.6

[a]s = surface water, m = mid depth, b = bottom water. [b]NA= not applicable.

of methane in marine sediments produce GDGTs with 1-3 cyclopentane moieties as major membrane lipids (Pancost et al., 2001; Blumenberg et al., 2004).

The branched GDGTs V-VII were found in all sediment samples and appear to be the most important GDGTs in the POM and sediments of lakes from the northern part of the studied transect (Fig. 4). These GDGTs were discovered in a Dutch peat (Sinninghe Damsté et al., 2000) and were subsequently detected in coastal sediments, but not in open marine sediments (Schouten et al., 2000; Hopmans et al., 2004). An extended analysis of soils revealed that branched GDGTs occur ubiquitously in soils and are the most important GDGTs (Weijers et al., 2006b). Taken together, this implies that the branched GDGTs are soil-derived and are transported into the aquatic environments predominantly through erosion of soils. The stereochemistry of the glycerol moieties of the branched GDGTs was found to be the bacterial 1,2-di-O-alkyl-sn-glycerol stereoconfiguration and not the 2,3-di-O-alkyl-sn-glycerol stereoconfiguration as in archaeal membrane lipids (Weijers et al., 2006a). This demonstrated the bacterial origin of these GDGTs. However, the mesophilic anaerobic bacteria that are thought to produce these membrane lipids are as yet unknown.

2.4.2. Influence of methanogenesis on GDGT distributions

Approximately half of the lakes investigated in our study are meso- to eutrophic. Because of the relatively high primary productivity in the lakes, there is a substantial organic matter flux to the sediments, which rapidly become anoxic. The dominant anaerobic mineralisation process in lake sediments is methanogenesis. In some of the lakes, even part of the water column is anoxic, so methanogenesis can also occur in the water column. Consequently, methanogenic Archaea may be an important source of GDGTs in POM and sediments of lakes.

The ratio between GDGT-0 and crenarchaeol can be used to investigate whether methanogenic Archaea are a major source of GDGTs in these sediments. The rationale behind this ratio is that crenarchaeol as well as GDGT-0 can be derived from Group I Crenarchaeota, whereas methanogens synthesize GDGT-0, but no crenarchaeol. Using compound - specific carbon isotope analyses of biphytanes released from GDGTs, Schouten et al. (1998) have shown that in sediments where GDGT-0 was much more abundant than crenarchaeol, there was a significant offset in the stable carbon isotopic compositions of the acyclic and tricyclic biphytane. This suggested an additional, probably methanogenic source of the acyclic GDGT. The lakes that cluster in the right hand corner of the ternary diagram (Fig. 3a) are characterized by high relative concentrations of GDGT-0, which is indicative of methanogenic activity in the lake. In this ternary diagram, the line for GDGT-0/crenarchaeol ratio = 2 is plotted: all samples that fall below this line probably have a source for GDGT-0 other than Group I Crenarchaeota. A substantial fraction (47%) of both sediment and POM samples fall in this area. However, within this group there is substantial variation: for the sediments, the GDGT-0/crenarchaeol ratio can be as high as 250, whereas for POM the highest value is 19. In nine of the lakes (Lago Grande di Monticchio, Lago di Vico, Pfäffikersee, Sempachersee, Mondsee, Titisee, Arendsee, Hjälmaren, and Navarn) the GDGT-0 versus crenarchaeol ratio for both water column and sediment shows significant differences (Fig. 4), with higher values of the ratio in the sediment, indicating that GDGT-0 is predominantly derived from methanogens in the sediment. For the other lakes, the values for the ratio are identical. These results strongly suggest that methanogenic Archaea can be an important source of GDGTs in lake settings. However, the fact that in some POM samples from the aerobic part of the water column GDGT-0/crenarchaeol ratios were also >2 indicates that in some settings other Archaea than methanogens and Group I Crenarchaeota also produce GDGT-0.

The GDGT-0/crenarchaeol ratio of the sediment from Sempachersee (i.e. 7.8) was substantially higher than that of POM (i.e. 1.6). To investigate the potential contribution of in situ GDGT production by sedimentary methanogenic Archaea, one-centimetre slices of the first 5 cm from the core top sediment were analysed. A change in the GDGT-0/crenarchaeol ratio was observed, with values increasing from 3.8 in the first centimetre to 14.3 at 4-5 cm depth (Fig. 5). This strongly suggests in situ production of GDGT-0 in the sediments from Sempachersee because of ongoing methanogenic activity, altering the GDGT distribution of the lake sediments.

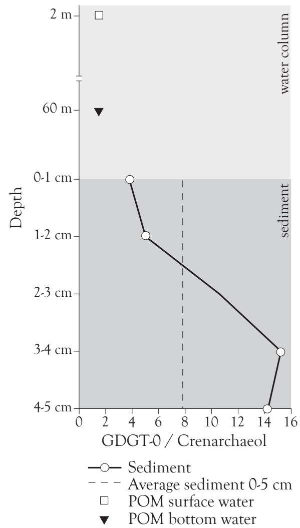


Fig. 5 Ratio between GDGT-0 and crenarchaeol, versus depth in the water column and in the top 5 cm sediment from Sempachersee (Switzerland). The stippled line indicates the value of the BIT index for the 0-5 cm surface sample and reflects the average of the five 1 cm slices.

2.4.3. Influence of soil organic matter input

In soil, the GDGT composition is dominated by branched, glycerol dialkyl glycerol tetraether membrane lipids (Fig. 3b; Weijers et al., 2006a), which are most likely produced by anaerobic bacteria involved in organic matter mineralization (Weijers et al., 2006b). In many of the lake sediments, the GDGT distribution is similarly dominated by branched GDGTs (Fig. 3b). In marine settings, branched GDGTs are thought to be brought in by rivers through erosion of soils (Hopmans et al., 2004; Herfort et al., 2006; Kim et al., 2006). In this way, the BIT index is considered to represent the input of terrestrial (i.e. soil) organic matter. Weijers et al. (2006b) measured, in pure soil samples, values for the BIT index mainly between 0.8 and 1 (Fig. 3b). A similar approach can be used for lake settings, although we lack hard evidence that branched GDGTs are not produced in situ in lake waters or sediments. For the set of lakes studied here, BIT index values ranged between 0.08 (Lac du Bourget) and 1.00 (Arendsee) (Table 1; Fig. 4) for the sediment and between 0.02 (Lago Maggiore) and 1.00 for two lakes at high latitude

(Hapsajaure, Vuolgamjaure) for POM (Table 2; Fig. 4). Out of the 47 lake sediments and 35 POM samples, 38 and 29, respectively, had BIT values higher than 0.4 (Fig. 3a), a value indicative of a substantial input of terrestrial GDGTs. Significant differences between POM and sediments could be observed in the case of Lago Maggiore, where the values measured in the sediment are higher than the ones from the water column. On the other hand, in Lago Albano the BIT values in the sediment are lower than the ones from the water column. These differences could be explained by the fact that the composition of POM represents only a snapshot of the conditions present in the lakes during the year. The contribution of soil organic matter to the lake, and thus the input of branched GDGTs, may vary through the year, whereas we do not know anything about variations in the seasonal abundance of Group I Crenarchaeota in lakes. In the North Sea there is a strong seasonal cycle in their abundance, with high densities in winter and undetectable levels in summer (Wuchter et al., 2006).

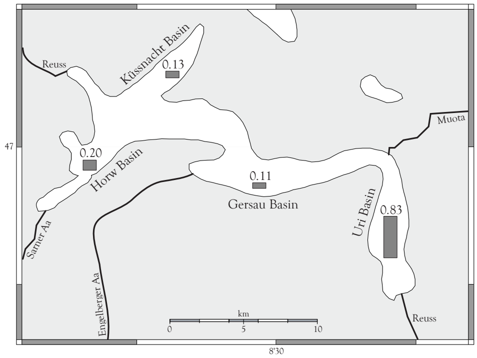


Fig. 6 Map of Lake Lucerne showing the four different basins and the corresponding BIT values measured in the surface sediments.

Sediment cores from four different basins in Lake Lucerne were analysed (Fig. 6). Sediments from the Uri basin are dominated by branched GDGTs, as the BIT index has a value of 0.83, while in the other three basins the index values are 0.1 – 0.2 (Fig. 4, 5). A major tributary, the river Reuss, enters Lake Lucerne through the Uri basin thus contributing to the soil organic matter input which is reflected by the GDGT distribution. The Uri basin is situated in a rectilinear valley exposed to frequent storms that lead to efficient turnovers of the lake (Bührer and Ambühl, 2001). This could potentially result in enhanced resuspension of organic matter. However, based on the low BIT index of the other connected sub-basins of Lake Lucerne, this organic matter is apparently not effectively transported further. The decrease in the relative contribution of branched GDGTs to the total GDGTs along the four basins shows that the branched GDGTs are likely not produced in situ in the lake, but rather, originate from soil erosion and are brought into the lake by river inflow.

On the European north-south lake transect (Fig. 4), we observe that the GDGT composition of the northern lake sediments and, to a lesser extent, POM, is dominated by branched GDGTs. This contrast between the northern and southern lakes is likely due to differences in soil erosion in the catchments, soil and bedrock types, precipitation characteristics, the abundance of vegetation hydrology, topography, etc. It may also be related to the in situ aquatic production of archaeal GDGTs in the lakes; most northern lakes are oligotrophic, whereas southern lakes are meso- to eutrophic. Since mesophilic Crenarchaeota in lakes are probably nitrifiers, as in the marine environment (e.g. Wuchter et al., 2006), their production rate is likely dependent on the availability of ammonium, which is primarily derived from decay of organic matter produced by primary producers. At lower in situ production rates of Crenarchaeota, and thus of crenarchaeol, input of soil-derived branched GDGTs may become dominant, which is reflected by high BIT indices.

2.4.4. Group I Crenarchaeota and TEX_{86} palaeothermometry

The abundance of crenarchaeol in some of the lake sediments and POM samples confirms that Group I Crenarchaeota occur not only in marine environments, but also in lakes (cf. Powers et al., 2004; Powers, 2005). Crenarchaeol is detected in almost all lake sediments and POM samples (Tables 1 and 2). However, crenarchaeol has also been reported to occur in soils, albeit in small relative amounts (Leininger et al., 2006; Weijers et al., 2006b), and the GDGT distribution of the lakes studied indicates that many of them have a GDGT distribution comparable to the one of soils (Fig. 3b). In these cases, the presence of crenarchaeol should not be taken as an indication of an active population of Group I Crenarchaeota in the lake.

An interesting application in palaeolimnology is the use of the distribution of fossil GDGTs of Group I Crenarchaeota in the reconstruction of past lake temperature (Powers et al., 2004; Powers, 2005). The TEX_{86} palaeothermometer is based on the distribution of GDGTs present in relatively low abundance (GDGT I-III and IV') (Schouten et al., 2002). As a consequence, TEX_{86} palaeothermometry can only be performed if the source of sedimentary GDGTs is Group I Crenarchaeota. In lake settings, two other known major sources of archaeal GDGTs may impact the TEX_{86}-based palaeotemperature reconstructions: i) methanogenic Archaea, and ii) Archaea from soils. GDGT-0 is produced by methanogenic Archaea (Koga et al., 1998) and analysis of environmental samples has led to the belief that they may also produce some of the cyclised derivatives (though in much smaller amounts) (Weijers et al., 2006b; Pancost and Sinninghe Damsté, 2003), although this is not confirmed by culture studies (see Table 1 in Schouten et al., 2007b). As explained earlier, if the GDGT-0/crenarchaeol ratio is >2, a non-Group I crenarchaeotal origin is evident for GDGT-0, and we reckon that in that case GDGTs with cyclopentane moieties may also be derived, in part, from methanogenic Archaea. Therefore, in such a case, we feel it is not appropriate to calculate TEX_{86} values and infer past lake temperatures.

Table 3 Morphometric and hydrologic characteristics of lakes with abundant aquatic GDGTs and low BIT values.

	Catchment area (km^2)	Area (km^2)	Depth (m)	Trophic state	Turnover	ALST (°C)	WLST (°C)	pH-water	References
Lac du Bourget	560	42	145	mesotrophic	meromictic[1] monomictic[2]	15.5	6.22	8.3	Jacquet et al. (2005) Paolini (unpublished data)
Lake Lucerne (Küssnachter-, Gersauer-, Horwerbecken)	2124	113.6	214	oligotrophic	meromictic[1] monomictic[2]	11.5	5.3	8.6	Bührer and Ambühl (2001)
Lago di Albano	4	6	175	mesotrophic	meromictic	17.7	14	8.3	Cioni et al. (2003) Messineo et al. (2006)
Zugersee	204	39	198	eutrophic	meromictic[1], monomictic[2]	6.9	5.7	8.0	DBGZ Switzerland
Lake Ohrid	2600	358	288	oligotrophic	oligomictic	15.7	6.3	8.3	Ocevski and Allen (1977)
Silsersee	46	4	71	oligotrophic	dimictic	2	0		Blass et al. (2005)
Lago Maggiore	6600	213	370	oligotrophic	monomictic[2]	13.2	7.2	8.4	Morabito et al. (2002)

[1] Lake not thermally stratified during circulation period, may mix completely in some years
[2] Lake may show an inverse stratification during extremely cold years

Branched GDGTs, produced by anaerobic bacteria, are derived and transported in the lakes through soil erosion. Soils also contain small amounts of isoprenoidal GDGTs, including the ones used for TEX_{86} palaeothermometry (Weijers et al. 2006b). Therefore, the BIT index should not be >0.4 (cf. Weijers et al., 2006b) when TEX_{86} will be used for palaeotemperature reconstructions. These constraints define an area in the ternary diagram (Figs. 3a, b) in which lake sediment values should fall if TEX_{86} is to be applied. Of the 47 lakes studied, only Zugersee, Lake Lucerne (Horwerbecken), Lake Lucerne (Küssnachterbecken), Lake Lucerne (Gersauerbecken), Silsersee, Lago Maggiore, Lac du Bourget, Lago di Albano and Lake Ohrid had the full complement of GDGTs necessary for calculating $TEX_{86,}$ BIT values <0.4, and GDGT-0/crenarchaeol ratios <2 (Fig. 3b, Table 3).

When the TEX_{86} values (Table 1) from these 9 lakes are plotted against annual lake surface temperature, together with data from the study of large lakes by Powers (2005), eight of nine data points follow the general trend (Fig. 7a), although the European lakes studied here cover only a relatively small temperature range. In the case of Silsersee, the TEX_{86} value translates into an unrealistic lake surface temperature of 29.5 °C, whereas the true mean annual temperature is 2 °C. In comparison with the other lake sediments, Silsersee had relatively low GDGTs concentrations. Even though the GDGT concentrations were sufficient to be taken into account in the present analysis, it is unclear why this lake represents an outlier. It may be related to an additional, but unknown source of GDGTs. Nevertheless, for calibration purposes we eliminated this data point.

Linear regression of the TEX_{86} with the mean annual lake surface temperature for the eight lakes, together with the previously published data set of large lakes, gave the following equation:

$$TEX_{86} = 0.018*ALST + 0.19 \ (r^2 = 0.76, n=18) \qquad (5).$$

TEX_{86} values were also plotted against mean winter lake surface temperatures, in which case the correlation coefficient was slightly higher:

$$TEX_{86} = 0.017*WLST + 0.27 \ (r^2 = 0.84, n=18) \qquad (6).$$

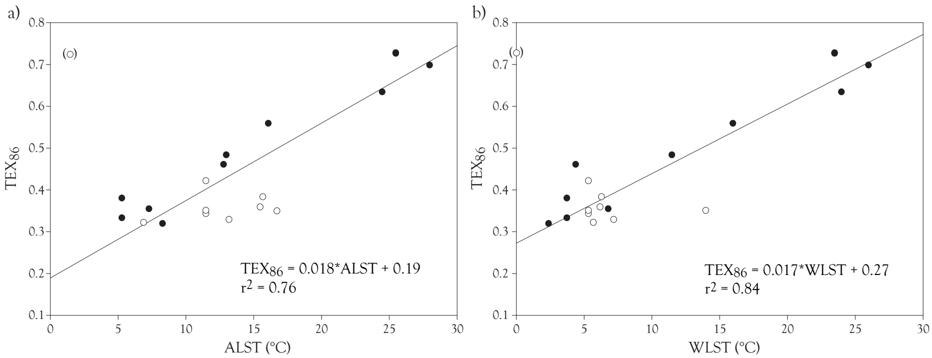


Fig. 7 Linear regression and correlation of TEX_{86} with: (a) annual mean lake surface temperature and (b) winter mean lake surface temperature. White dots represent lakes from the European north-south transect from this study; black dots represent large lakes sampled by Powers (2005). The data point for Silsersee is between brackets as it was not included in correlation calculations.

The relationship between TEX_{86} and winter mean temperature appears to be stronger, suggesting that Crenarchaeota bloom in winter or during the early spring months. Indeed, we found in some of the southern lakes that were sampled in winter that the BIT index of POM was substantially lower than that of the surface sediment, implying a higher winter flux of crenarchaeotal GDGTs compared with terrestrial GDGTs. This is in agreement with observations made in the high-latitude lakes by Powers (2005), as well as with time series from the North Sea (Wuchter et al., 2005, 2006).

These results, together with the ones from previous empirical studies, suggest that in some of the lakes GDGTs are being synthesized by mesophilic Crenarchaeota in amounts that allow TEX_{86} temperature reconstructions. Although GDGTs are present also in smaller lakes, the influence of the factors described above limits the application of TEX_{86} palaeothermometry in these lakes. The large scatter in the lake TEX_{86} calibration calls for a detailed investigation of Crenarchaeota ecology in lakes, this to better understand, for instance, how seasonal changes and water depth influence the relative abundance of the GDGTs in lake systems.

2.5. Conclusions

Our study shows that GDGTs derived from Group I Crenarchaeota are ubiquitous in lakes of all sizes in northern, central and southern Europe, based on the analysis of a wide variety of core-top sediments and water-column POM samples. Production of GDGTs by methanogens in the water column or in the sediments potentially hinders TEX_{86}-based temperature reconstructions. Furthermore, we suggest that the BIT index, as a measure for the input of soil-derived GDGTs, is a reliable tool for assessing which lake sediments are suitable for application of the TEX_{86} palaeothermometer. It also seems that not only large lakes (Powers et al. 2004) are suitable for TEX_{86} palaeothermometry, but that this palaeotemperature proxy can be applied to reconstruct past climate changes in some intermediate-sized lakes. In some lakes, the ecology and abundance of freshwater Crenarchaeota or other environmental factors might contribute to an offset of TEX_{86} values from the general temperature calibration equation.

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Chapter 3

Branched glycerol dialkyl glycerol tetraethers in lake sediments: Can they be used as temperature and pH proxies?

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submitted to *Organic Geochemistry*

A series of surface sediments from 82 lakes, of variable water depths and sizes, was analyzed for glycerol dialkyl glycerol tetraethers (GDGTs) in order to investigate the potential of the MBT/CBT (methylation ratio/ cyclization ratio of branched tetraethers) as a continental palaeothermometer in lacustrine environments. Branched GDGTs dominate in most sediments as indicated by the high BIT values. We observed that the CBT and MBT varied substantially among the lake sediments. Mean annual air temperatures (MAAT reconstructed) and pH values were calculated using the CBT and MBT values and the calibration from the global soil data set [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]. The MBT/CBT inferred temperatures were considerably lower than measured values. Nevertheless, there is a significant correlation between MAAT reconstructed and MAAT measured on site although there is still considerable scatter (r^2 = 0.47). Lacustrine sediments integrate organic remains of organisms living in the lake and its drainage basin thus offering a unique opportunity for calibrating MBT and CBT, as small-scale variability is averaged out. However, it is not clear yet whether only temperature and pH in the catchment area are the driving factors, since the source of the branched GDGTs in lake sediments remains unknown.

3.1. Introduction

Understanding past environmental change is crucial for improving our capability to predict future responses to expected climatic change. For understanding natural climate variability, a key issue is the improvement of high-resolution climate reconstructions using reliable, accurate and well calibrated proxies, from both marine and terrestrial realms. Various geochemical proxies based on inorganic and organic fossil remains have been applied in attempts to reconstruct continental and sea surface temperatures. The $\delta^{18}O$ (Erez and Luz, 1983) and Mg/Ca ratios of foraminifera (Elderfield and Ganssen, 2000) are commonly used as inorganic sea water temperature proxies. Marine temperature reconstructions from organic fossil remains are generally based on the alkenone unsaturation index U_{37}^{k} proposed by Brassell et al. (1986), but more recently also based on the TEX_{86} proxy (Schouten et al., 2002). For the terrestrial environment few quantitative temperature proxies exist. For example palaeoclimatic reconstructions from palaeosoils using fossil plant assemblages (Utescher and Mosbrugger, 2007) yield snap shots of past environments and are relatively scarce throughout the fossil record. Lake sediments on the other hand represent good and continuous archives of temporal and spatial variations in climate on the continent. Several proxies have been developed to reconstruct continental climate based on lake sediments, using either the preserved fossil parts of organisms, such as pollen (e.g. Seppä and Hammarlund, 2000; Finsinger et al., 2007), diatoms (e.g. Radle et al., 1989; Fritz et al., 1991), ostracodes (e.g. Forester, 1987; Smith, 1993) and chironomids (e.g. Heiri and Lotter, 2005), or using the TEX_{86} proxy (e.g. Powers et al., 2005; Blaga et al., 2009).

Recently, branched glycerol dialkyl glycerol tetraethers (GDGTs) have attracted significant attention as a new potential palaeoenvironmental tool for continental climate reconstructions (Weijers et al., 2007b). GDGTs containing branched alkyl chains (I-III) were initially discovered in peat deposits (Sinninghe Damsté et al., 2000). Based on their branched alkyl chains and the bacterial 1,2-di-O alkyl-sn-glycerol stereochemical configuration at C-2 in the glycerol backbone, Weijers et al. (2006a) attributed the production of these GDGTs to bacteria, most likely at least facultative anaerobes. Weijers et al. (2006b, 2007a) showed that GDGTs occur ubiquitously in soils. These compounds are transported as a component of the soil organic matter by rivers to lakes (Blaga et al., 2009; Powers et al., 2009), and also to coastal marine sediments (Hopmans et al., 2004; Herfort et al., 2006; Kim et al., 2006; Walsh et al., 2008; Rueda et al., 2009). Run-off is also considered an important factor in the accumulation of branched GDGTs in lacustrine sediments (Sinninghe Damsté et al., 2009; Verschuren et al., 2009). Based on the relative abundance of the soil-derived branched GDGTs versus the mainly aquatically produced isoprenoidal GDGT - crenarchaeol, the Branched versus Isoprenoid Tetraether (BIT) index was introduced as a proxy for soil organic matter input in aquatic environments (Hopmans et al., 2004; Weijers et al., 2006b).

In a study of globally distributed soils, Weijers et al. (2007a) observed that specific structural features, such as the degree of methylation and the number of cyclopentyl moieties of branched GDGTs in soil are related to temperature and soil pH. The cyclisation ratio of the branched tetraethers (CBT) related empirically to soil pH, while the degree of methylation, expressed by the methylation index of branched tetraethers (MBT) was correlated with mean annual air temperature and to a lesser extent also with soil pH. By combining the CBT and MBT ratios, reconstructions of annual mean air temperatures (MAAT) became possible (Weijers et al., 2007a). This method was successfully applied to a core from the Congo Fan containing branched GDGTs which were delivered from the Congo River drainage basin through the river (Weijers et al., 2007b), resulting in a temperature reconstruction spanning the last 25,000 years. Sinninghe Damsté et al. (2008) studied an altitudinal transect of different soils from Mt. Kilimanjaro and found that the distribution of branched GDGTs changed with altitude and consequently with temperature. The temperatures inferred by the MBT/CBT, based on the initial calibration of Weijers et al. (2007a) were slightly higher than the MAAT measured in situ, suggesting the potential need for local calibrations. Peterse et al. (2009a) studied a series of soils from a transect away from two hot springs in California and confirmed that MBT is controlled by soil temperature and pH whereas CBT is related to pH. However, in a recent study of soils on Svalbard and coastal marine sediments, Peterse et al. (2009b) showed that the branched GDGTs in soils actually reflect MAAT but that the distribution of GDGTs in coastal marine sediments is quite different from that of the soils and cannot be used to reconstruct MAAT. This is due to the minimal transport of soil organic matter to the ocean and the in situ production of at least part of the branched GDGTs in marine sediments. Therefore, they suggested that the MBT/CBT proxy should only be used at sites with a substantial input of soil OM relative to the amount of marine OM, i.e. at sites close to the mouth of rivers with a catchment area where sufficient soil formation takes place and the soil thus contains substantial amounts of branched GDGTs.

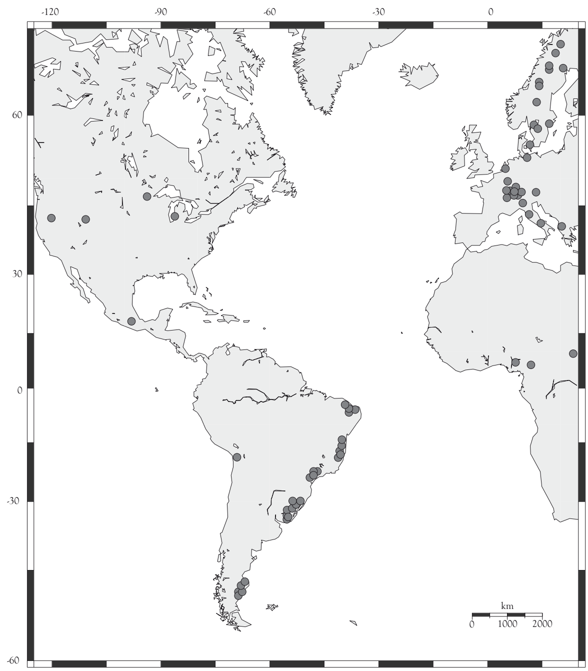

Fig. 1 Location of the lakes investigated for GDGT composition of its surface sediment. Some dots represent more than one lake.

Lake sediments have been shown to contain substantial amounts of branched GDGTs (Powers et al., 2004, 2009; Blaga et al., 2009). In the case of Lake Challa, Sinninghe Damsté et al. (2009) suggested that branched GDGTs from the sediment are predominantly allochthonous and brought into the lake from the catchment soils by run-off. Recently, Tierney and Russell (2009) investigated the distribution of branched GDGTs in soils, river sediments and lake sediments from Lake Towuti and found significant differences in the branched GDGT composition of soils and lake sediments. Based on the differences observed in the values of MBT and CBT for the lake sediments and catchment soils both studies also proposed in situ production of branched GDGTs in addition to soil erosion.

Here we studied the GDGT composition of a large number (82) of surface sediments from lakes in Europe, the Americas and Africa to a) examine the relative abundance and distribution of branched GDGTs in lake sediments; and b) to assess whether the MBT/CBT can be used as a continental temperature proxy in lacustrine environments.

3.2. Material and methods

The surface sediments used for this study were collected during different fieldtrips in South America (2004/5) and Europe (January and July 2006). In addition, previously collected samples from African and North American lakes, stored at the National Lacustrine Core Repository (LacCore, University of Minnesota) were obtained. The lakes (Fig. 1) are characterized by different physiographic and climatic settings. They were chosen in order to cover a large gradient of temperatures, as well as a wide variety in maximum depth, volume, surface area, pH, trophic conditions, and sedimentary organic matter content.

Generally sediments were recovered using a gravity corer and represent the top 0-5 cm of sediment. Upon recovery samples were freeze dried and extraction was performed using an Accelerated Solvent Extractor (DIONEX ASE 200). A mixture of DCM/methanol (9:1; vol/vol) was flushed through the sediment samples at a temperature of 100 °C and a pressure of $7.6*10^6$ Pa three times, with 5 min intervals in between. Extracts were condensed and separated over an activated Al_2O_3 column into an apolar and polar fraction by using mixtures of hexane:DCM 9:1 (vol/vol) and DCM:MeOH 1:1 (vol/vol), as eluents, respectively. The polar fraction was dissolved in hexane:isopropanol 99:1 (vol/vol) by sonication and filtered prior to injection. GDGTs were measured (injection volume 10 µl) using HPLC/atmospheric pressure positive ion chemical ionization (APCI)/MS according to Schouten et al. (2007). Ion scanning was performed in a single ion monitoring mode adjusted to the masses of interest (m/z 1292, 1050, 1048, 1046, 1036, 1034, 1032, 1020, 1018, and 1016) in order to increase sensitivity and reproducibility. After an evaluation of the mass chromatograms, peaks that were at least one order of magnitude greater than the background noise were integrated and used for MBT and BIT calculation. CBT and MBT values were determined according to the equations given by Weijers et al. (2007a):

$$MBT = I+Ib+Ic/I+Ib+Ic+II+IIb+IIc+III+IIIb+IIIc \quad (1),$$

$$CBT = -LOG\ [(Ib+IIb)/(I+II)] \quad (2),$$

where I – III b-c refer to GDGT structures presented in Fig. 2.

BIT index values were calculated according to the equation given by Hopmans et al. (2004) as follows:

$$BIT = I+II+III/I+II+III+Cren \quad (3).$$

The pH of lake sediments was determined after soaking freeze dried sediments in distilled water (1:5 vol/vol). Mixtures were vigorously shaken for 1 min and particles were left to settle for 30 min. Values were subsequently measured with a pH meter (Consort C830) equipped with a glass electrode (QIS).

We used the program CANOCO 4.51 (ter Braak and Smilauer, 1998) to statistically evaluate the distribution in abundance of GDGTs and to assess the relationship between relative GDGT abundance and environmental factors. A detrended correspondence analysis (DCA) (Lepš and Šmilauer, 2003) was used to identify if a unimodal (gradient length >2 S.D.) or linear (gradient length <2 S.D.) response model was appropriate. According to the gradients a linear-based ordination method - principal component analysis (PCA) - was used for further analysis.

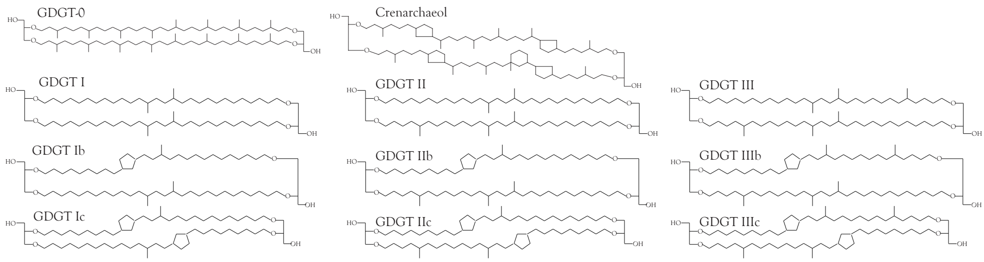

Fig. 2 The structure of GDGT 0, crenarchaeol and branched GDGTs (I-III b-c) occurring in lake sediments.

3.3. Results

From 82 lakes, predominantly from Europe and South America but also from North America and Africa (Fig. 1), the distribution of GDGT lipids in surface sediments was determined (Fig. 3). All of the lake sediments contain isoprenoidal GDGTs and branched GDGTs in varying amounts. The variation in the distribution of the membrane lipids can be visualized in a ternary diagram (Fig. 4) where the relative abundance of crenarchaeol (specific GDGT of Crenarchaeota), GDGT-0 (general GDGT) and the summed branched GDGTs (bacterial GDGTs) is presented. Of the isoprenoidal GDGTs present in the lake sediments GDGT-0 varies from 1% to 78% (on average 22% of total GDGTs). Crenarchaeol was found in varying amounts ranging from 0.2 to 85% (on average 13% of the total GDGTs). Branched GDGTs, with and without cyclopentyl moieties, varied from 0.0% to 48.5% with an average of 13.8% (GDGT III b-c); 1.6% to 52.5% with 27.2% on average (GDGT II b-c) and 0.5% to 74.5% with 24.1% on average (GDGT I b-c).

Within the branched GDGTs those without cyclopentyl moieties (I-III; Fig. 2) are consistently more abundant than the ones with cyclopentyl moieties ((I-III b-c; Fig. 2). In some of the sediments branched GDGTs with cyclopentyl moieties were below the detection limit. Of all branched GDGTs, GDGT II summed with GDGT IIb and IIc (on average 27% of all GDGTs) is the most abundant component, followed by GDGT I. BIT index values are between 0.1 and 0.4 for ten lakes, while for the other 72 lakes BIT values are almost always >0.9 (Table 1; Fig. 3). The MBT index varies between 0.1 and 0.87, while the CBT index varies between 0.14 and 1.67 (Table 1).

Table 1 Morphometric and hydrologic characteristics of lakes, BIT-index, CBT, MBT, and reconstructed pH and MAAT values. NA= Not available/applicable.

Lake name (code)	Latitude (°)	Altitude (m)	Depth (m)	Av. Depth (m)	Area (km^2)	Volume (km^3)	MAAT (°C)	water pH	sediment pH	BIT	CBT	pH	MBT	$MAAT_{recon}$
Laguna Santa Laura (AR73)	-54.6	166	12	3	1.049	0.003151	15.0	7.8	4.7	0.99	0.47	7.5	0.54	16.3
Lago del Pescado (AR71)	-54.5	473	2.25	0.9	0.552	0.000514	10.4	7.2	NA	1.00	0.82	6.6	0.22	-2.5
Digue San Jose (AR74)	-51.5	408	4.2	2.1	0.367	0.000779	14.4	9	4	0.99	0.69	7.0	0.16	-4.5
Laguna del Cisne (AR76)	-50.3	225	0.95	0.5	0.396	0.000219	13.7	9	72	1.00	0.52	7.4	0.22	0.2
Santa Barbara (AR30)	-38.8			1.3	0.782	0.001057	23.7	8.5	NA	0.94	0.60	7.2	0.20	-1.8
El Bagual (AR28)	-38.0	200	1	0.8	0.836	0.000668	18.8	9.1	NA	0.94	0.41	7.7	0.22	1.2
El Paraiso (AR25)	-37.6	213	1.65	1.1	1.135	0.001263	26.3	9	7.6	0.96	0.60	7.2	0.32	4.3
Laguna Rosita (AR82)	-36.1	2	1	0.9	2.419	0.002413	23.9	8.7	7.5	1.00	0.59	7.2	0.28	2.3
Las Encadenadas o San Carlos (AR19)	-35.3	42	1	0.7	0.380	0.00025	24.2	9	7.6	0.99	0.51	7.4	0.31	4.5
Estancia Bellavista (AR20)	-35.2	42	1.2	0.8	0.328	0.000289	28.6	9	7.7	0.98	0.55	7.3	0.32	4.8
Laguna del Barro (UY15)	-34.9	12	1.8	1.2	0.216	0.000274	24.7	5.5	3.2	0.94	0.95	6.3	0.54	12.0
Laguna Clotilde (UY17)	-34.3	2	3.8	2.4	0.167	0.000409	26.9	7.5	3.9	0.95	0.49	7.5	0.45	11.6
BR01	-30.6	20	7	3.0	0.464	0.001396	22.3	7	4.1	0.98	0.73	6.8	0.56	15.2
Lagoa da Lavagem (BR04)	-30.4	29	2.5	1.5	0.771	0.001174	23.2	7	4.8	0.93	0.60	7.2	0.57	16.6
Lagoa da Tapera (BR08)	-30.1	12	2.3	1.4	0.859	0.001252	25.9	7	NA	0.98	0.69	6.9	0.59	16.9
Lagoa do Rincão (BR11)	-29.9	6	2.5	1.5	0.835	0.001313	24.1	6.7	4.3	0.97	0.82	6.6	0.60	16.1
Lagoa Palacete (BR37)	-21.8	2	2.5	1.3	0.764	0.001055	25.5	8.5	7.4	0.98	0.99	6.1	0.20	-5.5
Jabaete (BR43)	-20.4	27	2.5	2.1	0.343	0.000734	25.0	6.7	4.3	0.99	1.07	5.9	0.79	23.5
Lagoa Nova (BR47)	-19.6	1	5	1.6	0.185	0.000298	27.1	6.7	4.9	0.97	0.62	7.1	0.76	26.0
Lagoa Boa Vista (BR48)	-19.6	1	3.2	2.3	0.483	0.001119	26.6	6.8	4	0.89	0.75	6.8	0.76	25.0
Lagoa da Viuva (BR49)	-19.5	1	4.4	2.2	0.499	0.001103	26.2	6.3	3.1	0.98	0.83	6.6	0.71	21.5
Laguna Seca	-18.2	1000	NA	NA	NA	NA	NA	4.7	NA	0.99	0.81	6.6	NA	NA
Acude Mondo Novo (BR68)	-6.4	189	4.9	3.6	0.875	0.002384	29.9	7.7	3.6	0.97	0.86	6.5	0.64	17.9
Acude das Lajes Pintadas (BR67)	-6.1	318	4.5	2.3	0.243	0.000551	29.3	8.4	4.4	0.96	0.39	7.7	0.43	12.0
Boa Aqua (BR52)	-6.0	17	5.5	1.6	0.625	0.00226	29.4	8.7	7.6	0.99	0.77	6.7	NA	NA
Acude Recreio (BR64)	-5.9	121	4.1	1.4	0.199	0.000292	28.0	6.8	NA	0.99	1.11	5.8	NA	NA
Lagoa do Cujueiro (BR62)	-5.6	67	2.1	2.2	0.275	0.000442	27.8	5.7	3.4	0.98	0.63	7.1	0.63	19.5
Lagoa Cutias (BR59)	-5.4	7	4.7	2.7	0.615	0.001449	28.6	6.7	3.9	1.00	0.85	6.5	0.87	29.5
Lake Edward (EDW)	-0.3	912	112	17	2325	39.5	24	8.9	NA	0.59	0.66	7.0	0.39	7.1
Lake Oku (OKU)	6.2	300	NA	NA	NA	NA	18.6	NA	NA	0.64	0.61	7.1	0.38	7.1
Lake Nyos (NYOS)	6.4	1091	208	NA	1.6	0.15	24	5.2	NA	0.92	1.67	6.3	NA	NA
Lago Zirahuen (ZIR)	19.4	2090	NA	NA	NA	NA	16	NA	NA	0.55	0.50	7.4	0.30	4.0
Lago Grande di Monticchio (MONT)	40.9	656	36	8.7	0.405	0.0035	12	NA	NA	0.99	0.79	6.7	0.27	-0.1
Lake Ohrid (OHR)	41.0	695	286.7	163.7	358	55.4	11	9.3	7.3	0.28	0.14	8.4	0.10	-2.3
Lago di Albano (ALB)	41.7	293	175.1	77	6	0.453	15	7.1	6.7	0.15	0.40	7.7	0.13	-3.4
Bear Lake (BEAR)	42.0	1806	63.00	19.0	280.0	8.02	14	8.8	NA	0.98	0.52	7.4	0.13	-4.7
Lago di Vico (VIC)	42.3	507	48.5	21.5	12.1	0.26	14	8.1	5.7	0.98	0.35	7.8	0.27	3.9
Crater Lake (CRATER)	42.6	1883	594	350	53.0	18.7	12.5	7.7	NA	0.35	0.53	7.4	0.12	-5.2
Lago Trassimeno (TSM)	43.1	259	5.5	4.7	124.3	0.59	13	8.3	7.7	0.87	0.16	8.3	0.26	5.5
Yellowstone Lake (YELLOW)	44.5	2376	120	42	350	NA	5	7.2	NA	0.61	0.41	7.7	0.11	-4.5
Lac Bourget (BGT)	45.7	231	145	80	42	3.5	10.1	7.5	6.7	0.09	0.45	7.6	NA	NA
Lago Maggiore (MGR)	45.9	193	370	177	212.5	37.1	12.1	7.8	6.2	0.40	0.69	6.9	NA	NA
Lago di Poschiavo (POS)	46.3	962	85	NA	1.98	0.12	NA	7.8	NA	0.41	0.61	7.1	0.21	-1.4
Silsersee (SILS)	46.4	1796	71	35	4.1	0.137	NA	7	4.4	0.29	0.84	6.5	NA	NA
Hinterburgsee (HIN)	46.4	1514	11.00	NA	0.1		NA	7.6	NA	0.93	0.62	7.1	NA	NA
St. Moritzersee (ST.MOR)	46.5	1768	44	25	0.078	0.02	8	7.2	5.5	0.92	0.69	6.9	NA	NA
Lac Morat (MOR)	46.6	453	45.00	NA	22.8	0.55		7.3	6.2	0.98	0.43	7.6	0.17	-1.9

Table 1 (continued) Morphometric and hydrologic characteristics of lakes, BIT-index, CBT, MBT, and reconstructed pH and MAAT values. NA= Not available/applicable.

Lake name (code)	Latitude (°)	Altitude (m)	Depth (m)	Av. Depth (m)	Area (km^2)	Volume (km^3)	MAAT (°C)	water pH	sediment pH	BIT	CBT	pH	MBT	$MAAT_{recon}$
Lac de Joux (JOX)	46.6	1004	33	21	9	0.16	7	8.2	7	0.98	0.42	7.7	0.20	-0.1
Hagelseewli (HAG)	46.7	2339	18.5	13	0.03	0.000196	3.4		3.9	0.49	0.46	7.6	0.15	-2.7
Lake Lucerne Urnerisee (VW UR)	47.0	434	192	117	113.6	11.8	9	8.2	7.6	0.80	0.92	7.8	0.35	2.6
Lake Lucerne Gersauerbecken (VW GER)	47.0	434	214	117	113.6	11.8	9	8.2	NA	0.11	0.41	7.7	0.19	-0.5
Lake Lucerne Küssnachterbecken (VW KUS)	47.0	434	214	117	113.6	11.8	9	8.2	7.1	0.13	0.42	7.7	0.19	0.5
Lake Lucerne Horwerbecken (VW HO)	47.0	434	214	117	113.6	11.8	9	8.2	NA	0.18	0.29	8.0	0.27	4.8
Zugersee (ZUG)	47.1	417	198	NA	38.2	3.18	9	7.9	6.9	0.13	0.37	4.4	0.25	2.7
Sempachersee (SMP)	47.2	504	87	44	14.4	0.624	9	7.9	6.8	0.85	0.41	7.7	NA	NA
Elk Lake (ELK)	47.2	400	59.00	NA	NA	NA	NA	NA	NA	1.00	0.53	7.4	0.18	1.8
Baldeggersee (BA)	47.2	463	66	33	5.2	0.173	7.7	7.8	6.9	0.51	0.42	7.7	NA	NA
Greiffensee (GR)	47.2	435	32.00	18	8.5	0.148	9	7.6	7.3	0.73	0.43	7.6	0.28	3.7
Türlersee (TUR	47.3	643	22	13	0.5	0.006485	8.	7.9	NA	0.65	0.40	7.7	NA	NA
Pfäffikersee (PFA)	47.3	537	36	18.5	3.3	0.058	9	7.9	7.4	0.96	0.44	7.6	NA	NA
Mondsee (MDS)	47.8	481	68.3	36	14.2	0.51	9	8.1	7.1	0.93	0.42	7.7	0.22	0.9
Titisee (TTS)	47.9	846	39.2	20	1.08	0.0225	10	7.3	4.6	0.98	1.00	6.1	0.35	1.9
Lac de Blanchemer (LBL)	48.0	984	NA	NA	NA	NA	NA	NA	3.9	0.93	1.18	5.7	0.45	5.6
Lac de Gerardmer (GRD)	48.1	660	38.4	13	1.16	0.01951	9	NA	5.4	0.99	0.87	6.5	0.32	1.6
Maarssevenseplassen (MSV)	52.1	1	30.8	20	0.7	0.0848	10	NA	7.3	0.98	0.62	7.1	0.34	-5.3
Arendsee (ARN)	52.9	22.8	48.7	28.6	5.2	0.147	10	NA	6.6	1.00	0.56	7.3	NA	NA
Grosser Plöner See (GPS)	54.2	21	58	12.4	30	0.372	9	8.1	6.9	0.99	0.44	7.6	NA	NA
Furesø (FUR)	55.8	80	37.7	16.5	7.4	0.122	8	7.3	6.9	0.99	0.28	8.0	0.19	0.8
Lake Vättern (VAT)	58.5	89	128	39	1893	77.6	10.9	7.6	6.3	0.71	0.56	7.3	0.16	3.5
Lake Vänern (VAN)	59.0	44	106	27	5648	153	6	7.2	6.4	0.61	0.70	6.9	0.27	0.8
Lake Hjälmaren (HJA)	59.1	22	22	6.1	483	3.005	7	7.	6.2	0.99	0.41	7.7	0.20	0.2
Lake Siljan (SIL)	60.9	161	134	27	292	8.089	8.7	7	NA	0.83	1.26	5.4	0.37	0.6
Lake Navarn (NVN)	62.6	280	51.5	10	9.57	0.11	8.4	6.	5.3	0.97	0.98	6.2	0.21	-4.6
Kalsjön (KAL)	63.7	380	134	40	158	6.14	2.5	7.3	5.4	0.95	1.39	5.1	0.44	2.7
Melan Risjön (MRI)	64.7	443	8.3	4	1.6	0.017	7.31	6.	5.2	0.92	1.10	5.9	0.37	2.0
Malgomaj (MA	64.8	341	148	117	101	3.117	NA	6.8	NA	0.91	1.38	5.1	0.41	1.3
Vojmsjön (VOJ)	64.9	420	145	39	70	3.114	NA	7	5.8	0.59	1.23	5.5	0.32	-1.6
Vuolgamjaure (VUO)	65.7	437	15	4.5	2	0.01075	10.3	6.	5	0.99	1.05	6.0	0.26	-2.7
Hornavan (HO	66.2	425	228		283	11.234	9.2	7.	5.2	0.80	1.15	5.7	0.24	-4.8
Hapsajaure (HPS)	67.0	413	9.5	6	1.1	NA	NA	NA	4.3	1.00	1.09	5.9	0.25	-4.0
Stora Lulevatten (LUV)	67.1	365	28.5	9.3	155	1.31	9.4	7.1	5	0.94	1.27	5.4	0.33	-1.6
Lake Törnetransk (TOR)	68.4	341	168	51	332	17.1	-1	7	6.3	0.74	0.75	6.8	0.25	-0.7

3.4. Discussion

3.4.1. Factors controlling the distribution of GDGTs

The ternary diagram showing the relative abundance of GDGTs present in the lake sediments indicates that the GDGTs are often dominated by branched GDGTs (Fig. 4) and for more than 85% of the sediments the BIT index has values >0.4. All shallow lakes cluster in the

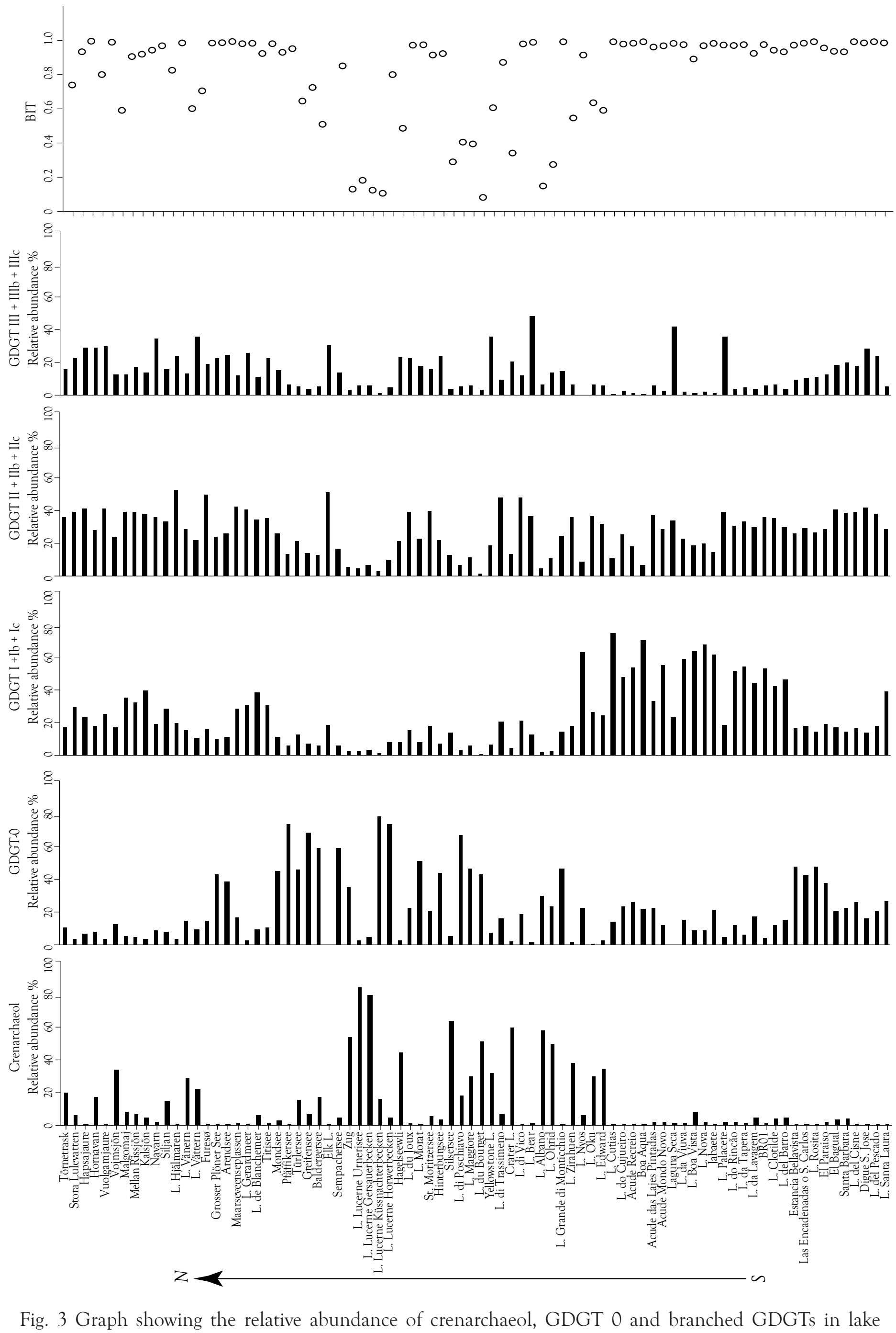

Fig. 3 Graph showing the relative abundance of crenarchaeol, GDGT 0 and branched GDGTs in lake sediments and the corresponding BIT values.

lower left side of the diagram and have a BIT index >0.8, indicating that the branched GDGTs are most abundant in these sediments. However, GDGT-0 is the most abundant individual isoprenoidal GDGT, while in ten deep lakes, mostly situated in the Alps, crenarchaeol is the dominant membrane lipid. These two isoprenoidal GDGTs are more abundant in the deeper lakes (Fig. 4).

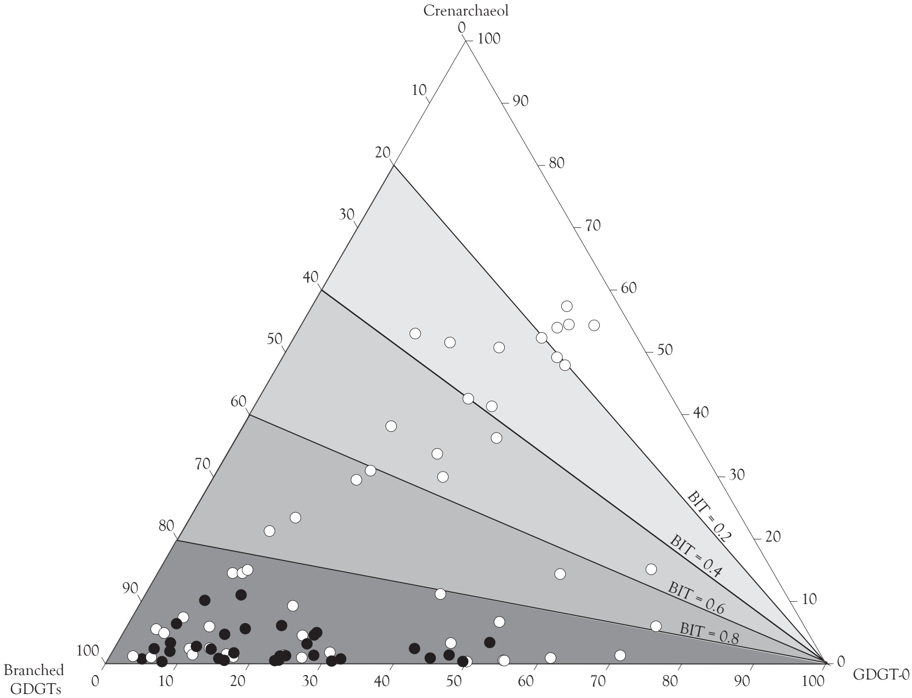

Fig. 4 Ternary diagram showing the relative abundance of crenarchaeol, branched GDGTs and GDGT 0 in the analysed lake sediments. Grey scales indicate increasing values for BIT. Open circles represent deep (>15 m) lakes, filled circles represent shallow (<15 m) lakes.

To examine which factors control the variability in GDGT distribution, we performed a principal component analysis (PCA) of the relative abundance of GDGTs. The PCA of the lake GDGT data showed that together the three principal components (PC) explain 85% (44% + 24% + 17%) of the observed variance in the dataset. A biplot of the samples and GDGT scores on the first and second PCA axes for the different lakes shows that the vectors for GDGT-0 and crenarchaeol plot on the right side of the diagram together with the deep lakes (>15m) which in general score positively on the first PC (Fig. 5a). In contrast, the samples from the shallow lakes plot on the left side, together with the branched GDGTs (Fig. 5a), reflecting the difference in GDGT distribution between the two types of lakes. Most of the variability (44%) is explained by the first principal component, with the relative abundance of crenarchaeol having the highest positive loading ($r = 0.93$), whereas relative abundances of branched GDGT I and branched GDGT II have negative loadings ($r = -0.77$ and -0.75, respectively). Variability in abundance of crenarchaeol and the branched GDGTs is also reflected by the BIT index (Hopmans et al., 2004). The passive projection of the BIT index into the ordination space (Fig. 5a) shows that BIT plots together with the branched GDGTs, in the opposite direction from crenarchaeol. Because the first PCA axis reflects the same variance in the data set as the BIT index, a substantial proportion (44%) of the variability in the GDGT data set is explained by the relative contribution of soil-derived

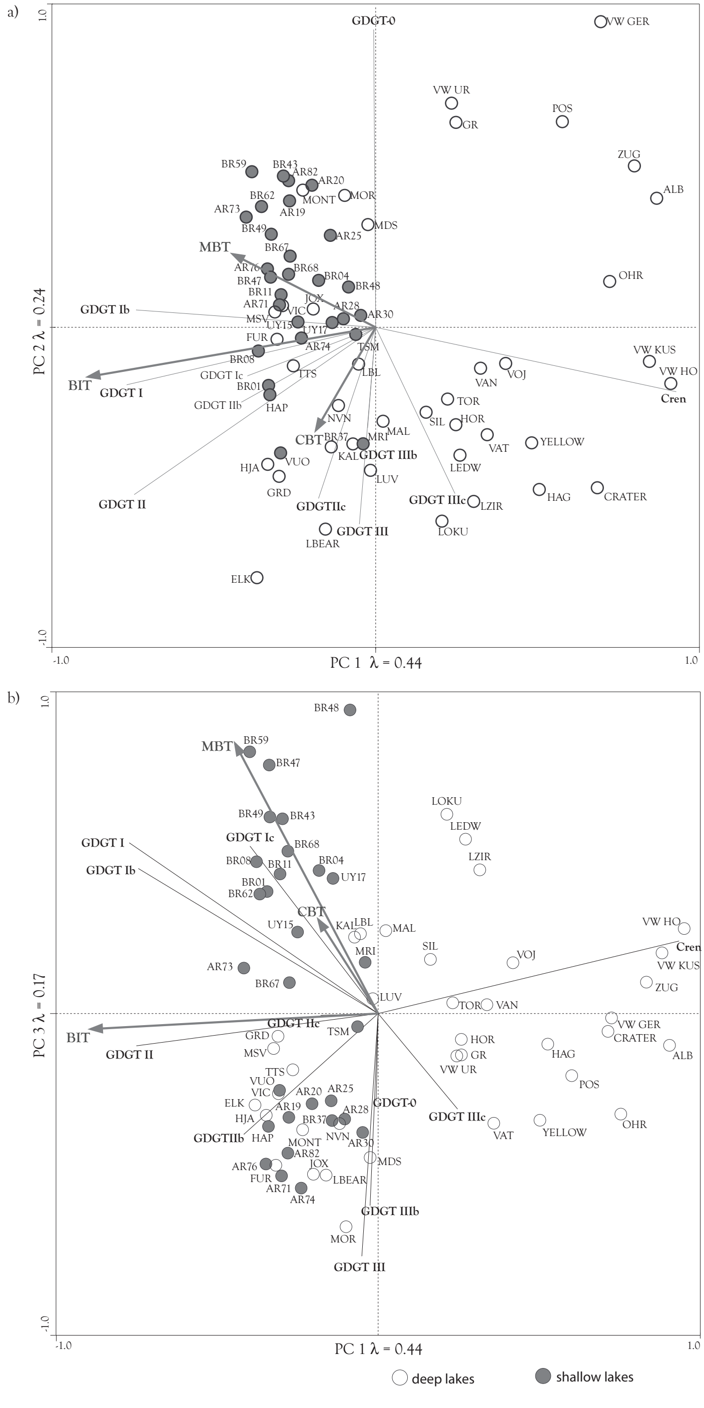

Fig. 5 Ordination diagram from the PCA for crenarchaeol, GDGT 0, branched GDGTs, BIT, MBT and CBT: a) PCA axes 1 and 2; b) PCA axes 1 and 3. Cren = crenarchaeol. Open circles represent deep lakes, filled circles represent shallow lakes.

branched GDGTs. In soils BIT index values usually range between 0.8 and 1 (Weijers et al., 2006b; Kim et al., 2006; Sinninghe Damsté et al., 2008; Peterse et al., 2009a, b). Analyses of soils, riverbed sediments as well as surface sediments from the shelf and canyons in the Golf of Lyon (Kim et al., 2006), Têt river (Kim et al., 2007), Angola Basin (Hopmans et al., 2004) and North Sea (Herfort et al., 2006) show that BIT values are nearly always >0.8 in soils and riverbeds and vary between 0.01 and 1 in marine sediments decreasing from the inner shelf towards the open ocean. In our set of lake sediments the BIT index has low values between 0.1 (Lac du Bourget) and 0.4 (Lago Maggiore) in the sediments of ten deep lakes. This probably reflects a combined effect of relatively low input of soil organic matter and substantial aquatic production of crenarchaeol by Crenarchaeota. For the other lake sediments BIT values >0.8 are observed in the sediments from 59 lakes, with an average of 0.9, close to the terrestrial end-member value of BIT, which seems to indicate a nearly pure soil origin for the branched GDGTs in the sediments from these lakes.

On the second PCA axis, which explains 24% of the observed variance, crenarchaeol has no appreciable loading (Fig 5a). This axis is determined mainly by a positive loading of GDGT-0 ($r = 0.92$) and a negative loading of branched GDGT III ($r = - 0.61$). It seems to mainly reflect a relative abundance of GDGT-0. GDGT-0 is a ubiquitously occurring GDGT within the Archaea and thus can be derived from both methanogenic Archaea and Group 1 Crenarchaeota. However, since crenarchaeol has no appreciable loading on the second PC, this component may indicate the relative contribution of methanogens to the GDGT distribution. The third PCA axis, explaining 16% of the observed variability in the data set, is primarily determined by GDGT III ($r = - 0.75$) (Fig. 5b). In addition GDGT I ($r = 0.53$), Ic ($r = 0.52$) and GDGT IIIb ($r = - 0.6$) show minor loadings on axis 3. The passively plotted MBT index has its strongest loading on the third axis, in the same direction as GDGT I, Ib and Ic, with the other branched GDGTs pointing in the opposite direction (Fig. 5b).

3.4.2. Factors controlling the distribution of branched GDGTs

Branched GDGTs were found to be ubiquitously present, in varying relative abundances, in the large set of surface lake sediments (Figs. 3 and 4). This is in line with previous studies of aquatic environments (Powers et al., 2004, 2009; Blaga et al., 2009; Sinninghe Damsté et al., 2009; Tierney and Russell, 2009). In a study of globally distributed soils Weijers et al. (2007a) observed that the branched GDGTs I-III not containing cyclopentyl moieties were more abundant than the GDGTs with one or two cyclopentyl moieties (I-III b-c). Similarly, in lake sediments branched GDGTs containing cyclopentyl moieties (I-III b-c) are one to two orders of magnitude less abundant than GDGTs I-III and in some cases even below the detection limit.

Even though some GDGTs were below the detection limit, the full sample set was analyzed by PCA and evaluated against environmental factors by replacing the missing values with an average value of the relative abundance (cf. Lepš and Šmilauer 2003). PCA analysis of the branched GDGTs distributions (Fig. 6) resulted in the first two PCA axes together explaining 84% (60% + 24%) of the variance in the data. GDGT I has the highest positive loading ($r = 0.94$) on axis 1, whereas GDGT III has the highest negative loading ($r = - 0.97$). When projecting the MBT index passively into the ordination space it also has a high positive loading ($r = 0.99$) on axis 1, indicating that the MBT index is an appropriate way to express the largest variance in the data. As in the global soil calibration set (Weijers et al., 2007a), we note higher MBT index values (and higher scores on PCA axis 1) in lakes from warm locations [e.g. Lagoa Boa Vista (BR48), Laguna del Barro (UY15)], while lakes from colder regions [e.g. Lac Bourget (BGT)] are characterized by lower MBT indices and lower scores on axis 1.

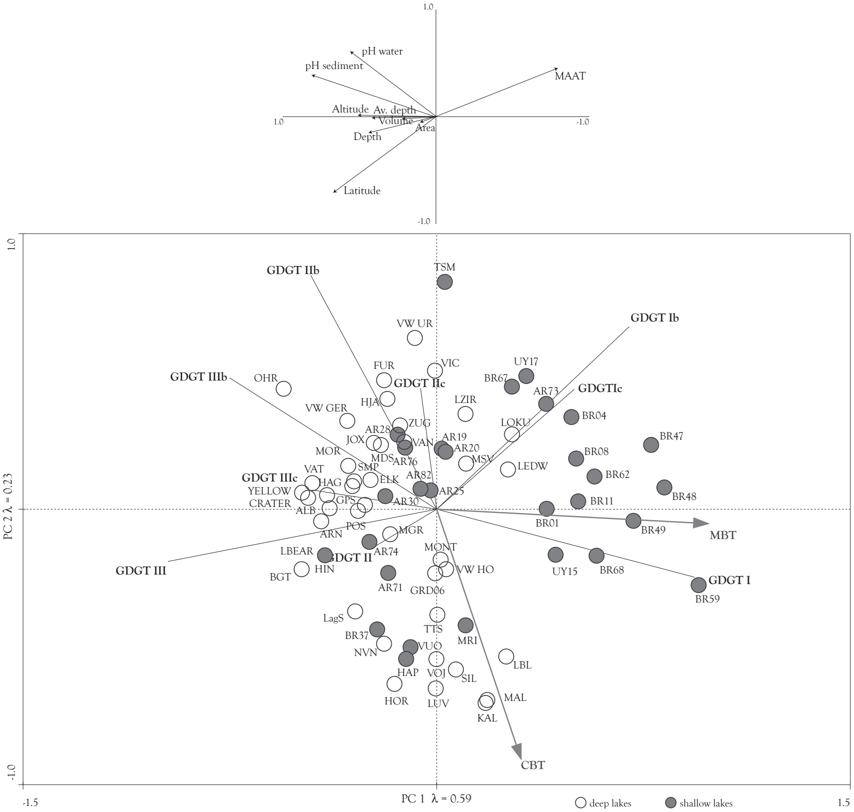

Fig. 6 Ordination diagram from the PCA for branched GDGTs, MBT and CBT. Biplot diagram summarizing the effects of the environmental factors upon the branched GDGT composition. Open circles represent deep lakes, filled circles represent shallow lakes.

GDGT IIb and GDGT Ib have the highest positive loading (r = 0.85 and r = 0.66, respectively) on axis 2. The CBT index clearly shows a high negative relation with PCA axis 2 (r = - 0.99), confirming that this index, in addition to the MBT index, is a good descriptor of the variance in the dataset. This is again in line with the study of Weijers et al. (2007a) that introduced the CBT index to distinguish soils with relatively high versus relatively low abundances of cyclopentyl containing branched GDGTs.

3.4.3. Estimation of MAAT and soil pH using branched GDGTs in lake sediments

To establish the potential of using the MBT and CBT proxies in lake sediments to reconstruct past continental temperatures, we reconstructed MAAT and pH using the soil-based MBT/CBT calibration set off by Weijers et al. (2007a).

$$CBT = 3.33 – 0.38*pH \ (r^2 = 0.70) \quad (4)$$

$$MBT = 0.122 + 0.187*CBT + 0.020*MAAT_{recon} \ (r^2 = 0.77) \quad (5).$$

This approach is based on the assumption that the branched GDGTs are primarily derived from soils in the watershed of the lake, warranted by the observed high values of the BIT index in most shallow lakes. The CBT index ranges between 0.14 and 1.67 which, using the published calibration (Weijers et al., 2007a) corresponds to calculated pH values between 4.4 and 8.4 (Table 1). The MBT index varies from 0.09 to 0.87, which according to the calibration (Eq. 5) for MBT/CBT, translates into a $MAAT_{recon}$ range of between - 5.6 °C and 29.5 °C (Table 1).

When we plot the MBT/CBT inferred temperature values ($MAAT_{recon}$) against measured temperatures ($MAAT_{obs}$) a significant correlation (r^2 = 0.47) with $MAAT_{recon}$ is observed though with considerable scatter and with consistently lower $MAAT_{recon}$ than the $MAAT_{obs}$ (Fig. 7). These results are in line with the observations of Tierney and Russell (2009) in Lake Towuti, where the MBT/CBT values of the branched GDGTs in the lake sediments also seem to record colder $MAAT_{recon}$ than expected, and with observations of Sinninghe Damsté et al. (2009) in Lake Challa, where the distributions of branched GDGTs were not identical to those of soils in the watershed. The lakes with relatively low BIT values (and thus an assumed smaller relative input of soil-derived branched GDGTs) do not consistently show a larger off-set from the 1:1 line than the lake sediments with higher BIT indices (Fig. 7) as would be expected if soil-derived branched GDGTs would mix with in situ produced branched GDGTs. An influx of branched GDGTs from soils from higher and thus colder altitudes in the catchment area could potentially explain the offset. Lakes at higher altitudes are often surrounded by steep mountain slopes, facilitating the input of large quantities of allochthonous organic matter from higher catchment regions. However, no appreciable correlation was observed between the difference in reconstructed and measured MAAT and lake altitude (r^2 = 0.16). This implies that the difference between reconstructed and measured temperature cannot be solely explained by the enhanced input of branched GDGTs from higher up the mountain slopes surrounding the lakes.

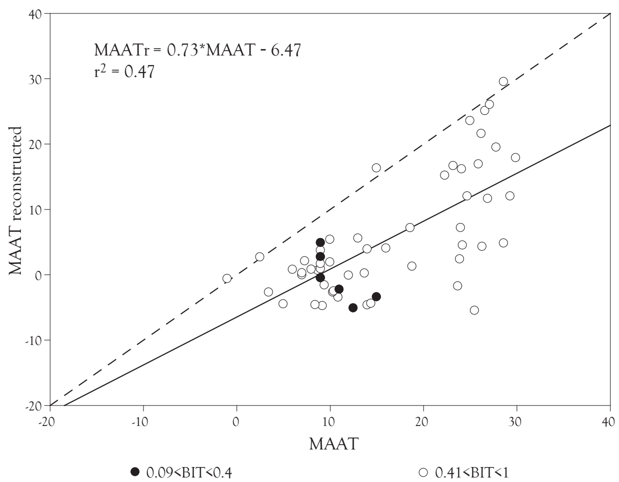

Fig. 7 Scatter plots showing the relation between $MAAT_{recon}$ and $MAAT_{obs}$.

These data seem to indicate that it is unlikely that the branched GDGTs in the lake sediments are derived from soils only in the watershed. Therefore, an additional source of branched GDGTs has to be taken into account to explain the mismatch in reconstructed and measured MAAT (Fig. 7). This could be an in situ production of branched GDGT in the water column or sediments as suggested previously (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009).

3.4.4. Are branched GDGTs produced in situ in lakes?

PCA of the branched GDGT distributions in lake sediments clearly revealed that much of the variance can adequately be described by the MBT and CBT ratio (Fig. 6). If the available environmental parameters are plotted in the ordination space, a clear positive correlation of MBT with MAAT and a negative correlation of CBT and pH of lake water, and with sediment pH are observed (Fig. 6). Unfortunately, lake water temperature was not available as a parameter for most lakes. However, it is well known that lake water temperature and MAAT are strongly correlated (Livingstone and Lotter, 1998) and this may perhaps explain the existing correlation between MBT and MAAT even if the branched GDGTs are produced in situ in the lake waters. The observed relation suggests a mixed signal due to transport of GDGTs from different types of soils and different locations in the catchment area as well as in situ production.

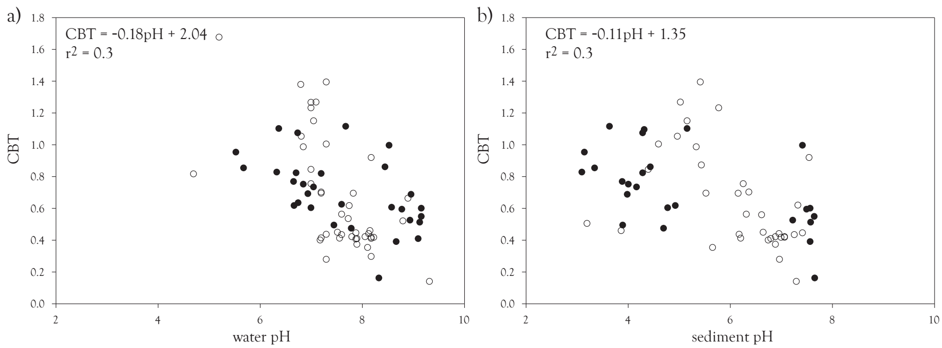

Fig. 8 Scatter plots showing the relationship between CBT and: a) water pH; b) sediment pH. Open circles represent deep lakes, filled circles represent shallow lakes.

Comparing the CBT values with the in situ measured water pH and sediment pH (Fig. 8) could potentially reveal allochthonous versus autochthonous source for the branched GDGTs as the pH of lake waters and surrounding soils in the watershed are much less coupled than are MAAT and lake water. When we plot the CBT values against lake water pH and sediment pH, only a weak correlation (r^2 = 0.3) is observed (Fig. 8 a, b). If the branched GDGTs are primarily derived from in situ production in the lake, this relationship would be expected to be stronger. Therefore, assuming that the CBT index of in situ produced branched GDGTs in lakes also shows a dependence of pH as reported for soils (Weijers et al., 2006), this suggests that the branched GDGTs in lakes are derived from mixed sources.

3.5. Conclusions

Analysis of 82 globally distributed lake surface sediments shows that the relative abundance of branched GDGTs is generally high as reflected by the high (>0.8) values of the BIT index for the majority of lakes. The relationship found between reconstructed and measured MAAT indicates that temperature played only a partial role in setting the MBT/CBT indexes. The high observed residual variability in the GDGT composition makes it important to establish source and origin of the branched GDGTs. As branched GDGTs occur ubiquitously in soils worldwide as well as in aquatic environments it is likely that in lake sediments they represent a mixed signal, which is difficult to untangle.

Acknowledgements

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Chapter 4

Seasonal changes in glycerol dialkyl glycerol tetraether concentrations and fluxes in an alpine lake: Implications for the use of the TEX_{86} and BIT proxies

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submitted to *Geochimica et Cosmochimica Acta*

To determine where and when glycerol dialkyl glycerol tetraether (GDGT) membrane lipids in lakes are produced, we collected descending particles in Lake Lucerne (Switzerland) using two sediment traps (at 42 and 72 m water depth) with a monthly resolution from January 2008 to late March 2009. Suspended particulate matter (SPM) was monthly filtered from the water column at three different depths in the water column. The potential application of GDGTs in palaeoenvironmental and palaeoclimatic reconstructions was investigated comparing core lipids (CLs) and intact polar lipids (IPLs), and their relative GDGT distribution, with lake water temperatures throughout the year. Fluxes of GDGTs and concentrations in the water column vary according to a seasonal pattern, showing a similar trend in the SPM and sediment traps. Fluxes and concentrations of isoprenoid GDGTs increase with depth, maximum values being observed in the deeper part of the water column, indicating production of isoprenoid GDGTs by Group 1 Crenarchaeota in the deep (~50 m), aphotic zone of Lake Lucerne. The flux-weighted averages of TEX_{86} (0.27) and BIT (0.03) based on the total extracted GDGTs are similar at both trap depths. The flux-weighted average of TEX_{86} in the IPL fraction is slightly higher, probably due to a minor contribution of other Archaea to this fraction. A sediment core from the same location showed that in the first few centimetres of the core TEX_{86} and BIT values of 0.29 and 0.07, respectively are similar to those recorded for descending particles and SPM, indicating that the sedimentary TEX_{86} records the annual mean temperature of deeper waters in Lake Lucerne. TEX_{86} values are slightly higher below 20 cm in the core. This offset is apparently caused by the present-day trophic state of the lake, which probably resulted in a deeper niche of the Crenarchaeota. Branched GDGTs represent only a minor fraction of the total GDGTs in the lake and it remains unclear if they also have an allochtonous origin. However, the low BIT values during the eutrophic lake phase suggest that the BIT reliably reflects the relative contribution of soil-derived organic matter. Our data reveal that GDGTs in lakes have a large potential for palaeoclimatic studies but indicate that knowledge of the system is important for accurate interpretation.

4.1. Introduction

Lake sediments provide an important archive for reconstructing past climates in continental interiors (e.g. Meyers, 1997). Recently the application of TEX_{86} (TetraEther Index of 86 carbon atoms), MBT/CBT (Methylation index/Cyclization index of Branched Tetraethers) and BIT (Branched and Isoprenoid Tetraether) proxies in lake sediments emerged. These proxies have been applied to reconstruct lake water and related continental air temperatures as well as the input of soil organic material to the lake (Powers et al., 2004, 2009; Weijers et al., 2004, 2007) and variations in rainfall (Verschuren et al., 2009).

The TEX_{86} palaeothermometer, which is based on membrane lipids derived from aquatic Crenarchaeota an abundant group of prokaryotes, was initially proposed as an organic geochemical proxy for sea surface temperatures (Schouten et al., 2002). Crenarchaeota are ubiquitously distributed in the ocean and produce glycerol dialkyl glycerol tetraethers (GDGTs) membrane lipids with a variety of cyclopentane moieties (from 0 to 4), but also crenarchaeol, a specific GDGT with four cyclopentane moieties and one cyclohexane moiety (Sinninghe Damsté et al., 2002). Mesocosm studies (Wuchter et al., 2004) showed that the increase of cyclopentane moieties in the GDGTs is an adaptation to temperature change as previously observed in their (hyper)thermophilic relatives (Gliozzi et al., 1983). Analysis of a suite of over 300 marine surface sediments revealed that the TEX_{86} ratio, as defined by Schouten et al. (2002), correlates linearly with annual mean sea surface temperature (Kim et al., 2008):

$$T = 56.2 * TEX_{86} - 10.78, \ r^2 = 0.94, \ n = 223 \qquad (1).$$

The presence of crenarchaeotal GDGTs in lake surface sediments (Powers et al., 2004; Escala et al., 2007; Sinninghe Damsté et al., 2009) confirmed the widespread occurrence of Crenarchaeota in freshwater aquatic environments previously assessed by molecular ecological studies (Keough et al., 2003). Therefore, the application of TEX_{86} index was extended to freshwater systems with an initial lacustrine calibration of TEX_{86} (Powers et al., 2004) that closely resembled the marine calibration. Subsequently, this calibration was improved and the applicability of TEX_{86} in lakes constrained, when surface sediments from 47 European lakes (Blaga et al., 2009) and 46 globally distributed lakes (Powers et al., 2009) were analyzed for their GDGT content. Lake palaeotemperatures were reconstructed using the TEX_{86} proxy from sediment cores from Lake Malawi and Lake Tanganyika (Powers et al., 2005; Tierney et al., 2008) and revealed past climatic changes. Recently, Sinninghe Damsté et al. (2009) determined the provenance and distribution of isoprenoid GDGTs in suspended particulate matter and descending particles from the water column and in sediments of a small crater lake (Lake Challa) at the border of Kenya and Tanzania. The sediment trap time series revealed that crenarchaeol and related isoprenoid GDGTs were predominantly produced in January and February, following the local prominent short rain season. The TEX_{86}-inferred temperature derived from sedimenting particles corresponded well with lake surface-water temperature at this time of largest crenarchaeol flux. However, in situ production of isoprenoid GDGTs in deeper waters or surface sediment influenced the isoprenoid GDGT distribution in such a way that the sediments could not be used for TEX_{86} palaeothermometry. Soils also contain isoprenoid GDGTs (Weijers et al., 2006) that may affect in situ produced GDGT distributions in the lake. A high input of these allochtonous isoprenoid GDGTs may, therefore, also hamper the straightforward application of TEX_{86} in lakes (Blaga et al., 2009).

In addition to isoprenoid GDGTs, also branched GDGTs were found in soils (Weijers et al., 2006) often dominating quantities (>90%). This group of GDGTs is produced by an as yet unknown group of anaerobic soil bacteria, possibly belonging to the group of acidobacteria (Weijers et al., 2009). Their abundance, relative to that of isoprenoid GDGTs in aquatic systems, was quantified using the branched versus isoprenoid tetraether (BIT) index (Hopmans et al., 2004). This index can be applied as a means to determine the relative changes in input of soil organic matter (OM) to lacustrine environments (Hopmans et al., 2004; Blaga et al., 2009). Sinninghe Damsté et al. (2009) noted that in Lake Challa the main flux of branched GDGTs to the sediment during the short rainy season was most probably derived from eroded catchment soils and delivered through surface run-off. Verschuren et al. (2009) reconstructed variations in rainfall over the past 25,000 years using a high-resolution BIT record from the sediment of this lake. However, Tierney and Russell (2009) showed that for an Indonesian lake in situ production of branched GDGTs in the water column or in the sediment cannot be excluded.

An approach to distinguish between in situ production and allochthonous sources for GDGTs is to discriminate between core lipids (CL) and intact polar lipids (IPLs). IPL GDGTs are phospho- and glycolipids composed of glycerol units containing tetraether linked isoprenoid chains. They are often the main constituents of archaeal membranes and are quickly turned over after the death of a cell, as the polar headgroups of the IPLs are quickly lost (White et al., 1979, Harvey et al., 1986). In a biologically active system most of the IPLs will, therefore, represent either living, or recently died biomass. After the loss of their polar headgroups, CLs accumulate in the environment and over time can be traced back as fossil biomarkers. The analysis of IPLs is thus considered a suitable approach in attempting to detect biomass of living Archaea (Rütters et al., 2002, Zink et al., 2008, Lipp et al., 2008, Pitcher et al., 2009a). Comparing intact and core lipids, Pitcher et al. (2009b) determined relative contributions of in situ produced versus fossil archaeal GDGTs in two Californian hot springs and their surrounding soils. There have been no studies to date that investigate intact polar versus core lipid composition of fresh lacustrine organic matter, which could provide a better translation of primary proxy signals to the fossil record.

Here we present the results of an integrated seasonal study, in which we quantified GDGTs in SPM, descending particles and surface sediments, to shed further light on the application of GDGTs as proxies for reconstructing palaeoclimatic and palaeoenvironmental changes in lakes. Lake Lucerne was selected for this study based on the initial identification of ubiquitous GDGTs in surface sediments (Blaga et al., 2009) and the potential of this lake as a recorder of regional climate since the last glacial maximum (Schnellmann et al., 2006). The lake was sampled at a monthly resolution, using in situ lake-water filtration of surface and deeper waters, and sediment traps deployed at two depths. In this way we determined when and where the different GDGTs are produced, transported through the water column, and ultimately buried in the sediment. Core and intact polar lipids in the collected particulate organic matter from the water column and sediment traps were compared to the CLs of the sediment to estimate selective decomposition. The assessment of spatial and temporal variability proved to be important for evaluating the proxy potential of the GDGTs.

4.2. Materials and methods

4.2.1. Setting

Lake Lucerne is an oligotrophic lake at the border of the Alps (434 m above sea level, 113 km^2 surface area, 104 m mean depth, 3.4 years residence time) situated in Central Switzerland.

As an oligomictic lake a complete overturn occurs on average every six years. The lake has seven subbasins, separated by subaquatic sills formed by glacial bedrock-erosion and moraine deposits. The five subbasins that form a chain from the main inflow to the outflow (Lake Uri, Treib Basin, Gersau Basin, Vitznau Basin and Chrüztrichter Basin) (Fig. 1) are fed by four major alpine rivers: Reuss, Muota, Engelberger Aa and Sarner Aa, which drain a large part of the limestone and granite bedrock dominated catchment (2124 km^2) and at the same time provide ~80% of the lake's total water supply (109 m^3 s^{-1}) (Schnellmann et al., 2002). The study site Fig. 1) is located at the edge of the Chrüztrichter Basin that is characterized by a complex bathymetry as a result of its geomorphologic evolution, which was influenced by the nearby front of the alpine naps and two major confluencing alpine glaciers. The sediment trap was positioned at each deployment within a narrow area on the moraine-built sill separating the Chrüztrichter Basin from the Vitznau Basin in water depths between 80 to 90 m. The sediment core was taken in the same area at a water depth of ~90 m. Limnological parameters (temperature, oxygen, conductivity, pH profiles) were measured each time the sediment traps were deployed and recovered at the sampling site using a Conductivity-Temperature-Depth recorder (Seabird CTD SBE-19).

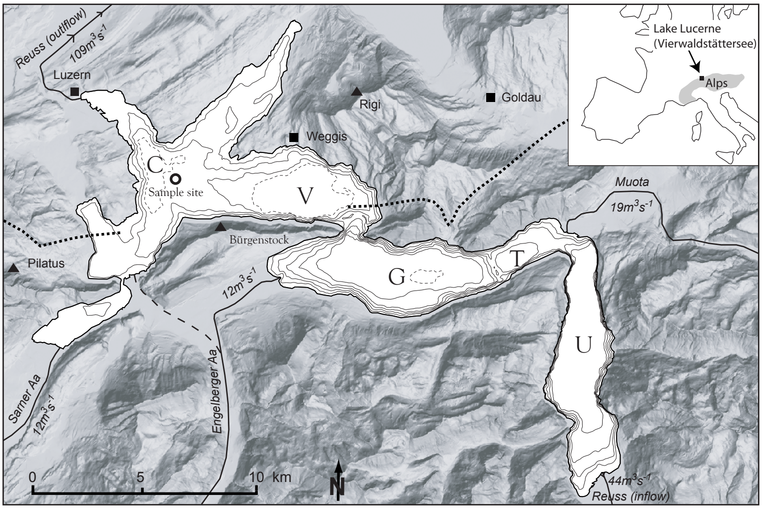

Fig. 1 Location of the sampling site in Lake Lucerne. Capital letters indicate names of sub-basins: C = Chrüztrichter, V = Vitznau, G = Gersau, T = Treib and U = Uri Basins. Major rivers are indicated.

4.2.2. Sample collection

Eight cylinder sediment-traps (height 101cm, ø 18.8cm) were deployed every first week of the month, with four cylinder traps at 42 m water depth and four cylinder traps at 72 m. Three thermistors (Minilog, Vemco, Canada) were attached to the mooring at water depths of 30, 42 and 72 m and logged water temperatures at 10 minute intervals, to study the temperature regime of Lake Lucerne. Sinking particulate organic matter was collected with a monthly resolution, during a 13 months period starting January 2008 and ending March 2009. In March 2008 the sediment trap was recovered later than usual and not immediately re-deployed, to avoid a too short sampling interval. For this reason the sediment trap deployment was continued until end of March 2009, completing a full annual cycle. No preservatives were used in the traps.

After the sediment traps were recovered the overlying water layer was drained and samples were centrifuged at 6500 rpm for 20 min. The centrifuged particles were subsequently kept at -20 °C and freeze-dried after returning to the home laboratory. Particulate matter was weighted after freeze-drying to calculate particle fluxes (g m^{-2} d^{-1}).

Water was filtered through a 0.7 μm ashed glass fibre filter (GFF) (ø 142 mm) using an in situ pump (McLane WTS-LV08) close to the sediment trap site. Samples were taken at 2, 42 and 72 m depth in the water column. The in situ pump filtered between 25 and 175 l, depending on when the capacity of the filter was reached.

A gravity core (111 cm long) was taken from the same site in November 2009. Using marker horizons, a cross correlation of this core with core 4WS00-4P (Schnellmann et al., 2002), taken in close vicinity, was made, indicating that the new core covers the last ~1200 years of sediment deposition.

4.2.3. Sample preparation

A small aliquot of each sediment trap sample and several down-core sediment samples was treated with a solution of HCl (0.5 N, and 6 N respectively) to remove any authigenic carbonate and further analyzed for total organic carbon (TOC) content using a C, N and S Fisons NA 1500 elemental analyzer (EA).

A known aliquot of the freeze-dried sediment collected in the traps was extracted 3 times using an accelerated solvent extractor (ASE; DIONEX2000), with a solvent mixture of dichloromethane (DCM)/methanol (MeOH) 9:1 (vol/vol) at a temperature of 100 °C and a pressure of 7.6 x10^6 Pa for 5 min. The total extracts were rotary evaporated under vacuum and separated over an activated Al_2O_3 column, using hexane/DCM 9:1 (vol/vol) to obtain the apolar fraction and DCM/MeOH 1:1 (vol/vol) for the polar fraction containing the GDGTs. The later fraction was dried under a continuous flow of N_2, ultrasonically dissolved in a mixture of hexane/2-propanol 99:1 (vol/vol) at a concentration of 2 mg/ml and filtered through a 0.45 μm PTFE filter (ø 4 mm) prior to HPLC/APCI-MS analysis.

A new chromatographic method to quantify the distribution of CL- and IPL-GDGTs (Pitcher et al, 2009a) was also applied to the trapped particulate matter. For this purpose another known aliquot of the freeze dried sediment was extracted three times using a modified Bligh-Dyer technique (Bligh and Dyer, 1959). The sample was extracted in an ultrasonic bath for 10 min by using a solvent mixture of MeOH/DCM/phosphate buffer (2:1:0.8 vol/vol/vol). DCM and phosphate buffer were added to give a new volume ratio (1:1:0.9 vol/vol/vol). The methanol-phosphate buffer phase was removed after centrifugation at 2500 rpm for 5 min, and the DCM phase was collected in a round-bottom flask and reduced under a rotary vacuum and dried over a Na_2SO_4 column. The total Bligh-Dyer extract was fractionated over a pre-activated silica gel (60 mesh) with 3 column volumes of hexane-ethyl acetate (3:1 vol/vol) to obtain the CL-GDGT fraction and was then fractionated with 3 column volumes of ethyl acetate followed by 3 column volumes of MeOH to obtain an IPL-GDGT fraction according to methods described previously by Oba et al. (2006) and Pitcher et al. (2009a). The IPL-GDGT fraction was subjected to acid hydrolysis to cleave polar head groups by refluxing in 2 ml of 5% HCl in MeOH (96%) for 3 h. The pH of the cooled solution was adjusted to pH 5 with 2 N KOH-MeOH (1:1 vol/vol). Bidistilled water was added to a final ratio of H_2O-MeOH of 1:1 (vol/vol), and this mixture was washed three times with DCM. Intact polar lipids and CLs were quantified by adding a known amount of C_{46} internal GDGT standard (Huguet et al., 2006) to both the IPL-GDGT fraction (before acid hydrolysis) and the CL-GDGT fraction.

The GFF filters were freeze dried and ultrasonically extracted with MeOH, DCM/MeOH (1:1, vol/vol) and DCM, each three times. The total lipid extracts from the different extraction steps were combined after rotary evaporation and separated over an activated Al_2O_3 column similar to the sediment trap material.

The top 5 cm of the core was sampled continuously into 1 cm slices, continuing deeper in the core with a 10 cm resolution, subsequently analyzing samples with a similar method as the sediment trap material using ASE extraction.

4.2.4. HPLC/APCI-MS

Polar fractions from both sediment traps and water filtrates as well as CL- and IPL-GDGT fractions were analysed using high performance liquid chromatography/atmospheric pressure chemical ionization - mass spectrometry (Agilent 1100 series/Hewlett Packard 1100 MSD), equipped with an auto-injector and Chemstation chromatography manager software according to Schouten et al. (2007). The separation was achieved in normal phase on an Alltech Prevail Cyano column (150mm x 2.1 mm; 3 µm). Injection volume was 10 µl. An eluent consisting of hexane/propanol 99:1 (vol/vol) was used for 5 min to elute the GDGTs isocratically. The flow rate was set at 0.2 ml/min. Ion scanning was performed in single ion monitoring (SIM) in order to obtain higher sensitivity. GDGTs were quantified by integration of the peak areas. Absolute amounts of GDGTs injected on column were quantified by adding a known amount of C_{46} internal GDGT standard. TEX_{86} and BIT indices were calculated according to the following equations by Schouten et al. (2002) and Hopmans et al. (2004):

$$TEX_{86} = \text{GDGT-II+GDGT-III+CREN isomer/GDGT-I+GDGT-II+GDGT-III+CREN isomer} \quad (2),$$

$$BIT = \text{GDGT-V+GDGT-VI+GDGT-VII/CREN+GDGT-V+GDGT-VI+GDGT-VII} \quad (3),$$

where CREN, CREN isomer and I – VII refer to GDGT structures (Blaga et al., 2009, chapter 2).

4.3. Results

4.3.1. Temperature pattern of the water column

Water temperature of Lake Lucerne varied between January 2008 and March 2009 from 4.9 to 21.8 °C, as a function of season and depth (Fig. 2). The lake did not freeze during the winter, and in both the winter of 2008 and 2009, complete water-column mixing was revealed by homothermic conditions of 5.9 °C over the entire water column. Surface waters started to warm up early April 2008. During May 2008 the onset of stratification is observed with a depth temperature gradient starting from the surface. A stable stratification with an epilimnion comprising the upper 15 m was complete by June. Through the year, the mixed layer gradually deepened and reached a depth of 20 - 25 m by the end of October 2008. At the beginning of December 2008 the water body showed first signs of mixing, while in January 2009 a homogeneous temperature of 5.9 °C was again registered.

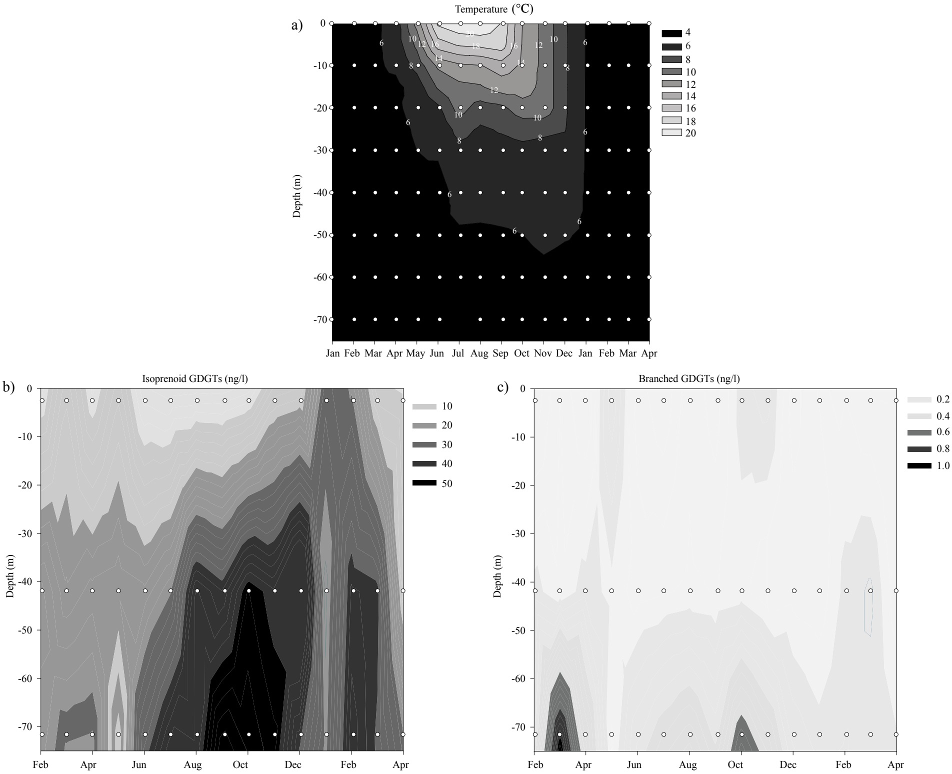

Fig. 2 Contour plots of (a) in situ water temperature measured at different depths during the study period; (b) concentrations of isoprenoid GDGTs in SPM, and (c) concentrations of branched GDGTs in SPM. Sampling grids are indicated with open white circles.

4.3.2. Particle fluxes

The temporal variation of the particulate mass flux determined from the trap deployed at 42 and 72 m is shown in Fig. 3. For the duration of the study, average sediment fluxes were 0.7 and 1.0 g m^{-2} day^{-1}, for the shallow and the deep trap, respectively. For both depths the flux of sinking particulate matter starts to increase early spring, both reaching a first maximum in June, and a second, less pronounced peak in September. After that, fluxes generally decrease towards the winter (Fig. 3). The lower trap shows two additional maxima, one in April 2008, the other at the end of the study in March 2009, both not observed in the mass-fluxes of the upper trap. During the annual cycle mass flux values range between 0.31 and 1.9 g m^{-2} day^{-1} in the sediment trap deployed at shallow depth and between 0.27 and 1.8 g m^{-2} day^{-1} for the deeper trap. The TOC content of the trapped particles varies from 3.8 to 8.8%. Particulate organic carbon fluxes generally mimic total particulate matter fluxes and vary between 0.02 and 0.07 g OC m^{-2} day^{-1} (Fig. 3). The C_{org}/N_{tot} ratio of the descending particles is relatively constant (~7.1) through time as well as between the two trap depths.

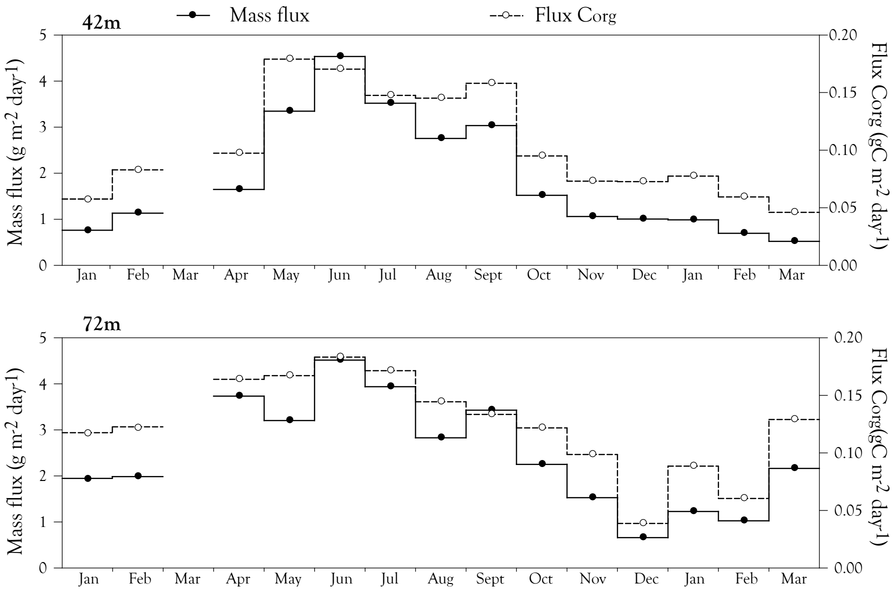

Fig. 3 Annual variation in mass flux of descending particles and organic carbon flux measured in sediment traps deployed at 42 and 72 m in Lake Lucerne.

4.3.3. GDGTs in Lake Lucerne

4.3.3.1. GDGTs in the suspended particulate matter

Isoprenoid and branched GDGT distributions at three different depths in the water column were compared and several differences were observed (Fig. 4a). Crenarchaeol and GDGT-0 dominate at all depths, while the branched GDGTs represent only a minor fraction. In the suspended material collected from 42 m, GDGT-0 was slightly more abundant than at the other two depths. On the other hand branched GDGTs show a contrasting pattern, with higher abundances in the surface waters and at 72 m compared with the material from 42 m. Concentrations of SPM-associated isoprenoid GDGTs in Lake Lucerne vary between 0.6 and 58 ng l^{-1}, while summed branched GDGT concentrations vary between 0.04 and 1 ng l^{-1}. Concentrations of the different GDGTs change through time and differ with sampling depth (Fig. 5). In the SPM from 72 m taken between June and December 2008 highest isoprenoid GDGT concentrations (35 - 60 ng l^{-1}) are observed, with maximum GDGT values in September 2008. Concentrations at 42 m are slightly lower, with maximum concentrations measured between August and December 2008 varying between 40 - 60 ng l^{-1}. In February and March 2009 a second GDGT maximum is observed at both 42 and 72 m. A different temporal evolution of GDGT concentrations is exhibited at the lake water surface compared with the other two depths. Isoprenoid GDGT concentrations at the surface are substantially lower than in the deeper waters, varying between 1 - 30 ng l^{-1}. In March and May 2008 two minor peaks are observed, while maximum concentrations were measured later in the year from November 2008 to March 2009 with the highest concentration in January 2009 at the time of the overturn of the water column (30 ng l^{-1}).

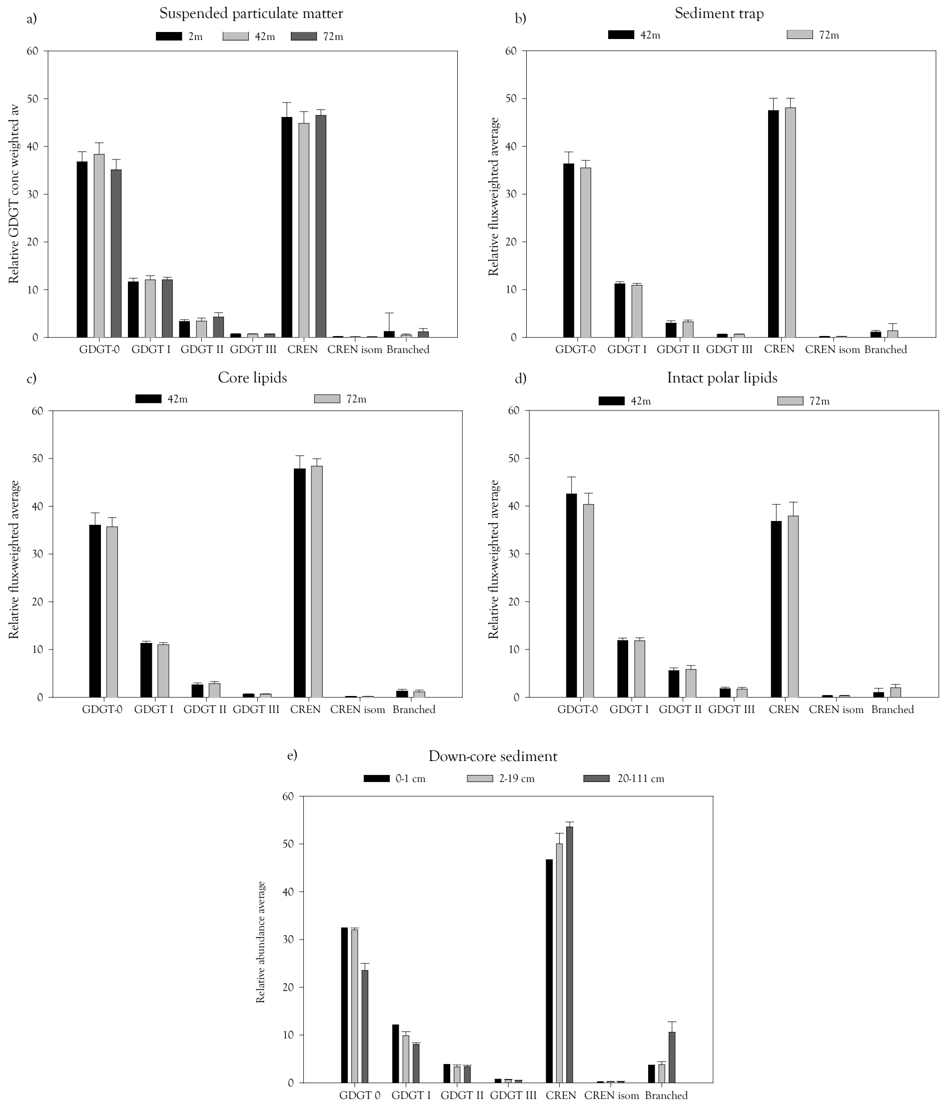

Fig. 4 GDGT distributions showing(a) concentration-weighted average for SPM,(b-d) flux-weighted average of total GDGTs (ASE method; b), CL- and IPL- GDGTs (Bligh-Dyer method; c-d) in sediment trap material, (e) average of specified sediment intervals. Error bars indicate the standard deviation of the average.

The low concentrations of branched GDGTs are also expressed by the low BIT index values, varying between 0.01 and 0.24 at 2 m, 0.005 and 0.02 at 42 m and 0.01 and 0.07 at 72 m water depth (Fig. 6). The TEX_{86} varies between 0.24 and 0.34 at 2 m, 0.22 and 0.30 at 42 m and 0.26 and 0.36 at 72 m depth. The changes observed in BIT and TEX_{86} follow a seasonal pattern; highest BIT values are observed during summer (principally at shallow depth), maximum TEX_{86} values are observed during late summer to autumn.

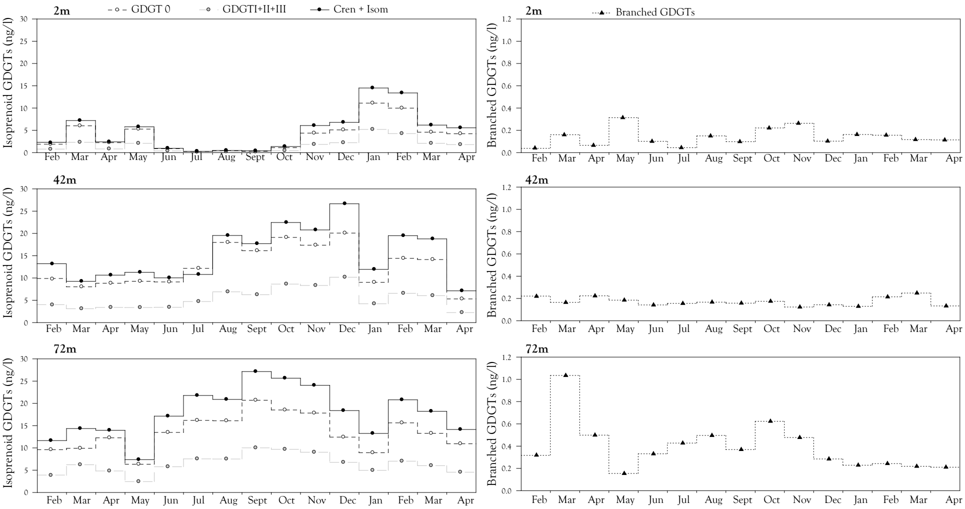

Fig. 5 Annual variation in concentrations of isoprenoid (left panels) and branched (right panels) GDGTs in SPM at 2, 42, and 72 m in Lake Lucerne.

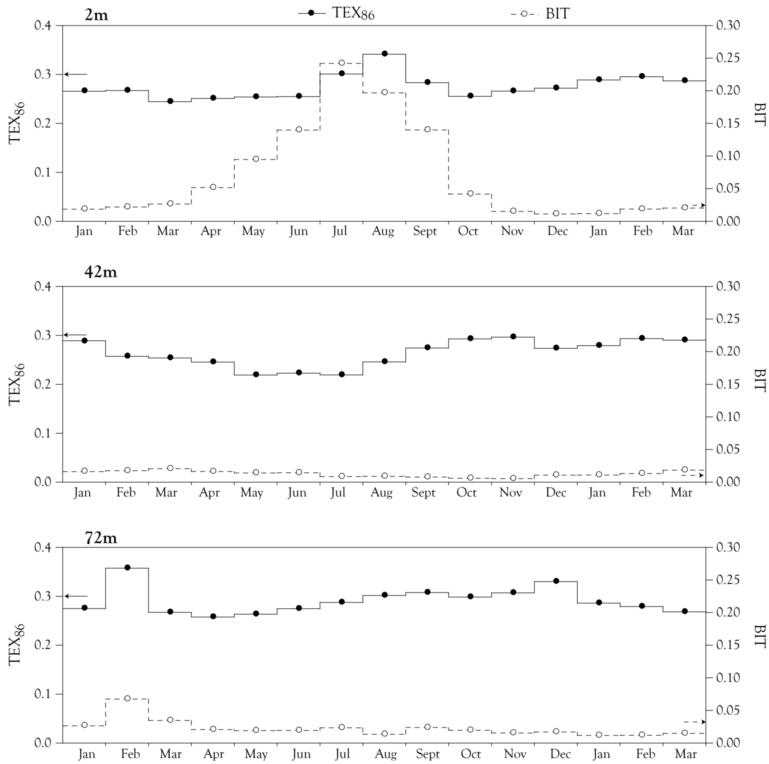

Fig. 6 Annual variation in TEX_{86} and BIT indices in SPM at 2, 42, and 72 m in Lake Lucerne. Arrows indicate indices values determined from the concentration-weighted average.

4.3.3.2. Distribution and fluxes of total GDGTs, CL-, and IPL-GDGTs

The results of the sediment trap study revealed nearly identical distribution for the GDGT in descending particles at different depths (Fig. 4b). The flux-weighted average distribution of GDGTs is dominated by crenarchaeol (48%), followed by GDGT-0 (36%), with branched GDGTs representing only a minor component (Fig. 4b).

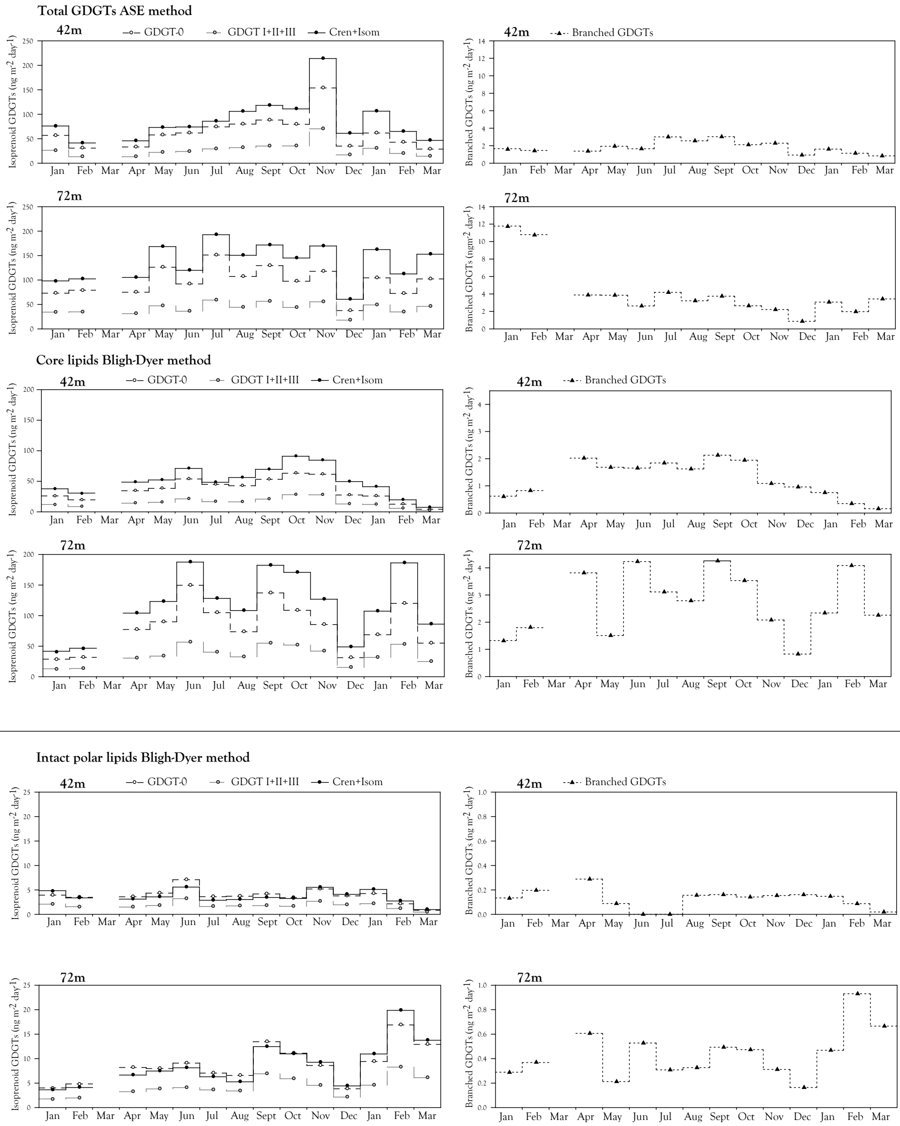

Fig. 7 Annual variation in fluxes of isoprenoid (left panels) and branched (right panels) GDGTs in descending particles at 42 and 72 m in Lake Lucerne. Distinction is made between total GDGTs (ASE method); CL- and IPL-GDGTs (Bligh-Dyer method) (see text for details).

For the trap deployed at 42 m isoprenoid GDGTs fluxes range between 0.08 and 0.4 μg m^{-2} day^{-1}. In the deep trap fluxes are similar and vary between 0.1 and 0.4 μg m^{-2} day^{-1} (Fig. 7). Throughout the study isoprenoid GDGT fluxes remained generally constant in the deep trap, whereas in the shallow trap all isoprenoid GDGT fluxes gradually increase over the year, culminating in a distinct maximum in November 2008. A conspicuous minimum in all isoprenoid GDGT fluxes is observed during December 2008 at both depths. Branched GDGT fluxes are between 0.84 and 3.0 ng m^{-2} day^{-1} in the shallow trap, whereas branched GDGT fluxes measured in the deep trap are between 0.87 and 11.7 ng m^{-2} day^{-1} (Fig. 7). For branched GDGT a distinct high flux is observed for the deep trap in January and February 2008. Overall isoprenoid GDGTs make up 99% of the total GDGT flux, the branched GDGT represent only a minor component.

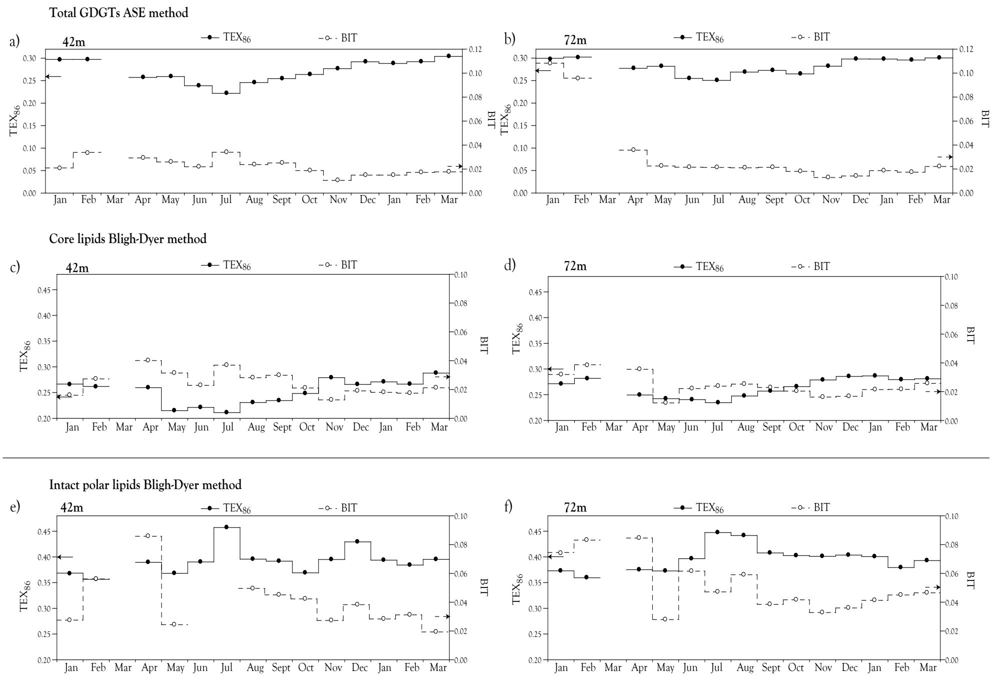

Fig. 8 Annual variation in TEX_{86} and BIT indices of GDGTs present in descending particles at 42 (left panels) and 72 m (right panels) in Lake Lucerne. Distinction is made between total GDGTs (ASE method; a-b); CL- and IPL- GDGTs (Bligh-Dyer method; c-f) (see text for details). Arrows indicate indices values determined from the flux-weighted average.

The relatively low amounts of branched GDGTs are reflected by the low BIT values, which varied from 0.01 to 0.03 for the shallow trap and from 0.01 to 0.11 for the deep trap (Fig. 8a, b). The TEX_{86} values for the material collected in the upper sediment trap were on average 0.27 and almost identical values (average of 0.28) were observed for the deep trap.

Using a modified Bligh-Dyer extraction method and subsequent fractionation technique (Pitcher et al., 2009a), CL- and IPL-GDGTs were analyzed in the material collected in the sediment traps. Analyses by HPLC-MS revealed subtle differences in the distribution of both CL- and IPL-GDGTs (Fig. 4c, d). Crenarchaeol, followed by GDGT-0, are the most abundant CL-GDGTs at both depths and, as observed for the total GDGTs (Fig. 4b); the branched GDGTs represent only a minor fraction. Core lipids extracted using a Bligh-Dyer method and total GDGTs determined by ASE method, have an identical distribution of GDGTs. In contrast to the CL-GDGTs, GDGT-0 was slightly more abundant in the flux-weighted average distribution of IPL-GDGTs (40 - 43% of total GDGTs) than crenarchaeol (ca. 37%) (Fig. 4). Fluxes of CL-derived isoprenoid GDGTs are higher at 72 m with fluxes varying between 0.08 and 0.4 μg m^{-2} day^{-1} compared with 0.01 and 0.2 μg m^{-2} day^{-1} at 42 m (Fig. 7). The fluxes of the IPL-derived isoprenoid GDGT are consistently more than one order of magnitude lower than the CL-GDGT fluxes and show similar patterns but with higher fluxes at 72 m (Fig. 7). CL- and IPL- branched GDGTs fluxes are very low (0.2 - 4.3 ng m^{-2} day^{-1} and 0 - 1 ng m^{-2} day^{-1}, respectively).

The flux-weighted averaged BIT value determined for the CL-GDGTs is 0.027 for the shallow trap and 0.023 at 72 m, while the TEX_{86} values are 0.23 and 0.25, respectively (Fig. 8c, d). IPL-GDGT based BIT values average to 0.027 (42 m) and 0.05 (72 m) and TEX_{86} average value is 0.4 at both sampling depths (Fig. 8e, f), substantially higher than for the CL-GDGTs and total GDGTs.

4.3.3.3. GDGTs in sediments

Sixteen sediment intervals from an ~1 m long core were analyzed for their total GDGT distribution and content (Fig. 9). A slight change in the GDGT distribution can be observed down core. For surface sediments the GDGT distributions are dominated by crenarchaeol

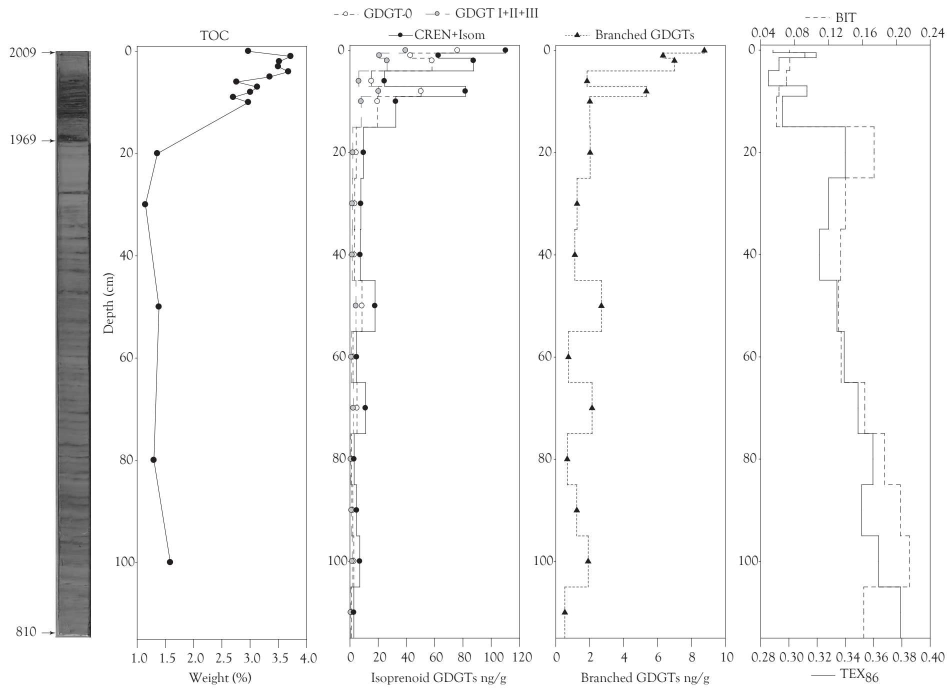

Fig. 9 Down-core profiles (0-100 cm) of TOC, concentrations of isoprenoid and branched GDGTs and TEX_{86} and BIT indices. The photograph at the left shows the core with the darker sediments at the top representing deposition of sediments enriched in TOC during the eutrophic period of the lake (last 45 years of deposition).

(52%) followed by GDGT-0 (27%), and with increasing depth there is a shift towards higher relative abundances of the former over the latter. Sediments from the top 10 cm are characterized by high concentrations of isoprenoid GDGTs varying between 0.1 and 110 ng g^{-1} compared with the deeper part of the core where concentrations barely reach 18 ng g^{-1} (Fig. 9). A similar down core shift towards higher abundances in the last 80 cm of the core can be observed for the branched GDGTs. Relatively low concentrations of branched GDGTs (0.3 - 4.1 ng g^{-1} in top 10 cm and 0.1 - 1.3 ng g^{-1} in the rest of the core) are observed also in the sediments, also revealed by the low BIT index which ranges between 0.06 and 0.2 (Fig. 9). The values for TEX_{86} increase from an average of 0.29 in the top 10 cm to an average of 0.34 in the deeper part of the core.

4.4. Discussion

4.4.1. Crenarchaeotal GDGTs in Lake Lucerne

The distribution of isoprenoid GDGTs in SPM, descending particles, and the surface sediments of Lake Lucerne are almost identical (Fig. 4), indicating one dominant source for these components. This distribution, dominated by crenarchaeol, and to a lesser extent by GDGT-0, strongly suggests that the isoprenoid GDGTs are derived from Group 1 Crenarchaeota. These Archaea are so far the only organisms demonstrated to produce crenarchaeol (Pitcher et al., 2009c and references therein). Group 1 Crenarchaeota were also shown by molecular ecological studies to be important members of the prokaryotic community of Lake Lucerne (Vissers et al., in prep.).

Changes in the concentrations of isoprenoid GDGTs in the SPM likely reflect the dominant niches of the aquatic Crenarchaeota over time and space. Isoprenoid GDGTs in the suspended organic matter generally have highest concentrations in the deepest part of the water column (Fig. 2b). Concentrations of GDGT were consistently lower in the surface waters, except for winter 2008 and 2009 when the water column mixed and Crenarchaeotal cells were probably transported from deeper waters to the surface. This indicates that the main niche for Crenarchaeota producing the isoprenoid GDGTs is the deeper part of the water column. In the SPM measured in the deeper water column (both at 42 and 72 m), the isoprenoid GDGTs concentrations reveal a seasonal pattern with an increase in concentration during the late summer and autumn (Figs. 2 and 5). The production of isoprenoid GDGTs by Group 1 Crenarchaeota in the deeper part of the water column of the lake, and the seasonal changes therein, are in good agreement with the physiology of these organisms. They are thought to be predominantly nitrifiers (Konneke et al., 2005; Wuchter et al., 2006; Pitcher et al., 2009a), depending on the release of ammonium from the decomposition of particulate organic nitrogen, predominantly derived from phytoplankton communities in the surface waters of the lake.

The 14-month sediment trap study revealed a change from lower to higher biological activity over the annual cycle as reflected by relatively high mass fluxes during summer (Fig. 3). Maximum isoprenoid GDGT fluxes occurred shortly after the peak in mass flux (Fig. 7). This implies that the isoprenoid GDGTs are not transported to the sediment as part of the regular lake algal bloom and associated authigenic carbonate precipitation, but rather follow such blooms with a time lag. This is in good agreement with our interpretation on the basis of the SPM data that a deeper residing community of Crenarchaeota depends on the delivery of ammonium from decaying organic matter produced by phytoplankton in the surface waters. In Lake Challa a high flux of isoprenoid GDGTs also occurred shortly after a peak in the organic carbon flux (Sinninghe Damsté et al., 2009). In contrast to our study, however, crenarchaeol fluxes in Lake Challa remained much lower during the rest of the year.

Quantification of the GDGTs in the IPL- and CL-GDGT fractions showed that the contribution of fossil GDGTs to the total GDGT fluxes is always dominant; i.e. the IPL isoprenoid GDGTs represent only 12% of the total isoprenoid GDGTs. This indicates that the isoprenoid GDGTs associated with particles descending through the water column of Lake Lucerne primarily originate from dead Crenarchaeotal cells. The slightly higher flux of isoprenoid GDGTs at 72 than at 42 m is probably due to a thriving community of Crenarchaeota at mid-water depth (Fig. 2). Also, the higher concentration of IPL isoprenoid GDGTs in the trap deployed at 72 m compared to that at 42 m, suggests in situ production at mid-water depth of GDGTs by Crenarchaeota. The Bligh-Dyer extraction method revealed another difference in CL- and IPL-GDGT distribution in descending particles. The IPL-GDGT distribution is characterized by a slightly higher GDGT-0 relative abundance than in the CL-fraction (Fig. 4d). This likely indicates a minor additional source for GDGT-0 in the IPL-fraction, probably through methanogens residing in anoxic niches of the descending particles. Such a contribution of GDGT-0 in deeper waters from anaerobic Archaea was also evident in the permanently stratified and anoxic Lake Challa (Sinninghe Damsté et al., 2009) but was significantly more substantial than in Lake Lucerne. In any case, this additional source for GDGT-0 has to be minor since the crenarchaeol to GDGT-0 ratio is identical in the water column and the surface sediment.

The sedimentary isoprenoid GDGTs also do not reveal a substantial contribution of methanogens (producing predominantly GDGT-0) since relative GDGT-0 concentrations decrease instead of increase down-core (Fig. 4e). Substantial changes in the concentration of isoprenoid GDGTs down core are observed (Fig. 9). Although this may partially be due to diagenesis, it is more likely that this relates to changes in the lake (eu)trophic status.

Between 1955 and 2001, Lake Lucerne went through four periods of varying trophic state: an oligotrophic period before 1969; a period of accelerated eutrophication (1970-1977) with total phosphorus (TP) concentrations reaching 30 mg m^{-3} and nitrate-nitrogen (N-NO_3) 500 mg m^{-3}; a moderate mesotrophic period (1978-1988) when TP values decreased but N-NO_3 increased and a fourth period of growth limiting P concentration (1989-2001) with TP concentrations between 5 and 10 mg m^{-3} and N-NO_3 concentrations between 600 and 700 mg m^{-3} (Bürgi and Stadelmann, 2002). The transitions between the four periods are clearly revealed in the short core by the transition from greyish sediments with a lower TOC, to finely-laminated black coloured sediments with a higher TOC content (Fig. 9). Lake Lucerne is now P limited as it was before the eutrophication period but the N concentration has tripled and consequently the present-day oligotrophic conditions in the lake are different from former conditions. This has a strong impact on the species assemblages, which also differ from the previous ones. Due to the increase in nutrients the shift in species community was rapid but during the re-oligotrophication the response time is longer and it takes much longer for the original (i.e. before 1969) oligotrophic community to re-establish (Bürgi and Stadelmann, 2002). The present oligotrophic structure of the lake characterized by an oxygenated water column with relatively high N concentrations and may thus well be capable to support a higher density of crenarchaeotal cells compared to the microbial community existing prior to 1969 in the lake.

Comparing the GDGT concentration in the water column with the GDGT flux captured in the sediment traps, shows that on average 20% of the SPM standing stock of GDGTs is exported annually to the sediment. The burial efficiency of the GDGTs can be calculated by comparing the flux in the sediment trap at 72 meter, which is about 18 meters above the lake floor, with the GDGT accumulation rate ($GDGT_{acc.\ rate}$) in the sediment. The burial efficiency (BE) was calculated according to:

$$BE = GDGT_{acc.\ rate} / \text{Flux of GDGT} * 100\% \qquad (4).$$

Because the lake is presently restored to an oligotrophic state again, we compared present day GDGT fluxes with the GDGT accumulation rate before the lake became eutrophic. Although we acknowledge that the current oligotrophic state is different from that before the eutrophication of the lake, with probably slightly different crenarcheotal production, it is not possible to compare the GDGT accumulation rates at the top of the sediment because this would not include the ongoing sedimentary degradation. Moreover bioturbation at the top of the sediment ad-mixes organic rich sediments and GDGTs originally deposited during the eutrophic state of the lake. The accordingly calculated average BE of the GDGTs is ca. 18%, which is similar to oxic marine sediments (Sinninghe Damsté et al., 2002b). No appreciable differences are observed in BE between individual GDGTs.

4.4.2. Consequences for the interpretation of TEX_{86} in Lake Lucerne

TEX_{86} values for SPM are similar to those observed in the trapped particles, with a flux weighted average value of 0.27, and the average TEX_{86} value of the surface sediment of 0.29. This is consistent with the almost identical contributions of isoprenoid GDGTs in these different compartments (Fig. 4). TEX_{86} values based on isoprenoid GDGTs present as IPL are slightly higher (aprox. 0.35 - 0.40; Fig. 7), probably due to the fact that there is a minor contribution of other Archaea to this fraction. A detailed study of Lake Challa has revealed that a deep water or sedimentary population of Archaea may seriously impact TEX_{86} values (Sinninghe Damsté et al., 2009). However, in Lake Lucerne this contribution is so minor that it apparently does not affect TEX_{86} values to a significant extent, as the TEX_{86} values in the surface sediments are similar to those of SPM and sedimenting particles.

TEX_{86} values of ~0.28 translate into a relatively low water temperature of ~2 °C, if we apply the lake core top calibration of Powers et al. (2004, 2009). This temperature has a relatively large error since it is at the low end of the calibration curve (Powers et al., 2009) and as shown for marine systems by Kim et al. (2008) the TEX_{86} calibration for temperatures <10 °C is non-linear. Mean annual lake surface temperatures for Lake Lucerne are ~11 °C (Bührer and Ambühl, 2001) and during the study period fluctuated between 6 and 22 °C (Fig. 2a). This suggests a large discrepancy between the TEX_{86} – inferred and actual temperature. However, our SPM data indicate that most of the Crenarchaeota reside deeper in the water column (Fig. 2b). The temperature of the water at this depth fluctuates between 5 and 8 °C over the year (Fig. 2a) and this is consistent (within the calibration error) with the TEX_{86} – inferred temperature. Consequently, these large changes in the temperature of the surface waters would not influence the TEX_{86} values in this lake system to a significant extent.

This is substantially different from what is typically seen in marine systems where TEX_{86} was found to reflect upper water temperature only, even though Crenarchaeota occur throughout the water column (Wuchter et al., 2005), because grazing processes effectively only transfer particles from the surface ocean to the sediment and to a much lesser degree from deeper waters (see also Wakeham et al., 2003). However, the surface mixed layer in the ocean is at least 100 m thick, whereas in lakes it is much smaller. This explains why there can be such a large offset between TEX_{86} – inferred temperatures and mean surface lake temperatures.

The top few centimeters of the core collected from the study site show average TEX_{86}

values of ca. 0.3, in line with the water column observations. However, below the interval characterized by elevated organic matter contents deposited during the time when the lake was eutrophic, TEX_{86} values are about 0.34 (Fig. 9), which corresponds, using the calibration by Powers et al. (2009), to a slightly higher average lake temperature of about 5 °C. Since lake temperatures before the 1970's were likely not higher (Bührer and Ambühl, 2001) than in the period of 1980 to today, the eutrophication phase of Lake Lucerne clearly influenced also the archaeal community in such a way that it affected the distribution of GDGTs and thus also TEX_{86}. It may be that the reduced primary production before the eutrophication led to Crenarchaeota residing, on average, in shallower waters and recording slightly higher TEX_{86} values. The GDGT distribution in the surface sediments is similar to that of sediments deposited during the eutrophic state of the lake (Fig. 4). This suggests that the archaeal community in the present-day re-oligotrophic state (with only P limitation but not the former multi-nutrient limitation) is still occupying the same niche as the eutrophic state of the lake the present and, consequently is recoding the same TEX_{86} values.

4.4.3. Branched GDGTs and BIT as recorders of soil organic matter input

Branched GDGTs represent only a small fraction of all GDGTs in the SPM, settling particles, and sediments. This is consistent with a previous study in which sediments from four basins of Lake Lucerne were analyzed for their GDGT distribution (Blaga et al., 2009), showing that the relative abundance of branched GDGTs was lowest in the Chrüztrichter Basin. This probably reflects the position of this basin relative to the main sites of river inflow (Fig. 1). Recent studies suggest that in situ production of branched GDGTs in marine sediments (Peterse et al., 2009) and in lake waters and sediments (Sinninghe Damsté et al., 2009, Tierney and Russell, 2009) cannot be excluded as a source in addition to input from soil erosion by run-off. The observed 1 to 2 orders of magnitude higher concentration of branched GDGTs in the deeper water SPM of Lake Challa suggested production in the water column (Sinninghe Damsté et al., 2009), whereas the higher branched GDGT concentration of Lake Towuti sediments compared to its tributaries and surrounding soils suggested either water column or in-sediment production (Tierney and Russell, 2009).

In Lake Lucerne the concentrations of branched GDGTs in the SPM at 0 and 42 m are somewhat lower compared to that at 72 m but this difference is only marginal. The maxima in branched GDGT concentrations at 72 m are not observed at the more shallow sampling depths (Figs. 2 and 5). This could be caused by deep water in situ production of branched GDGTs but also by resuspension events (the surface sediments contain higher relative amounts of branched GDGTs) or lateral advection of water masses containing relatively higher amounts of branched GDGTs, possibly derived from incoming rivers transporting soil-derived GDGTs. As branched IPL-GDGTs may be considered markers for the in situ microbial production, their mere presence (Fig. 7) in descending particles may be considered proof for in situ production, although this is based on the presumed instability of IPLs (which strongly depends on the type of IPL; Harvey et al., 1986). Still, IPL-branched GDGTs barely contribute 10% to the total (CL plus IPL) branched GDGTs, suggesting a predominant fossil origin for the branched GDGTs. Since the branched GDGT lipid composition in the suspended particulate matter was not extracted with the Bligh-Dyer method, the observed increase in branched GDGTs during the spring and autumn months in the surface-water, cannot be assigned confidently to either in situ production or allochtonous sediment or soil input.

Our results clearly show that the most common GDGTs are isoprenoidal, which is reflected also in the low BIT values. For SPM at 42 m and 72 m the index values are low for the entire duration of the study (>0.02), while at the lake surface slightly increased values (>0.07) are observed. Higher values in the surface waters are recorded between May and October, coinciding with the lowest concentrations of isoprenoid GDGTs. The low crenarchaeol production in the surface waters are the most likely cause for the higher BIT values rather than in situ production of branched GDGTs in surface waters. Although these higher BIT values of surface water SPM were also recorded in the material recovered from the sediment traps, due to the low particle flux at the time, it had only a small impact on the flux-weighted average. Clearly, the BIT is determined by the annual cumulative GDGT flux.

The BIT measured in the first centimeters of the sediment core was slightly higher compared to the particulate organic matter and the material collected in the sediment traps. This suggests that sporadic events, not captured by our sampling period, provide an additional source of branched GDGTs to the lake sediments, thus influencing the ratio between isoprenoid and branched GDGTs. Such events are more likely related to the sudden influx from soil-derived branched GDGTs than in situ production. Further down-core, prior to the 1960's-1980's eutrophication period, higher BIT values are observed. At that time also the concentrations of isoprenoid GDGTs are relatively low, which could explain the higher BIT values, since the ratio is based on relative concentrations. In situ bacterial production of branched GDGTs in the lake is, however, also expected to be stimulated by the higher fluxes of organic matter at this time, increasing accumulation of branched GDGTs. The fact that the concentrations of branched GDGTs only increased marginally at this time and that the BIT was, consequently, much lower suggests that BIT values in the sediments are mainly controlled by the input of soil derived branched GDGTs.

4.5. Conclusions

Our study reveals both seasonal and vertical changes in isoprenoid and branched GDGT concentrations and fluxes although the distribution of GDGTS is remarkably constant. In situ production of isoprenoid GDGT, by Group 1 Crenarchaeota, takes place mainly in the deeper part of the water column and is influenced by seasonal variability in primary production from the upper layers. Branched GDGT membrane lipids are also present in the water column and sediments of Lake Lucerne but in significantly lower concentrations and fluxes. Comparing TEX_{86} values from the water column and the surface sediment shows similar values, which implies that crenarchaeotal GDGTs produced in lake water dominate the sedimentary GDGTs. Although the TEX_{86} values show seasonal changes, they do not reflect recorded annual surface water temperature changes. The SPM data indicate that most of the Crenarchaeota reside deeper in the water column. The temperature of the water at this depth fluctuates between 5 and 8 °C over the year and this is consistent (within the calibration error) with the TEX_{86} – inferred temperature. Down core a change in TEX_{86} values is observed that coincides with the change in trophic state of the lake (from eutrophic to oligotrophic), suggesting that the niche of the archaeal community, and consequently TEX_{86} changed. During this eutrophication period the BIT was low due to enhanced production of crenarchaeol, indicating that the flux of branched GDGTs was not affected by the trophic state and also that the branched GDGTs in Lake Lucerne are primarily derived from soil erosion in the catchment of the lake.

Acknowledgements

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Chapter 5

Late Glacial to Holocene temperature variability of Lake Lucerne (Vierwaldstättersee, Switzerland)

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We applied the TEX_{86} temperature proxy to a sediment core from Lake Lucerne (Vierwaldstättersee) to reconstruct in almost decadal resolution temperature changes during the Late Glacial Interstadial, the Younger Dryas and the Early Holocene (~14,600 to 10,600 cal. yr BP). The TEX_{86} temperature record suggests a sequence of shifts during the late glacial period that strongly resemble the shifts in $\delta^{18}O$ values from the Greenland ice core record. The TEX_{86}-reconstructed lake temperature record indicates a step-wise pattern of climate changes across the studied interval with a shift from colder to warmer temperatures at the onset of the late-glacial interstadial, followed by an abrupt cooling at the onset of Younger Dryas and a rapid warming from 5.5 to 9 °C at the Younger Dryas/Holocene transition within less than 200 years. These results suggest a substantial thermal response of the Alpine region to the varying conditions during the Interstadial and quick shifts at the onsets of the Younger Dryas and the Holocene.

5.1. Introduction

The Late Glacial period was characterized by large and rapid changes in temperature and precipitation (e.g. Taylor et al., 1993; Birks and Ammann, 2000, Bard, 2002, Denton et al., 2005, EPICA 2006) marking the transition from the Last Glacial Maximum (LGM) to the Early Holocene. Most reconstructions of past temperatures focus to date on the Greenland and Antarctic ice cores and on marine records. In contrast, relatively little is known on how temperatures of the continental interiors fluctuated. Lake sediments provide an important archive of past changes in environmental conditions. Palaeoclimatic studies focusing on the last deglaciation showed unstable climatic conditions in Central Europe, based on correlations of isotope records, pollen, cladoceran and chironomids from lakes in Germany and Switzerland with the Greenland isotope records (e.g. von Grafenstein et al., 1998, 1999, Ammann et al., 2000, Lotter et al., 1992, 2000, Schwander et al., 2000, Heiri and Lotter, 2005). The reconstructed amplitude of the changes in July/summer temperature in Central Europe during the shifts from the Oldest Dryas to the Interstadial (i.e.Bølling/Allerød), from the Interstadial to the Younger Dryas, and finally from the Younger Dryas to the Holocene are believed to range between 3 and 6 °C (e.g. Coope et al., 1998, Lotter et al., 2000). Ostracod oxygen stable isotope signatures from perialpine lake sediments indicate that the annual mean air temperature at the onset of the Younger Dryas decreased by 5 °C, while the transition to the Holocene is marked by a rapid increase of 7 °C (Schwalb, 2003). From previous studies it is evident that reconstructing temperature and precipitation changes from continental interiors crucially depends on the availability of sensitive and well-calibrated proxies that can be applied to these records.

Schouten et al. (2002) introduced the TetraEther indeX of lipids with 86 carbons (TEX_{86}) as a paleotemperature tool for reconstructing sea surface temperature. Glycerol dialkyl glycerol tetraethers (GDGTs), with up to eight cyclopentane moieties, are major components of the membrane lipids produced by several groups of Archaea (de Rosa and Gambacorta, 1988). By changing the number of cyclopentane moieties of these lipids, adjustments are made in membrane fluidity as a response to fluctuations in temperature (Gliozzi et al., 1983). This temperature response of a specific group of aquatic Archaea, the so-called Group 1 Crenarchaeota, was quantified in TEX_{86} (Schouten et al., 2002). In order to calibrate the proxy, initially, an empirical correlation was established between TEX_{86} values of sediment core tops, from a variety of geographical locations, and annual mean sea surface temperatures. A more extensive, global calibration of the TEX_{86} paleothermometer was recently established by Kim et al. (2008) analyzing a much larger set of globally distributed core-top sediments. Comparing TEX_{86} values with sea surface temperatures of different seasons and water depths showed that the correlation is strongest with mean annual temperatures from the upper mixed layer.

Focusing on a number of worldwide spread lakes, Powers et al. (2004, 2009) showed that the archaeal membrane lipid based proxy can also be applied to freshwater sediments. However, in a survey of a large number of European lakes, Blaga et al. (2009) showed that not all lakes are suitable for a TEX_{86}-based temperature reconstruction. Moreover, this study established that the TEX_{86} proxy is primarily applicable to large lakes with a relatively high isoprenoidal GDGTs production compared to the input of soil-derived branched GDGTs (Hopmans et al., 2004). The calibration based on lacustrine core tops was similar to that reported by Schouten et al. (2002) for the marine environment.

On the basis of high isoprenoidal GDGT concentrations and limited input of terrestrial GDGTs (Blaga et al., 2009), Lake Lucerne (Vierwaldstättersee) was selected as a suitable lake for reconstructing past temperatures. We have recently performed a seasonal study of GDGTs in Lake Lucerne and determined concentrations of GDGTs in suspended particulate matter, determined fluxes of GDGTs in descending particles and determined GDGT distributions in surface sediments (Blaga et al., 2010). This revealed that the isoprenoid GDGTs in sediments are predominantly derived from Group I Crenarchaeota living in the deeper waters and that the TEX_{86} temperature signal reflects the annual mean temperature of the lake water at ca. 50 m below the surface. The aim of this paper is to contribute to a better understanding of the development of continental temperatures during the Late Glacial and the Early Holocene transition (~14,500 – 10,600 cal. yr BP) by applying the TEX_{86} proxy to a well-dated Lake Lucerne sedimentary record. We present an organic geochemical reconstruction of past absolute mean annual lake temperatures, across the Late Glacial period.

5.2. Material and methods

5.2.1. Lake Lucerne and its sediment record

Lake Lucerne (Vierwaldstättersee) is a peri-alpine, fjord-like lake of glacial origin (434 m a.s.l.) located in Central Switzerland (47°01'N, 8°24'E) at the northern alpine front. Its total surface area is 116 km^2. The entire Lake Lucerne consists of seven sub-basins morphologically separated by sub-aquatic sills formed by the glacial bedrock-erosion and moraine deposits. Five of these basins form a chain from main inflow to outflow: Lake Uri, Treib basin, Gersau basin, Vitznau basin and Chrüztrichter Basin (Fig 1). The basins of Lake Lucerne are fed by four major alpine rivers (Reuss, Muota, Engelberger Aa and Sarner Aa) that drain a large part of the catchment (2124 km^2) and at the same time provide ~80% of the lake's total water supply (109 $m^3 s^{-1}$) (Aeschbach-Hertig et al., 1996). All but one basin are characterized by elongated shapes, relatively steep slopes and flat intermediate basin plains. The lake's complex

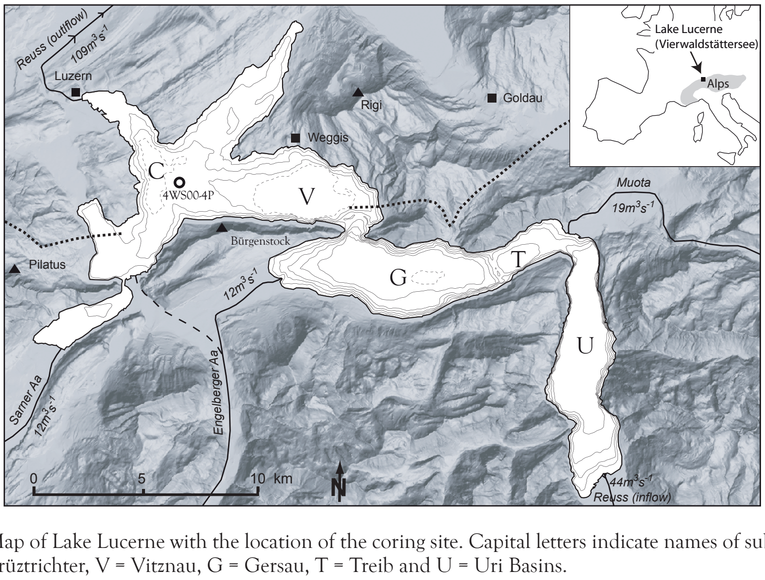

Fig. 1 Map of Lake Lucerne with the location of the coring site. Capital letters indicate names of sub-basins: C = Chrüztrichter, V = Vitznau, G = Gersau, T = Treib and U = Uri Basins.

shape and morphology result from efficient glacial erosion along weak zones associated with the regional geology. In this study we will concentrate on a core from the sill separating the Chrüztrichter from the Vitznau Basin (Fig. 1), which are the two last basins in the chain and most distant to the major river inflows. This sill is formed by a submerged moraine that was created by the confluence of two major alpine glaciers (Hantke, 2003). The site of the core is located north of the Northern Alpine Front in an area with a molassic substratum consisting mostly of sandstones and conglomerates. On the basis of the analysis of GDGT distributions in several down-core samples from this location, Blaga et al. (2009) showed that the input of soil organic matter, based on the Branched versus Isoprenoid Tetraether (BIT) index, is limited at site excluding the influence of allochthonous GDGTs.

In a study that investigated mass-movement processes and reconstructed the prehistoric mass-movement and earthquake history (Schnellmann et al., 2004, 2006) a series of long piston cores located along seismic profiles were retrieved from Lake Lucerne. This allowed us to select an ideal site with a continuous sedimentary record, avoiding the influence of large mass-movement deposits. Sediment core 4WS00-4P (825 cm length) was collected in 2000, on top of the subaquatic hill in the Chrüztrichter Basin (Fig. 1) at a water depth of 95 m, using a Kullenberg-type gravity piston corer. The core was split in 1 m-long sections and measured regarding the petrophysical properties of the sediments (P-wave velocity, gamma-ray density, and magnetic susceptibility), photographed and described macroscopically. The basal part of the studied section (625 - 825 cm) consists of very thinly laminated, light-gray to yellowish mud, changing gradually into laminated, medium to light-gray mud with a low organic matter content.

To determine the age of different points in the core, plant remains were used for AMS radiocarbon dating (Schnellmann et al., 2002). Preparation and pretreatment of sample material for radiocarbon dating was carried out by the ^{14}C laboratory of the Department of Geography at the University of Zurich (GIUZ). The dating itself was done by AMS (accelerator mass spectrometry) with the tandem accelerator of the Institute of Particle Physics at ETH Zurich. Furthermore, the Laacher See Tephra (LST) could be identified (Schnellmann et al., 2002), that was radiocarbon-dated by Friedrich et al. (1999). The last two sections (8-9) of core 4WS00-4P were sub-sampled in 1 cm slices, generating 200 individual samples for GDGT analysis.

5.2.2. GDGT analysis

Freeze-dried and ground samples of 3 to 9 g were extracted using an Accelerated Solvent Extractor 200 (ASE 200, DIONEX) with a mixture of dichloromethane (DCM) and methanol (MeOH) (9:1, vol/vol) at 100 °C and 7.6 x 10^6 Pa. The total extract was concentrated using rotary vacuum evaporation. The extract was subsequently dried under a gentle flow of nitrogen. The dried extract was re-dissolved in a mixture of hexane:DCM 9:1 (vol/vol) and applied over a column filled with activated alumina, where the apolar and polar compounds were sequentially eluted with hexane:DCM 9:1 (vol/vol) and DCM:MeOh 1:1 (vol/vol). The polar fraction was dried under a N_2 flow, ultrasonically dissolved in a hexane:2-propanol 99:1 (vol/vol) mixture at a concentration of 2 mg/ml and filtered through a 0.45 µm PTFE filter (ø 4 mm) prior to HPLC-MS analysis.

The analysis was performed with a HP 1100 series Liquid Chromatography–Mass Spectrometer (LC-MS) equipped with an auto-injector and ChemStation chromatography manager software, using a procedure modified from Hopmans et al. (2000) and Schouten et al. (2007). Separation was achieved on a Alltech Prevail Cyano column (2.1 x 150 mm; 3 μm) maintained at 30 °C. For the first five min, elution was isocratic with 90% A (hexane) and 10% B (hexane:isopropanol 9:1 vol/vol), followed by a linear gradient to 16% B for 34 min. The injection volume of the sample was 10 μl. To detect the different GDGTs, single ion monitoring of $[M+H]^+$ was used (Schouten et al., 2007). TEX_{86} and BIT indices were calculated according to the following equations by Schouten et al. (2002) and Hopmans et al. (2004):

TEX_{86}= GDGT-II+GDGT-III+GDGTIV'/GDGT-I+GDGT-II+GDGT-III+GDGTIV' (1),

BIT = GDGT-V+GDGT-VI+GDGT-VII/GDGT-IV+ GDGT-V+GDGT-VI+GDGT-VII (2),

where I – VII refer to the different GDGTs (Blaga et al., 2009, chapter 2).

5.3. Results

5.3.1. Age model

A first order chronology was based on correlation to previously identified and dated marker horizons in cores from different other locations in the Chrüztrichter and Vitznau basins (Schnellmann et al., 2004, 2006). Since these basins lack major active deltas, sedimentation rates are relatively low (~0.06 cm yr^{-1}) and, more importantly, they are characterized by dominantly hemipelagic sedimentation. Core-to-core correlation was established by comparing both petrophysical properties and visual characteristics. A series of stratigraphic event horizons related to past mass-movement activity was determined and dated in the Chrüztrichter and Vitznau basins based on characteristic layers such as deformed deposits, (mega)turbidite beds and sand layers (Schnellmann et al., 2002, 2006). In the core used in our study the following

Table 1 Dating of core 4WS00-4P section 8-9 using radiocarbon, marker beds and down-core pattern of magnetic susceptibility. Calibration (2 sigma range) was carried out with CALIB 4.4 software (Stuiver and Reimer, 1993)

Core depth (cm)	Cal. Years BP	Dating	References
596.3	9,965 (9,826–9,912: 9,870)	Lithological marker horizon M	Schnellmann et al., 2006
650	11,205 (10,764–11,546: 11,155)	^{14}C leaf remains	Schnellmann et al., 2006
752	12,972	Magnetic susceptibility peak attributed to the Laacher See Tephra	Radiocarbon dated by Friedrich et al., 1999 Schnellmann et al., 2006
786.6	13,720 (13,580–13,838: 13,710	Lithological marker horizon R	Schnellmann et al., 2006

marker beds were identified: the mass-flow and turbidite beds related to Events M and R, and the Laacher See Tephra (LST) (Schnellmann et al., 2006) (Table 1). In the magnetic susceptibility curve (Fig. 2) a distinctive peak was observed related to the LST layer at 752 cm. For constructing the age model the LST layer represents an absolute age constraint as this layer was radiocarbon dated to 11,063 ± 12 conv. radiocarbon years BP (Friedrich et al., 1999), which corresponds to a calibrated age of 12,930-13,000 cal. yr BP (one sigma range, IntCal04). At 650 cm depth in section 8 a fossil leaf was dated to 11,120 cal. yr BP (10,764–

11,546: 11,155). The mass-movement horizons M (9,826–9,912: 9,870) and R (13,580–13,838: 13,710) (Schnellmann et al., 2006) were deposited morphologically only below the sill of the core location so that the studied section comprises undisturbed sediments. Radiocarbon ages were transferred to calendar years BP (2σ-range) using the CALIB 4.4 software (Stuiver and Reimer, 1993) (Table 1). The age of the sediments between age control points were inferred using linear interpolation. The resulting sedimentation rate is relatively constant at 0.04 - 0.05 cm/yr, which is in accordance with previously dated cores from the same location. The lack of drastic changes in sedimentation rate indicates that our first order age model is relatively robust.

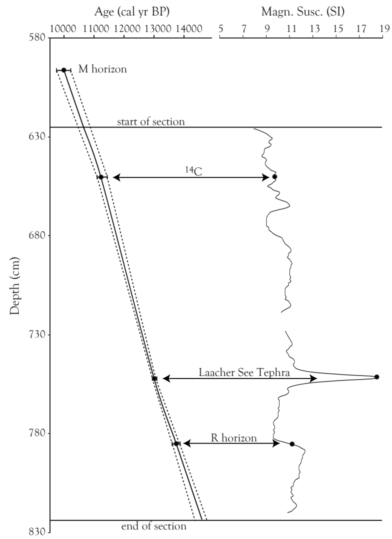

Fig. 2 Age-depth plot of the Lake Lucerne record for the studied sections. The marker horizons M and R, ^{14}C point and the Laacher See Tephra are indicated also in the magnetic susceptibility plot.

5.3.2. Late Glacial and Early Holocene changes in GDGTs

HPLC analyses on the sediment extracts revealed the ubiquitous presence of isoprenoidal and branched GDGTs as well as changes in their relative abundances throughout the core. Since the entire range of GDGTs occurs throughout the record, the BIT index can be used to reconstruct relative input of soil organic carbon into the lake. The BIT values for the two studied core sections vary between 0.15 and 0.55 (Fig. 3). The base of the studied interval shows high BIT values around 0.35, followed by a decrease to values around 0.2. At ~14,200 cal. yr BP, BIT values increase to a short peak, with values reaching 0.35. A longer plateau, with average BIT values around 0.25 follows, which sharply ends at about 12,750 cal. yr BP. The highest BIT values (0.3 - 0.55) are reached directly at the start of the Younger Dryas, followed by a gradual decrease towards BIT values of about 0.2, which after that remain relatively stable until the top of the studied interval.

The high-resolution TEX_{86} record from Lake Lucerne shows a range of values varying from 0.33 to 0.42 (Fig. 3). Around 14,600 cal. yr BP, at the onset of the Late Glacial Interstadial, the TEX_{86} values are low (0.33) but increase slightly towards 0.37. At around 14,100-14,000 cal. yr BP the TEX_{86} values slightly decrease again. From 14,000 cal. yr BP to 13,800 cal. yr BP TEX_{86} values vary between 0.35 and 0.38. Between 13,700 and 13,500 cal. yr BP the values decrease from 0.37 to 0.35 similar to the values observed for the interval between 13,300 and 13,000 cal. yr BP. Around 12,800 cal. yr BP we observe an abrupt decrease from 0.37 to 0.33 in TEX_{86} values. These values remain constantly low until around 12,000 cal. yr BP when they increased again to 0.37 at ca. 11,860 cal. yr BP and subsequently to 0.41 at 11,600 cal. yr BP. During the Early Holocene TEX_{86} values remain high at ~0.40 with small fluctuations.

5.4. Discussion

According to the established age model for core 4WS00-4P, the studied sediments cover the transition from the Oldest Dryas to the Late Glacial Interstadial (i.e. Bølling/Allerød), the Younger Dryas cold phase and the Early Holocene (Preboreal). Based on our age model the covered interval encompasses the time from ~14,600 to 10,600 cal. yr BP.

5.4.1. Lake Lucerne temperature changes during the deglaciation

Plotting the TEX_{86} record next to the NGRIP oxygen-isotope record on the GICC05 time scale (Fig. 3) shows that the major climate shifts during the Greenland Interstadial I and Stadial I (GI-1, GS-1, respectively, Björk et al., 1998) are reflected in both records. Although the chronologies of the two records are independent, the timing and the changes in the TEX_{86} record from Lake Lucerne closely resemble those observed in the $\delta^{18}O$ record of NGRIP Greenland ice core with only minor offsets (Fig. 3). In order to reconstruct absolute temperature changes based on the TEX_{86} temperature proxy first a temperature calibration has to be applied to the Lake Lucerne record. In recent years the application of GDGTs as temperature indicators for marine and freshwater environments has led to different TEX_{86}-to-temperature calibrations (Schouten et al., 2002; Kim et al., 2008; Powers et al., 2004, 2009). Application of these different calibrations results in different reconstructed absolute temperatures, however, the reconstructed temperature offsets between Oldest Dryas, the Interstadial, Younger Dryas and Holocene temperatures are insensitive to the calibration used. All calibrations consistently indicate a maximum offset of about 4 °C between Younger Dryas and Holocene, the most pronounced event in the TEX_{86} record. We applied the lake calibration established by Powers et al. (2009) as the most appropriate one and this resulted in the lake temperatures varying from 5-10 °C (Fig. 3).

The base of section 9 of the studied core shows relatively low TEX_{86} temperatures rapidly increasing at the onset of the Interstadial at ~14,600 cal. yr BP. Chronologically, this onset corresponds to a large shift in the NGRIP oxygen isotope record from oxygen isotope values of about - 42‰ to - 36‰ VSMOW at ~14,700 cal. yr BP and represents the transition from GS-2 to GI-1e (Fig. 3). The offset of ~100 cal. BP, observed between the timing of this event in Lake Lucerne and Greenland is well within the uncertainty range associated with our chronology. The section covering the GI-1e period has relatively constant high TEX_{86} temperatures of ca. 7 °C. Between 14,100 and 14,000 cal. yr BP (GI-1d; Aegelsee oscillation, see Lotter et al., 1992) lower TEX_{86} temperatures correspond with low $\delta^{18}O$ values from 14,080 to 13,980 cal. yr BP from the NGRIP record. This oscillation is known to have had a short duration (ca. 100 yr) during times characterized by a highly unstable environment, but still is reflected in the TEX_{86} record pointing to a high sensitivity of Lake Lucerne to record also short-lived climate fluctuations. Similar events later in the Interstadial are more clearly reflected by shifts in TEX_{86} values, with a strong similarity to the oxygen isotope records during the other three events that characterize this period [GI-1a, 1b (Gerzensee oscilation) and 1c]. Offsets in timing between the two curves are again minor. The short events during this period (GI-1a, 1b, 1c and 1d) can be observed as small shifts of about 1 °C in inferred temperatures.

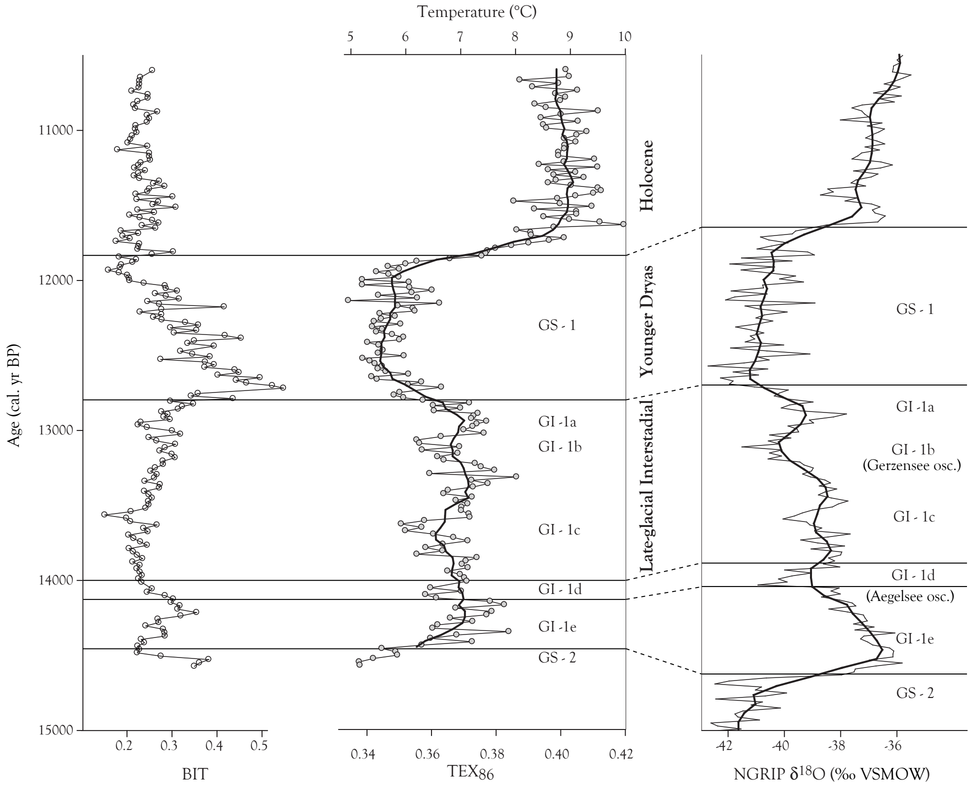

Fig. 3 Comparison of the high resolution BIT, TEX_{86} and TEX_{86}-inferred temperature record from sediments of Lake Lucerne with $\delta^{18}O$ values from the NGRIP record across the onset of the Late Glacial Interstadial, Younger Dryas and onset of the Holocene. Thick black line in the TEX_{86} temperature and $\delta^{18}O$ record represents the three-point moving average. The INTIMATE event stratigraphy (Björk et al., 1998) is presented together with the indices values.

The transition to the Younger Dryas is characterized by an inferred TEX_{86}-derived temperature drop from 7.2 °C during the Interstadial (GI-1a) to 5.5 °C during the Younger Dryas. The inferred temperatures remain stable between 5 and 6 °C during the Younger Dryas. Even with an increased contribution of branched GDGTs, and a substantial change in BIT values (Fig. 3), the Younger Dryas data clearly show that the TEX_{86} was not influenced over this interval, indicating no impact on inferred temperatures. At the onset of the Holocene, a sharp increase in temperature is observed with absolute temperatures going from an average of 5.5 °C to as high as 10 °C, in a transitional phase of at most 200 years.

Compared to the changes observed during the deglaciation, the Early Holocene is characterized by relatively constant TEX_{86} temperatures of aprox. 9 °C. These temperatures are comparable with those determined for a recently recovered short core from the same site covering the last 1200 years, except for the last 45 years when the trophic state of the lake changed markedly, inducing a shift in the crenarchaeotal community (Blaga et al., submitted). Based on oxygen isotope records, temperature shifts of 1 °C only have been detected for Swiss alpine lakes during the Holocene (Schwalb et al., 1994, von Graffenstein et al., 1998), in line with our TEX_{86} data.

Temperature estimates for the glacial (Oldest Dryas) period in the Alps region differ; oxygen isotopes indicate a cooling of 10 - 15 °C (Lake Zurich, Lister, 1989), 10 - 12 °C (Lake Ammersee, von Graffenstein et al., 1994) or 5 - 8 °C (Lake Neuchâtel, Schwalb et al., 1994) compared to present temperatures. Based on $\delta^{18}O$ values of authigenic lake carbonates temperatures increased by about 4 - 7 °C (Eicher et al., 1976, 1981) from Late-Glacial to Holocene values. The TEX_{86}-inferred temperature changes, independent from the calibration used, indicate shifts similar with the ones estimated from the $\delta^{18}O$ record of Lake Neuchatel (Schwalb, 2003) (3.5 - 5 °C between the Oldest Dryas and the Holocene and 3 - 4.5 °C between the Younger Dryas and the Holocene).

Climate proxy records available from both marine and terrestrial archives have improved our understanding of centennial- and millennial-scale variability in past climate. Unfortunately, most terrestrial records reflect only summer temperatures changes. The application of crenarchaeal GDGTs as palaeo-proxies in lake sediments is a relatively new approach but the Lake Lucerne record reflects, at a high-resolution scale, fairly accurate and rapid mean annual temperature shifts. The inferred temperature changes are in good agreement with other proxy records reflecting continental changes in the region indicating that the TEX_{86} proxy can be used as a continental paleotemperature reconstruction tool.

5.4.2. The BIT index as a proxy for soil erosion in the catchment of the lake

The oldest sediments of the core show high BIT values that rapidly decrease during the onset of the Interstadial at ~14,600 cal. yr BP (Fig. 3). In both, Greenland and the continent, the transition from GS-2 to GI-1e is characterized by a climatic warming. On the Swiss Plateau this warming is reflected in an increase in stable oxygen isotopes measured in many carbonate-rich lake-sediment successions that coincide with the onset of reforestation with juniper and birch (e.g. Lotter et al. 1992) and is confirmed by our TEX_{86} record (Fig. 3). Highest values for BIT index are observed shortly after the onset of Younger Dryas, the saw-tooth pattern in the BIT index showing a rapid increase in input of branched GDGTs relative to crenarchaeol, associated with the inferred cooling (Fig. 3). The BIT index reflects the relative input of aquatically-produced vs. soil-derived GDGTs and could, therefore indicate changes in either one. The onset of the Younger Dryas is, however, characterised by high accumulation rates of branched GDGTs (data not shown), indicating that additional soil-derived organic matter input has the largest effect. This suggests that soils, which developed during the warmer and probably more humid Interstadial were eroded during the expansion of the Alpine glaciers during the Younger Dryas. Physically removed soil was subsequently transported from the catchment in the lake. The vegetation during the Late-Glacial Interstadial on the Swiss Plateau and the northern Alps was first characterized by birch and later by birch-pine woodlands (Ammann et al., 1996). During the climatic cooling of the Younger Dryas, also reflected in our TEX_{86} record (Fig. 3), the birch-pine woodland opened up, especially at higher elevations, which enhanced soil erosion. Thus, the BIT record clearly reflects Late-Glacial landscape openness and soil erosion in the hydrological catchment, given that a large amount of the catchment area of Lake Lucerne is situated in the Alps at higher elevations. Values subsequently decrease towards the Holocene, indicating a gradual reduction in soil input during the Younger Dryas. The Younger Dryas/Holocene transition at ~11,800 cal. yr BP is marked by continuing low BIT values, and closely coincides with the final oxygen isotope transition at around 11,660 cal. yr BP. The reduction in input of soil organic matter during the second half of the Younger Dryas can be explained by either exhaustion of the soil layer or by a dryer climate, and consequently less run-off, during the second part of the Younger Dryas (e.g. Lotter et al., 1992).

Generally, the BIT values in the Lake Lucerne sediments are higher during periods that are characterized by a colder climate and by a more open vegetation, such as the Oldest Dryas or the Younger Dryas (Fig. 3), whereas during the warmer and more densely forested part of the Interstadial and the early Holocene BIT values are between 0.2 and 0.3. This differs from what is seen in tropical African lakes where BIT values are much lower during the Younger Dryas because of the reduced precipitation (Verschuren et al., 2009).

5.5. Conclusion

In this study we present a high-resolution record of temperature in the sediments from Lake Lucerne covering the Late Glacial up to Early Holocene. The comparison between the ice-core and the GDGT-based temperature records shows that there is a strong correlation between inferred temperature changes on Greenland and in the Alps region. It is also clear that our proxy, based on the isoprenoidal GDGTs found in the sediments of Lake Lucerne, is capable to reflect high-resolution records of rapid (decadal- to century-scale oscillations) environmental fluctuations, comparable with those obtained from ice cores. The rapid changes in temperature associated with the last deglaciation are reflected in the highest possible detail in the TEX_{86} record. The TEX_{86} estimated temperatures for Lake Lucerne genuinely reflect changes in absolute temperature across the studied interval and are in line with previous temperature reconstructions based on different proxies. Thus the present study shows that the GDGT-based proxy may be independently used - within the standard error - to reconstruct fluctuations in temperatures in lacustrine settings.

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Summary

Our ability to predict the future impact of climate change strongly depends on what we know about past climate change. Continents play an important role in global climate, which makes investigating terrestrial systems essential for understanding past and future climate forcing and feedbacks. Although increasing amounts of instrumental temperature records are available, they inevitably cover only a relatively short time interval, and are thus not able to capture the full range of natural variability. Geologic records provide a valuable tool to extend the instrumental data back in time, which is crucial to understand processes acting on longer times scales and to quantify natural variability in ecosystems prior to anthropogenic changes.

Recent studies in palaeoclimatology focus on the development and validation of quantitative proxies for environmental parameters sensitive to climate change. In lake sediments organic matter, for example, provides an important signal carrier of past environmental variability on the continents. Lacustrine sediments often contain relatively high amounts of organic matter because of limited bottom water oxygenation and relatively high sedimentation rates. Molecular ecological analyses revealed that Archaea, one of the three domains of life, are not restricted to extreme environments but are also present in more temperate environments such as lakes. The membrane lipids of Crenarchaeota, a major group of the domain Archaea, consist of isoprenoid glycerol dialkyl glycerol tetraether (GDGTs) containing cyclopentane moieties, a characteristic generally considered as an adaptation mechanism to temperature of the membrane. Previously the analyses of core top sediments from different locations worldwide showed that the distribution of these isoprenoid GDGTs varies with sea surface temperature (SST), a relation expressed in the TetraEther indeX of lipids with 86 carbon atoms (TEX_{86}). Besides isoprenoid GDGTs, branched GDGTs, whose potential biological origin is assigned to Bacteria, were also also detected in peat bogs, soils, and coastal marine and lacustrine sediments. The branched GDGT abundance in marine sediments was shown to decrease relative to crenarchaeol (an isoprenoid GDGT) with increasing distance from river mouths, indicating fluvial transport of branched GDGTs from land to aquatic environments. This relation was expressed in the Branched versus Isoprenoid Tetraether (BIT) index. The alkyl chains of branched GDGTs are composed of straight carbon chains containing a different number of cyclopentane moieties and also a different degree of methylation, which were shown to be related to air temperature and soil pH. This formed the basis for two newly developed proxies: CBT (Cyclisation ratio of Branched Tetraethers) showing the relation between the degree of cyclisation and soil pH; and MBT (Methylation index of Branched Tetraethers) expressing the correlation between the degree of methylation and annual mean air temperature and soil pH. This thesis describes the distribution and biological sources of GDGT membrane lipids in lacustrine environments, their potential use as temperature proxies and their application in reconstructing past continental temperatures.

Isoprenoid GDGTs were detected in variable amounts in particulate matter and the top 5 cm of the sediment from 47 European lakes, along a latitudinal transect from southern Italy to the northern part of Scandinavia. Branched GDGTs dominated, especially in the northern lakes, possibly related to high soil erosion rates. In many of the lakes, soil input affects the distribution of isoprenoidal GDGTs and prevents the reliable application of the TEX_{86} temperature proxy for lake water temperature, which is based on in situ crenarchaeotal

GDGTs production. Isoprenoid GDGTs derived from methane-producing Euryarchaeota, or allochthonous input of soil-derived isoprenoid GDGTs, could potentially bias lake surface temperature (LST) reconstructed with the TEX_{86} proxy. To assess this potential bias, the BIT index should be applied in settings where substantial amounts of soil organic matter may contribute to the lacustrine sediments as it is a reliable tool for determining which lake sediments are suitable for application of the TEX_{86} palaeothermometer. The results presented in this thesis show that not only large lakes but also smaller size lakes with high in situ productivity of isoprenoid GDGTs are suited for the use of TEX_{86}. After excluding lakes not suited for a TEX_{86} based temperature reconstruction the winter temperatures correlate better with TEX_{86}. This indicates that the isoprenoid GDGT producing organisms probably have their peak abundances during this season.

Because branched GDGTs dominate in many of the lake sediments, as indicated by high BIT values, the potential of the MBT/CBT as a continental palaeothermometer in lacustrine environments was investigated. The set of surface sediments from the European lakes was extended by including a series of lake sediments from North and South America, as well as some sediments from Equatorial Africa. The source for GDGT in these lakes is assumed to be largely soil-derived, resulting in high concentrations of branched GDGTs. We observed that the distribution of branched GDGTs as expressed in the MBT and CBT indices varied substantially among the lake sediments and that the MBT/CBT-reconstructed temperatures using the global soil calibration were consistently below annual mean air temperature of the catchment of the lake. Still, a significant correlation exists between the reconstructed temperature and the temperature measured on site, albeit with considerable scatter ($r^2 = 0.47$). It seems that the branched GDGTs in lake sediments are derived from both erosion of soil and in situ production and that the existing soil calibration cannot be used for lake sediments.

In order to determine where and when the GDGT signal is produced in the water column of lakes, we collected descending particles using two sediment traps (at 42 and 72 m water depth) with a monthly resolution from January 2008 to late March 2009 in Lake Lucerne. Suspended particulate matter (SPM) was monthly filtered from the water column at three different depths. The results of this study show that fluxes of GDGTs and concentrations in the water column vary according to a seasonal pattern, with a similar trend in SPM and sediment traps. Fluxes and concentrations of isoprenoid GDGTs increase with depth, maximum values being observed in the deeper part of the water column, indicating production of isoprenoid GDGTs by Group 1 Crenarchaeota in the deep (~50 m), aphotic zone. Temperature profiles of the water column were also measured and at this depth the values fluctuate over the year between 5 and 8 °C. This is consistent with the low values of the TEX_{86} proxy and with the inferred temperatures. Flux-weighted averages of the temperature proxy TEX_{86} (0.27) and the terrestrial input proxy BIT (0.03) are similar at both trap depths, and similar to the values measured in the surface sediments and SPM of Lake Lucerne.

To reconstruct temperature changes during the Late Glacial Interstadial, the Younger Dryas and the Early Holocene (~14,600 to 10,600 cal. yr BP) the relative distribution of GDGTs in a sediment core from the same location as the seasonal study was determined. The Late Glacial period was characterized by large and rapid changes in temperature and precipitation marking the transition from the Last Glacial Maximum (LGM) to the Early Holocene. The shifts in temperature for this interval are believed to range between 3 and 6 °C with a decrease in temperature at the onset of Younger Dryas and an abrupt increase at the onset of Early Holocene. The TEX_{86} record suggests a sequence of temperature shifts strongly resembling the $\delta^{18}O$ values recorded in the Greenland ice core. Reconstructed lake temperatures indicate a step-wise pattern of climate change, with a warming at the onset of the late-glacial interstadial, followed by an abrupt cooling at the onset of Younger Dryas and a rapid warming from 5.5 to 9 °C at the Younger Dryas/Holocene transition within less than 200 years.

In conclusion, the calibration and application studies presented in this thesis provide new insight into the TEX_{86} proxy as a tool for reconstructing past temperatures from lakes. Application of branched GDGTs in lacustrine environments still requires a detailed study in freshwater settings as the origin of these compounds in lakes is still largely unknown. Comparing the distribution of GDGT-0, crenarchaeol and branched GDGT membrane lipids in lacustrine environments the boundary conditions for the applicability of the TEX_{86} proxy were investigated. High resolution continental palaeoclimate records, comparable to the ice cores, can be obtained applying the TEX_{86} proxy to selected lakes.

Samenvatting

Hoe goed de gevolgen van toekomstige klimaatsveranderingen te voorspellen zijn hangt sterk af van wat we weten van dergelijke veranderingen in het verleden. Omdat het klimaat op aarde in belangrijke mate wordt beïnvloed door de continenten is het bestuderen van het landklimaat belangrijk om de rol daarvan en eventuele terugkoppelingen op klimaatveranderingen in het verleden en in de toekomst te begrijpen. De in toenemende mate beschikbare tijdseries met gemeten temperaturen beslaan slechts een kort interval en kunnen daardoor nooit de volledige omvang van de van nature aanwezige variabiliteit aantonen. Het geologisch archief maakt het mogelijk om de gemeten tijdseries verder terug in de tijd uit te breiden om op deze manier ook die processen te kunnen bestuderen die op langere tijdschalen een rol spelen en de van nature aanwezige variabiliteit in het klimaatsysteem te kwantificeren.

De ontwikkeling en het testen van kwantitatieve indicatoren voor parameters die gevoelig zijn voor klimaatveranderingen staat sinds enige tijd centraal binnen de palaeoklimatologie. Het organisch materiaal dat onderdeel uitmaakt van meersedimenten vormt een belangrijke informatiebron voor de reconstructie van veranderingen in het milieu op de continenten. Meersedimenten bevatten vaak veel organisch materiaal als gevolg van lage zuurstof concentraties van het bodemwater en de hoge sedimentatiesnelheden. Moleculair ecologisch onderzoek heeft aangetoond dat Archaea, één van de drie domeinen van het leven, niet beperkt zijn tot extreme milieus, maar veel algemener voorkomen, zoals onder andere in meren. De membraanlipiden van Crenarchaeota, een belangrijke groep binnen de Archaea, bestaan uit glycerol dialkyl glycerol tetraethers (GDGTs) met daarin een variabel aantal cyclopentaan eenheden, waarvan wordt aangenomen dat dit een aanpassing is van het membraan aan de temperatuur. Eerder toonde de analyse van oppervlakte sedimenten verzameld van locaties verspreid over de wereld aan dat de verhouding van de verschillende isoprenoïde GDGTs covarieert met de oppervlakte watertemperatuur. Deze afhankelijkheid kan beschreven worden met behulp van de zogenaamde TetraEther indeX voor lipiden met 86 koolstof atomen (TEX_{86}). Naast deze isoprenoïde GDGTs zijn in veenlanden, bodems, kustnabije sedimenten en meersedimenten ook GDGTs gevonden die opgebouwd zijn uit vertakte koolstofketens, waarvan wordt aangenomen dat deze worden gesynthetiseerd door bacteriën. Dat deze vertakte GDGTs, van het land naar het water getransporteerd worden, bleek eerder doordat hun concentratie in zeesedimenten ten opzichte van die van crenarcheol (een isoprenoïde GDGT) afneemt als een functie van de afstand tot riviermondingen. Deze relatie is vervolgens uitgedrukt in de vertakte (Branched) versus Isoprenoïde Tetraether (BIT) index. De membraan overspannende alkyl ketens van de vertakte GDGTs bestaan uit koolstofketens met 0-2 cyclopentaan eenheden en een verschillende mate van methylering, welke afhankelijk zijn van temperatuur en de pH van de bodem. Deze correlatie vormde de basis voor twee nieuwe indicatoren: de CBT (*Cyclisation ratio of Branched Tetraethers*) die de relatie tussen de aanwezigheid van cyclopentaan eenheden koppelt aan de pH van de bodem en de MBT (*Methylation index of Branched Tetraethers*) waarin de relatie tussen methylering, temperatuur en bodem pH wordt uitgedrukt. In dit proefschrift wordt de relatieve verdeling en biologische oorsprong van membraan GDGTs beschreven in lacustriene milieus, hun bruikbaarheid als temperatuursindicatoren en de toepassing voor het reconstrueren van continentale temperaturen in het geologische verleden.

In een transect van zuid Italië tot noord Scandinavië werden in 47 meren verschillende concentraties isoprenoïde GDGTs gevonden in zowel de bovenste 5 cm van het sediment als geassocieerd met het zwevend materiaal in de waterkolom. In met name de noordelijke meren waren de vertakte GDGTs het meest aanwezig, mogelijk gerelateerd aan de hoge mate van erosie van bodemmateriaal ter plaatse. In veel van deze meren beïnvloedt de aanvoer van bodemmateriaal de relatieve concentraties van isoprenoïde GDGTs en daarmee de toepasbaarheid van de TEX_{86} temperatuurindicator omdat deze gebaseerd is op uitsluitend ter plaatse geproduceerd crenarcheotische GDGTs. Isoprenoïde GDGTs afkomstig van methaan producerende Euryarchaeota of van de allochtone input van bodemmateriaal met isoprenoïde GDGTs kunnen beiden de met behulp van TEX_{86} gereconstrueerde lacustriene oppervlakte watertemperatuur (LOWT) beïnvloeden. In meren waar substantiële hoeveelheden organisch bodemmateriaal potentieel een rol spelen dient daarom vooraf eerst de BIT index toegepast te worden, om op die manier vast te stellen in welke meren de TEX_{86} indicator nog betrouwbaar is voor het reconstrueren van de temperatuur. De in dit proefschrift gepresenteerde data toont aan dat niet alleen grotere meren, maar ook meren met hoge lokale produktie van isoprenoïde GDGTs geschikt kunnen zijn voor het toepassen van de TEX_{86} methode. De data reeks laat zien dat na uitsluiting van die meren die niet geschikt zijn voor toepassing van TEX_{86}, deze beter correleert met de winter temperatuur. Dit geeft aan dat de organismen die deze isoprenoïde GDGTs produceren hun maximale productie tijdens de winter hebben.

Omdat de vertakte GDGTs in veel van de onderzochte meren relatief de hoogste concentraties hadden, zoals aangegeven door de BIT waardes, is de toepasbaarheid van de MBT/CBT continentale palaeotemperatuurindicatoren in lacustriene milieus onderzocht. De reeks oppervlakte sedimenten van de Europese meren zijn daarvoor uitgebreid met sedimenten van Noord en Zuid Amerikaanse meren en enkele sedimenten van meren uit Equatoriaal Afrika. Voor de onderzochte meren wordt aangenomen dat de GDGTs voornamelijk van bodems afkomstig zijn, resulterend in relatief hoge concentraties vertakte GDGTs. De onderlinge verdeling van de verschillende vertakte GDGTs, uitgedrukt in MBT en CBT, laat grote verschillen zien tussen de meren. De met behulp van de op bodemmonsters gebaseerde MBT/CBT–temperatuurkalibratie uitgerekende temperaturen liggen consistent onder de gemiddeldeluchttemperaturen in het drainagegebieden van de meren. Desondanks bestaat er, met een behoorlijke additionele ruis (r^2=0.47), een significante correlatie tussen gereconstrueerde temperaturen en ter plaatse gemeten temperaturen. Dit wijst erop dat de vertakte GDGTs in meersedimenten afkomstig zijn van zowel de erosie van bodemmateriaal in het drainagegebied als productie in het meer zelf, waardoor de bestaande kalibratie gebaseerd op bodemmonsters niet rechtstreeks kan worden geëxtrapoleerd naar meersedimenten

Om vast te stellen waar en wanneer het GDGT signaal wordt vastgelegd in de waterkolom van een meer zijn met twee sedimentvallen (op 42 en 72 meter diepte) de zinkende deeltjes bemonsterd in het meer van Luzern, met een maandelijkse frequentie vanaf januari 2008 tot eind maart 2009. In het water zwevende deeltjes (WZD) zijn maandelijks gefiltreerd uit de waterkolom op drie verschillende diepten, het meeroppervlakte en de diepten van de sedimentvallen. Concentraties en fluxen van de verschillende GDGTs in de waterkolom variëren met het seizoenen, met dezelfde trends in WZD en de sedimentvallen. Zowel de concentratie als de flux van isoprenoïde GDGTs neemt toe met de diepte, met de hoogste waardes in het diepste deel van de waterkolom. Dit geeft aan dat isoprenoïde GDGTs geproduceerd worden, door Type 1 Crenarchaeota, in het diepe (~50 m), afotische deel van de waterkolom. De temperaturen op deze diepte variëren over het jaar tussen de 5 en 8°C. De positie in de waterkolom en de daar heersende temperaturen komen goed overeen met de gevonden lage waarden voor de TEX_{86} temperatuurindicator. Flux-gewogen gemiddeldes van de temperatuurindicator TEX_{86} (0.27) en terrestrische aanvoer indicator BIT (0.03) zijn identiek op beide sedimentval dieptes en komen overeen met de waarden gemeten in het oppervlaktesediment en WZD in het meer van Luzern.

Van dezelfde locatie als de seizonale fluxstudie zijn de relatieve GDGT concentraties gemeten in een sedimentkern, om op die manier de temperatuur te reconstrueren gedurende het laat Glaciaal, De Jonge Dryas en het vroeg Holoceen (~14.600 to 10.600 cal. yr BP). De transitie van het laatste Glaciale maximum (LGM) naar het vroege Holoceen werd gekenmerkt door snelle en grote veranderingen in zowel temperatuur als neerslag. De temperatuursveranderingen gedurende dit interval zouden tussen de 3 en 6 °C zijn geweest, met een plotse afkoeling gedurende de jonge Dryas, gevolgd door een snelle opwarming bij het begin van het vroege Holoceen. De op TEX_{86} gebaseerde reconstructie suggereert een opeenvolging van temperatuursveranderingen die sterk overeenkomen met het patroon van $\delta^{18}O$ veranderingen zoals dat gevonden is voor dezelfde periode in het ijs van Groenland. De gereconstrueerde oppervlaktewater temperaturen van het meer van Luzern laten een stapsgewijze klimaatsverandering zien, met een opwarming gedurende de aanvang van het laatste Glaciale Interstadiaal, gevolgd door een plotse afkoeling als de jonge Dryas begint en wederom een opwarming van 5.5 naar 9 °C binnen 200 jaar tijdens de overgang van jonge Dryas naar het Holoceen.

De kalibratie en toepassingsstudies gepresenteerd in deze thesis geven nieuw inzicht in het gebruik van de TEX_{86} temperatuurindicator in meren. Toepassing van vertakte GDGTs in meren vraagt nog om een meer gedetailleerde studie in zoetwater milieus omdat de herkomst van deze verbindingen nog steeds grotendeels onbekend is. Door de concentratie verdeling tussen GDGT-0, crenarchaeol en de vertakte GDGT membraan lipiden te vergelijken tussen verschillende lacustriene milieus zijn de randvoorwaarden voor de toepasbaarheid van TEX_{86} voor de reconstructie van meerwatertemperaturen onderzocht. Het toepassen van de TEX_{86} temperatuurindicator in zorgvuldig geselecteerde meren maakt hoge resolutie reconstructies van het palaeoklimaat mogelijk, vergelijkbaar met die gebaseerd op ijskernen.

Rezumat

Modul în care putem prezice efectele determinate de schimbarea climei depinde în mare măsură de ceea ce ştim despre schimbările climatului survenite în trecutul geologic. Continentele joacă un rol important în ceea ce priveşte climatul global. De aceea studiul sistemelor terestre este esențial pentru înțelegerea schimbărilor climaterice din trecut şi viitor. Chiar dacă la ora actuală există un număr din ce în ce mai mare de baze de date în care au fost înregistrate schimbările de temperatură, inevitabil acestea acoperă doar perioade scurte de timp şi sunt astfel insuficiente pentru a îngloba întregul spectru al variabilității sistemelor naturale. Analiza depozitelor sedimentare reprezintă o modalitate potrivită prin care informațiile despre schimbările de temperatură înregistrate cu ajutorul instrumentelor pot fi extinse în trecut. În acest mod se pot înțelege procesele care acționează şi influențează pe termen îndelungat ecosistemele chiar şi în perioade când influența umană a fost nesemnificativă.

Studiile recente din paleoclimatologie se axează pe descrierea şi validarea unor indici cantitativi cu ajutorul cărora se pot observa modificările unor parametrii sensibili la schimbările climatului. Materia organică din sedimentele lacustrine acționează ca un important purtător de informație legată de diferitele schimbări din mediului terestru. Sedimentele din lacuri conțin cantități apreciabile de substanță organică datorită resurselor limitate de oxigen de la fundul lacurilor dar şi datorită unei rate de sedimentare mult mai ridicate decât în mediul marin. Studii de ecologie moleculară au pus în evidență faptul că organismele aparținând domeniului Archaea, unul din cele trei domenii de viață, nu sunt restricționate doar la medii de viață extreme ci pot fi găsite şi în medii mai temperate ca de exemplu în lacuri. Lipidele ce formează membrana celulară a Crenarchaeotelor, un grup major din domeniul Archaea, sunt formate din glicerol dialchil glicerol tetraeteri (GDGT) isoprenoizi ce conțin în structură cicluri cu 5 atomi de carbon. În general această caracteristică se consideră a fi un mecanism de adaptare al membranei la schimbările de temperatură. O serie de carote sedimentare marine provenind din diverse locații de pe glob au fost analizate pentru a determina prezența GDGT izoprenoizi. S-a observat că modul în care compuşii sunt distribuiți în diferite probe variază în funcție de temperatura masurată la suprafața apei mărilor. Această relație a fost exprimată ulterior prin intermediul unui nou indice de temperatură numit TEX_{86}. Pe langă GDGT izoprenoizi o serie de GDGT cu catenă ramificată au fost detectați în diferite medii precum turbării, soluri, sedimente din lacuri sau litoralul mărilor, sursa biologică fiind atribuită unui grup încă necunoscut de bacterii anaerobe ce trăiesc în soluri. Adundența acestor compuşi în sedimentele marine descreşte pe măsură ce distanța de la gura de vărsare a râurilor este din ce în ce mai mare, indicând faptul că aceşti compuşi ajung din mediul terestru în cel acvatic prin transport fluvial. Această relație a fost exprimată prin intermediul indicelui BIT care exprimă raportul dintre tetraeterii ramificați şi cei izoprenoizi. Catenele alchilice ale tetraeterilor ramificați conțin deasemenea un număr variabil de cicluri cu cinci atomi de carbon şi prezintă diferite grade de metilare. Aceste caracteristici au fost corelate cu temperatura aerului şi cu pH-ul solurilor prin intermediul indicilor CBT şi MBT. Proporția în care ciclurile cu 5 atomi de carbon variază în structura GDGT ramificați exrpimată prin intermediul indicelui CBT este determinată de pH-ul solului în timp ce gradul de metilare, exprimat prin intermediul MBT, este corelat cu temperatura medie anuală a aerului şi cu pH-ul solului. Scopul acestei teze este de a descrie distribuția şi originea biologică a acestor compuşi în mediul lacustru, potențialul

lor ca indicatori de temperatură şi utilizarea lor în reconstituirea paleotemperaturii.

GDGT izoprenoizi au fost detectaţi în cantităţi variabile în materia organică din apa şi sedimentele de suprafaţă colectate din 47 lacuri europene, distribuite de-a lungul unui transect latitudinal. GDGT ramificaţi domină spectrul compuşilor analizaţi preponderent în lacurile din nordul Europei, datorită ratei ridicate de eroziune a solurilor. În multe din lacurile analizate, distribuţia GDGT izoprenoizi este influenţată de prezenţa aceloraşi compuşi dar care provin din solurile din bazinul de drenaj sau sunt produşi de un alt grup de Archaea, Euryarchaea. Datorită acestui aport de compuşi cu origine diferită, temperaturile determinate cu ajutorul indicelui TEX_{86} pot fi eronate. Pentru lacurile în care aportul de substanţă organică din soluri este semnificativ se recomandă întâi de toate calcularea valorilor pentru indicele BIT şi apoi valorile pentru TEX_{86}. Rezulatele prezentate în această teză arată că pentru lacuri, indiferent de dimensiuni, dar în care GDGT izoprenoizi sunt produşi în cantităţi semnificative, este posibilă aplicarea noul indice pentru reconstituirea temperaturii. După ce au fost excluse lacurile ce nu îndeplinesc condiţiile menţionate mai înainte (ex. aport limitat de substanţă organică din sol) se observă faptul că indicele este corelat semnificativ cu temperaturile de iarnă indicând posibila producţie a acestor compuşi preponderent în acest anotimp.

Deoarece GDGT ramificaţi au fost găsiţi în abundenţă în majoritatea sedimentelor lacustrine, fapt indicat şi de valorile mari ale indicelui BIT, a fost testat potenţialul de paleotermometru al acestor compuşi prin intermediul indicilor MBT şi CBT. Pe lângă sediemntele din lacurile europene, au fost analizate şi o serie de sedimente din lacuri provenind din America de Sud şi Nord precum şi din Africa Ecuatorială. Datorită cantităţilor ridicate de GDGT ramificaţi, se presupune că în aceste lacuri GDGT provin din soluri. Şi în acest caz distribuţia GDGT variază între diferitele sedimente în timp ce temperaturile calculate prin intermediul MBT/CBT sunt considerabil mai scăzute decât cele măsurate în teren. Cu toate acestea o corelaţie semnificativă există între temperatura dedusă şi cea măsurată chiar dacă avem de a face cu un nor de puncte ($r^2 = 0.47$). Calibrajul pentru determinarea temperaturilor făcut într-un studiu anterior, pe diferite soluri este nepotrivit pentru mediul lacustru datorită faptului că GDGT ramificaţi ce se găsesc în sedimentele lacurilor pot proveni fie din soluri fie produşi in situ în sedimente.

O serie de probe de substanţă organică din lacul Lucerna au fost colectate lunar (între ianuarie 2008 şi sfârşit de martie 2009), cu ajutorul unor trape de sedimentare, pentru a determina unde şi când GDGT izoprenoizi sunt produşi în apa lacurilor. La momentul colectării a fost filtrată şi apa de la trei adâncimi diferite. Rezultatele acestui studiu arată că fluxul de GDGT din sedimente precum şi concentraţia acestor compuşi variază cu adâncimea de-a lungul unui ciclu sezonier. Fluxul şi concentraţile cele mai ridicate de GDGT izoprenoizi se înregistrează la adâncimi de aproximativ peste 50m indicând faptul că aceşti compuşi sunt produşi sub zona eufotică de organisme aparţinând grupului 1 Crenarchaeota. Profilele de temperatură măsurate de-a lungul studiului indică, la aceste adâncimi, temperaturi ce variază în timpul anului între 5 şi 8 °C. Temperaturile deduse cu ajutorul TEX_{86} sunt similare cu aceste valori. Valorile medii pentru TEX_{86} cât şi pentru BIT sunt asemănătoare între cele două adancimi cât şi cu cele determinate în probele de sediment şi substanţă organică din coloana de apă.

Utilizarea indicelui TEX_{86}, pentru reconstituirea schimbărilor de temperatură ce s-au produs de la ultima glaciaţiune până la începutul holocenului (14,600-10,600 ani BP), a fost testată pe o carotă din acelaşi lac Lucerna. Perioada studiată se caracterizează prin schimbări, de temperatură şi precipitaţii, majore dar de scurtă durată. Se presupune că în acest interval schimbările de temperatură au fost de 3 până la 6 °C. Valorile determinate pentru TEX_{86} indică o succesiune de schimbări de temperatură similare cu cele observate pentru isotopii de oxigen măsuraţi în carotele de gheaţă din Groenlanda. Temperaturile reconstituite pentru acest interval indică un model în formă de scară, cu o scădere a temperaturilor acum cca 14,200 ani BP şi o creştere abruptă de temperatură la începutul holocenului.

În concluzie, studiile prezentate în lucrarea de faţă clarifică o serie de probleme legate de calibrarea şi aplicarea indicelui bazat pe GDGT izoprenoizi pentru reconstituirea temperaturilor în mediul lacustru. Utilizarea celor doi indici MBT şi CBT în mediul lacustru se dovedeşte a fi mai dificilă deoarece nu se cunoaşte încă originea biologică a GDGT ramificaţi. Cu ajutorul investigaţiilor privind variaţiile în distribuţia GDGT (izoprenoizi şi ramificaţi) în lacuri s-a reuşit stabilirea unor condiţii ce determină aplicarea TEX_{86} în mediul lacustru. Utilizarea TEX_{86} pentru reconstituirea temperaturilor s-a dovedit a fi posibilă la o rezoluţie fină, astfel chiar şi schimbări de foarte scurtă durată putând fi reconstituite.

Acknowledgements

"This drop falling is time tapering to a point ... Time tapers to a point. As a drop falls from a glass heavy with some sediment, time falls."

V. Woolf

Here I should say that it has been a long chain of branched events leading straight to this point: the time when I have to write this chapter of the booklet. The TEXt that I have to write here has quite a BIT to do with all the people, from all different areas that made it possible for me to bring this thesis to the stage it is now. This Might Be Tiring for some but the page Can Be Turned aside.

A few words and special thanks go to my supervisor and co-promotor Gert-Jan Reichart (also the translator of the summary) and promotor Jaap S. Sinninghe Damsté who gave me the opportunity to work on this PhD project. It came as a surprise to them when at the first (fieldwork planning) meeting I mentioned that I do not swim; this when I would have to go on a rubber boat and sample several lakes. Once the samples where back in Utrecht and it came to figuring out the data and writing the manuscripts, Gert-Jan and Jaap were very efficient and helpful, taking all the necessary time to go through the different versions (and there were a number of them). Thanks to you my thesis is written in this form and all the chapters made it to or almost to the submission stage. I know several PhDs that envy this status and would like to be in the same position at the end of their PhD time. Many thanks also to Andy Lotter and Riks Laanbroek for collaborating in this project and for their useful discussions during our project meetings that helped improve the manuscripts.

I consider myself fortunate being involved in this project because it gave me the opportunity to go a lot in vacation. Oh sorry, I meant to say fieldwork. Liesbeth, Frederike, Koos, Oliver H. I don't think I will ever forget our "life in a van" with a boat as a trailer, a boat in the back and one on top of the van. I enjoyed being driven by you every single one of the ca. 10.000kms that we had to cover on the way to all those 32 lakes, X hotels and campings, Y restaurants, Z occasions for laughter ("sausage, dear?"), blood (Miss Milky), sweat (boxes in, boxes out) and tears (a passport, an engine on fire, a train station) a.s.o. Then came the second round with 16 monthly trips to beautiful Lake Lucerne. Thanks to Flavio Anselmetti who made it possible for us to do the extended study on this lake. I am grateful for all the assistance on the lake and in the lab provided by the very resourceful Wisi, Michi and Oliver S. from the EAWAG and to all the volunteer drivers (Arne, Koos, Wil, Dick, Els, Razvan, Julia, Eveline, Sascha, Riks).

I had the pleasure of working in a group of very nice colleagues that not only are of great scientific help but also know the importance of a sunny day, even when is pouring and we have to make it to town. Of course first my office mates Adriana and Elisabeth with whom many cups of solvents and cookies and dried sediments were shared. Then the group-thanks extend to Gert-Jan, Diana, Imogen, Gijs, Shauna, Eveline, Julia, Jordahna, Els, Jos, Klaas, Laura, Marieke, Johan, Mohamed, Aafke, België. A really great group of people! Further I have to pass by and mention Laurie, Celine, Siska, Côme, Thomas; the first floor Jose, Iana, Tom, Peter, Goulven, Ana, Claudia, Marie-Louise, Pien, Arnold, Helen, Dieneke and then two floors up to the ones from the third floor Francesca, Emi, Judith, Peter S., Appy, Micha, Emmy, Martin, João, Karolina, Anja, Lucy, Mariette. Fetelor - Iuliana, Emilia, Gabi, Marcela - pentru toate intalnirile (de scurta durata, in termeni geologici vorbind) la o supa, o salata, o maslina si o portie sanatoasa de limpezire a creierului - multumesc!

It didn't happen only once that I had to go "on the island", you know the one in the North, Texel, at NIOZ. Also there I had the pleasure of working with some very helpful people otherwise known as the MBT-MOB. Thank you Ellen, Jort and Stefan for all your help with the LC/MS analyses and also for teaching me all those new extractions techniques! I cannot forget how I improved my pipetting technique while filling internal standard vials. Angela, Thorsten, Andrea, Isla, Francien, Michiel, Marcel, Joost, Antje, Jayne, Arjan thanks guys for all the nice scientific (and not only) conversations over the famous coffee breaks and for making me feel like one of the group.

There have been plenty of good times but also some bad ones and my two paranymphs shared both with me, so I'm sure they will be able to act in case the debate will become too heated. My dear Lizz, you manage to be my tea provider, driver, partner in "the production line", listener of my playlist, mindreader, hairdresser etc. Ugh I don't know how you can still put up with me and be also my paranymph (hehe). I can hardly wait to "get that feeling" because you know we should be "On the road … Again". It was not only me having to commute from Leiden to Utrecht and so it happened that on the platform I met Simona, who strangely enough had her office 20m down the hall. Cara, I am so happy that the series of strange coincidences led to the opportunity of sharing such good times with you, delicious talks (because we were in the train) followed by dinners and evenings spiced with movies that we dared, without hesitation to watch. Grazie per essere la mia "paraninfa +"!

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Even if we see each other once a year and even then, maybe for only a couple of hours I have to especially mention the support of my family and friends from Romania (but not only). Dear Dea thank you for being there for me with an open heart at any odd hour! Ramona, Lavinia, Simona, Dora, Mara, Levi, Dani is always good to know that I will meet you any time I go back and you will be ready for some story-sharing time. La umbra de noapte!

Chiar daca un simplu multumesc nu ar ajunge vreau sa va multumesc voua mami si tati ca mi-ati fost alaturi si m-ati ajutat in acesti ani in ciuda distantei! Si tu Bogdane ca altfel fara tine si Diana nu erau nici povestile cu ce a mai facut Irina ca sa ma desprind de ale mele. Va pup cu drag pe toti!

Cornelia

Curriculum Vitae

Cornelia Iulia Blaga was born on the 6th of January 1981, in Cluj-Napoca, Romania. After she completed her secondary education in 1999, she studied Ecology and Sociology, both at Babes-Bolyai University in Cluj-Napoca. After she graduated with honours in 2003 she started her Master studies at University of Groningen. She conducted two research projects: one on the topic of social structure and dominance acquisition in an agent based model at University of Groningen. The second project was on the subject concerning the effects of spatial distribution of resources on the individual behavior of herbivorous insects at Victoria University of Wellington, New Zealand. In November 2005 she started her PhD studies at the Department of Earth Sciences - Geochemistry of the Faculty of Geosciences, Utrecht University under the supervision of Gert-Jan Reichart and Jaap S. Sinninghe Damsté. The PhD project, of which this thesis is the result, was partly funded by the Darwin Center for Biogeosciences.

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