Quaternary Science Reviews xxx (2011) 1–41

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

Invited review

A review of molecular organic proxies for examining modern and ancient lacustrine environments

Isla S. Castañeda [a,*], Stefan Schouten [a,b]

[a] NIOZ Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, PO Box 59, 1790 AB Den Burg, The Netherlands
[b] Department of Geosciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands

ARTICLE INFO

Article history:
Received 21 January 2011
Received in revised form
12 July 2011
Accepted 14 July 2011
Available online xxx

Keywords:
Lake
Biomarker
Organic geochemical proxies
Quaternary

ABSTRACT

Molecular organic geochemical proxies are increasingly being utilized to reconstruct past environmental conditions as new tools continue to be discovered and developed. To date, organic geochemical proxies have been developed mainly for use in marine systems and are widely used in paleoceanography. In contrast, organic proxies have been less commonly used on lacustrine sedimentary records. One reason for this is that the wide range in the physical and chemical properties of lakes complicates application of some organic geochemical proxies in lacustrine settings. Furthermore, in comparison to marine studies, presently only a small number of studies have conducted or are currently conducting fundamental research aimed at developing organic geochemical proxies for use in lacustrine settings. Despite this, an increasing number of (paleo)limnological studies are currently applying organic geochemical techniques to examine present and past environmental conditions. In this manuscript we review the use of a number of commonly utilized organic geochemical and isotopic proxies and discuss their potential for environmental reconstruction in Quaternary lacustrine deposits.

1. Introduction

Organic matter preserved in geologic materials (e.g. sediment, rock, coal, petroleum) provides a direct indicator of environmental conditions at the time of deposition and thus is important to paleoenvironmental studies. Although only a small amount of the organic matter produced is eventually preserved in the geologic environment, the geochemical properties of this preserved organic matter can provide a wealth of information. The bulk geochemical properties of organic matter, including total organic carbon (TOC) content, carbon to nitrogen (C:N) ratios, and carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopes, are routinely examined and applied to paleoenvironmental studies (e.g. Meyers, 2003). Examination of organic matter at the molecular level reveals contributions from the three domains of life: archaea, eukarya, and bacteria, and thus can often provide more specific information regarding past environmental conditions in comparison to bulk geochemical analyses, which reflect a mixture of allochthonous and autochthonous inputs.

Individual compounds, or compound classes, preserved in geological materials that can be traced to a particular source organism, group of organisms, or to a particular process (e.g. photosynthesis) are called "biomarkers" (Peters et al., 2005). There are numerous reasons why biomarkers are of particular interest to paleolimnologists. Examination of organic matter at the molecular levels allows for the separation of terrestrial, aquatic and sedimentary components and thus environmental conditions in both the water column and the surrounding watershed can be examined simultaneously (Fig. 1). Biomarkers also allow for the examination of certain groups of algae and microorganisms that lack hard silica or carbonate shells and typically are absent from the fossil record. Diatoms are widely used as a paleolimnological proxy because their silica tests are often abundant and well preserved in lacustrine sediments. While diatoms are important contributors to primary productivity in many lakes, other types of phytoplankton also can be important. Biomarkers such as botryococcenes and heterocyst glycolipids, produced by green algae and cyanobacteria, respectively, can be preserved in sediments thus providing information on the past abundance of these organisms, which are generally absent from the fossil record. Biomarkers of diatoms (e.g. loliolide) can be useful in conjunction with biogenic silica or diatom assemblage data, particularly in settings where silica dissolution has occurred. In recent years, organic geochemical proxies and compound-specific isotopic analyses have become increasingly utilized for paleoenvironmental reconstructions and have been used to address a wide range of research questions ranging from reconstructing

* Corresponding author. Present address: University of Massachusetts Amherst, Department of Geosciences, 611 N Pleasant St., Amherst, MA 01002, USA. Tel.: +1 413 577 1124.
E-mail address: isla@geo.umass.edu (I.S. Castañeda).

0277-3791/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.quascirev.2011.07.009

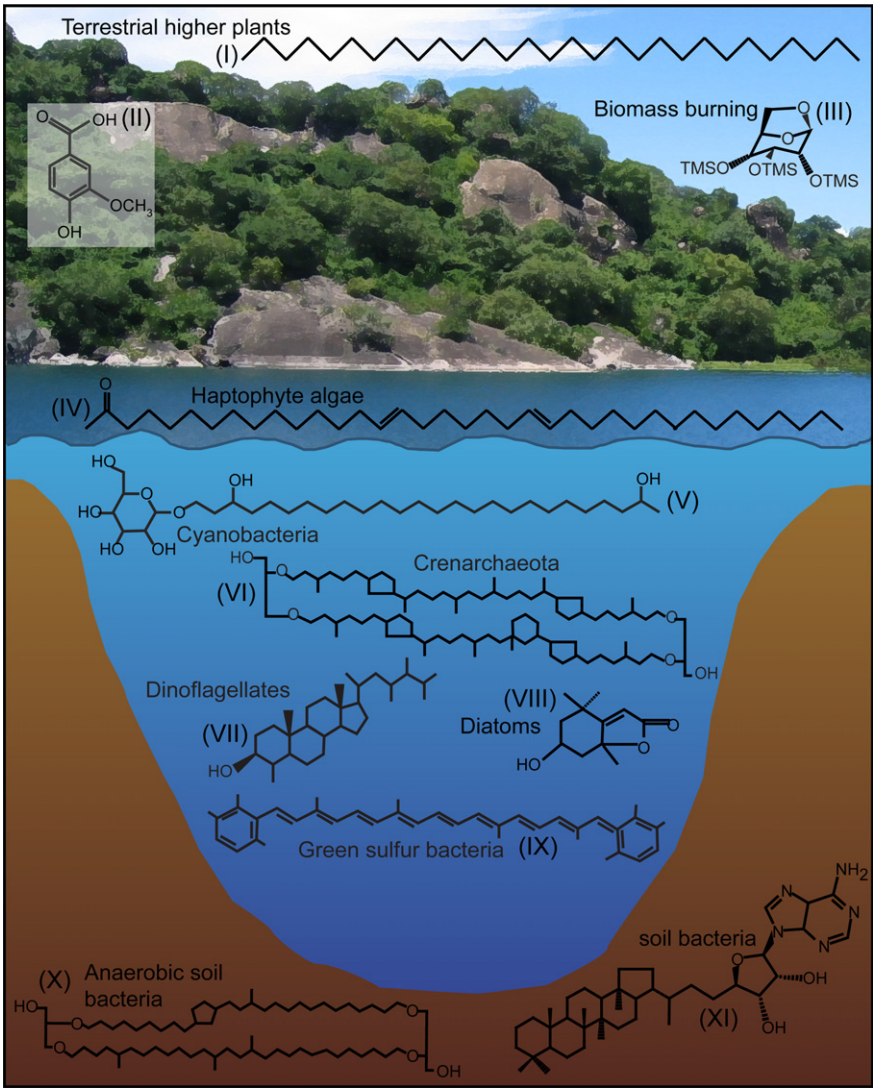

Fig. 1. The biomarker concept. Lacustrine sediments contain inputs from terrestrial and aquatic sources including higher land plants, microbes that live in the soils and sediments, and various types of algae and microorganisms that live in the water column. Using biomarkers, it is possible to examine contributions to sedimentary organic matter from the three domains of life, bacteria, archaea and eukarya, thus providing accurate paleoenvironmental information. There are also biomarkers of processes, such as photosynthesis or biomass burning. Structures shown include the (I) C_{29} *n*-alkane (a biomarker for terrestrial higher plants), (II) vanillic acid (a lignin phenol and biomarker for terrestrial higher plants) (Hedges and Mann, 1979), (III) levoglucosan (a biomarker for biomass burning) (Elias et al., 2001), (IV) the $C_{37:2}$ methyl alkenone (a biomarker for haptophyte algae), (V) 1-(*O*-hexose)-3,25-hexacosanediol (a heterocyst glycopid and biomarker for N_2-fixing cyanobacteria) (Bauersachs et al., 2009a), (VI) crenarchaeol (an isoprenoid glycerol dialkyl glycerol tetraether (GDGT) and biomarker for *Thaumarchaeota*) (Schouten et al., 2002), (VII) dinosterol (a biomarker for dinoflagellates) (Withers, 1983; Piretti et al., 1997), (VIII) loliolide (the anoxic degradation product of the pigment fucoxanthin, the major carotenoid present in diatoms) (Klok et al., 1984; Repeta, 1989), (IX) isorenieratene (a pigment produced by green sulphur bacteria that is used as an indicator of stratified conditions in ancient lake sediments) (Sinninghe Damsté et al., 2001a), (X) branched GDGT IIb (thought to be produced by anaerobic soil bacteria and a biomarker for soil organic matter) (Weijers et al., 2007b), and (XI) adenosylhopnane (an intact bacteriohopanepolyol (BHP) that has been proposed as a biomarker of soil bacteria) (Cooke et al., 2008a).

past terrestrial and aquatic ecosystems and environments (e.g. reconstructing lake surface temperatures, salinity, hydrological variability, vegetation type, soil organic matter input to aquatic environments, soil temperature and soil pH), for investigating biogeochemical cycling and carbon storage, and for examining the preservation and fate of organic matter in the geologic environment (Meyers, 1997; Killops and Killops, 2005; Peters et al., 2005; Eglinton and Eglinton, 2008). Biomarkers provide a wide range of opportunities for paleolimnological studies and the specific source information gained can complement or offer advantages over traditional paleolimnological proxies.

Lakes are sensitive recorders of climatic change and can provide excellent archives of past environmental conditions. In comparison to marine settings, many lakes are characterized by relatively high sedimentation rates, offering possibilities for high-resolution paleoenvironmental reconstructions. Some lakes are characterized by a seasonally or permanently anoxic water column, thus increasing the preservation potential of organic matter. Lakes also provide opportunities for examining local or regional paleoenvironmental conditions and provide information on continental paleoclimate. The paleoclimatic importance of lacustrine sedimentary archives has long been recognized and in recent years there have been increased efforts to obtain long lacustrine paleoclimate records by drill coring. These records have provided both continuous and high-resolution climate archives from a variety of locations around the globe and geochemical studies of these lake sediments has provided, and is currently providing, a wealth of new paleoenvironmental information (e.g. Brigham-Grette et al., 2007;

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Fritz et al., 2007; Hodell et al., 2008; Litt et al., 2009; Fawcett et al., 2011; Woltering et al., 2011).

The great majority of organic geochemical proxies that are of interest for reconstructing Quaternary paleoclimate were originally developed in and applied to marine systems, yet some can be directly applied to lacustrine environments. For example, primary producers such as diatoms, dinoflagellates and cyanobacteria are commonly found in both marine and lacustrine systems and there are diagnostic biomarkers for each of these groups (e.g. Volkman et al., 1998), allowing for past changes in primary productivity or shifts in algal community structure to be examined. However, for other types molecular proxies (e.g. paleotemperature proxies) application to lacustrine environments is not as straightforward due to additional complicating factors that are of importance in lacustrine systems: although the chemical properties of seawater vary somewhat between the different ocean basins, the range of variability in marine systems is quite small in comparison to the world's lakes. The physical (size, depth, basin morphology, catchment area) and chemical (temperature, salinity, pH, oxygen and nutrient concentrations) properties of lakes vary greatly. Here, we examine the application of commonly utilized organic geochemical and isotopic proxies to lacustrine sediments. Due to the extreme range in the chemical and physical properties of lakes it should be noted that the proxies and biomarkers discussed in this manuscript cannot simply be applied to all locations, and the applicability of many of the organic geochemical proxies to individual lakes needs to examined on a site-to-site basis.

The application of organic geochemical proxies to lacustrine sediments has been previously reviewed by Meyers (1997, 2003), who also examined bulk geochemical techniques, which are not discussed here. However, since these reviews, several new molecular proxies have been developed, which can largely be attributed to the application and development of relatively new analytical methods such as high performance liquid chromatography mass spectrometry (HPLC-MS) and compound-specific carbon and hydrogen isotope analysis. Therefore, the main goal of this review is to provide an overview of recently developed molecular and isotopic proxies that can be used to reconstruct paleoenvironmental conditions from Quaternary lacustrine deposits. We also will highlight the differences, when necessary, between application of molecular proxies in marine and lacustrine settings and discuss additional factors that need to be considered for application of molecular proxies to lacustrine environments. Finally, we highlight some recently developed molecular proxies that that have not yet been widely applied to lacustrine settings but that are likely to be useful for Quaternary studies.

1.1. A brief overview of analytical techniques for examining molecular fossils

Organic matter can be broadly separated into two classes; bitumen and kerogen. Bitumen is the solvent-extractable component of the organic matter while kerogen is the non-solvent-extractable component. This review focuses on biomarkers derived from bitumen since this is where the great majority of Quaternary paleoenvironmental studies have focused their research efforts, although we note that biomarkers are also present in kerogen that can provide paleoenvironmental information (see review of Vandenbroucke and Largeau, 2007).

The process of isolating biomarkers from a bulk sediment, culture, or water column filter sample typically begins by extraction with organic solvents followed by additional procedures to fractionate and purify compound classes of interest. Individual compounds (biomarkers) can be analyzed by a variety of techniques. Gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) are the most commonly applied techniques for quantifying and identifying individual compounds. GC-isotope ratio monitoring mass spectrometry (GC-IRMS) is a relatively newer technique (Hayes et al., 1990) and is used to measure the isotopic composition of individual compounds. Compound-specific carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$) and deuterium (δD) isotopes can be measured with a typical precision of 0.1–0.3‰, 0.3–0.7‰, and 2–5‰, respectively (see review of Sessions, 2006a). We also note that recently a technique for measuring compound-specific sulphur isotopes ($\delta^{34}S$) has been developed using GC together with multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), which has a precision better than 0.5‰ for samples containing as little as 6 pmol S (Amrani et al., 2009).

Another relatively new technique for quantifying and identifying biomarker lipids is high performance liquid chromatography (HPLC) with positive ion atmospheric pressure chemical ionization mass spectrometry (APCI-MS) (e.g. Hopmans et al., 2000). HPLC techniques have the advantage that they allow for larger (>1000 Da) and more polar compounds to be analyzed in comparison to traditional GC or GC/MS techniques. Additionally, HPLC coupled to mass spectrometry with electrospray ionization (HPLC/ESI-MS^n) allows for the detection of even more polar, charged compounds (Zink et al., 2003; Sturt et al., 2004) while HPLC with photodiode array UV–vis detection and APCI-MS can be used to examine sedimentary pigments (Keely et al., 1988; Eckardt et al., 1991; He et al., 1998; Ocampo and Repeta, 1999; Ocampo et al., 1999; Airs et al., 2001). Increased selectivity can be gained by using MS–MS (MS^2) techniques (note that MS^2 techniques are also used to increase selectivity in GC/MS). HPLC techniques are currently being utilized by an increasing number of studies and in the last decade have detected previously unknown biomarkers and provided a number of novel proxies (e.g. Hopmans et al., 2006; Talbot and Farrimond, 2007; Bauersachs et al., 2009b).

1.2. Framework of review

In the following parts of this manuscript the discussion is divided into sections by individual compound classes. In the section headings, we have indicated the main environmental parameter (e.g. temperature) that can be examined based on individual compound classes but note that for certain compound classes multiple environmental parameters may be reconstructed. We also indicate the methods that are commonly used to examine individual compound classes although for some compound classes analysis by multiple techniques (e.g. GC/MS and HPLC/MS) is possible. Thus, the reader should refer to the cited references for detailed analytical information. Throughout this review we use Quaternary case studies to highlight recent research developments or new insights that have come from applying molecular or isotopic techniques to lacustrine sediments.

2. Paleotemperature, paleosalinity and haptophyte input from long-chain alkenones

One of the oldest and most widely-applied organic geochemical proxies, the U^k_{37} Index, is based on long-chain alkenones (LCAs) and provides a method for reconstructing past sea surface temperatures, and in some cases, lake surface temperatures. LCAs are found in many marine and an increasing number of lacustrine sediments and comprise a series of C_{37}–C_{39} di-, tri-, and tetra-unsaturated methyl (Me) and ethyl (Et) ketones (Fig. 2), which are analyzed by GC and GC/MS techniques. The original U^k_{37} Index (Brassell et al., 1986) reflected the proportions of the di-, tri-, and tetra-unsaturated ketones (Table 1); however, subsequent research showed that there was no empirical benefit to including the tetra-

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

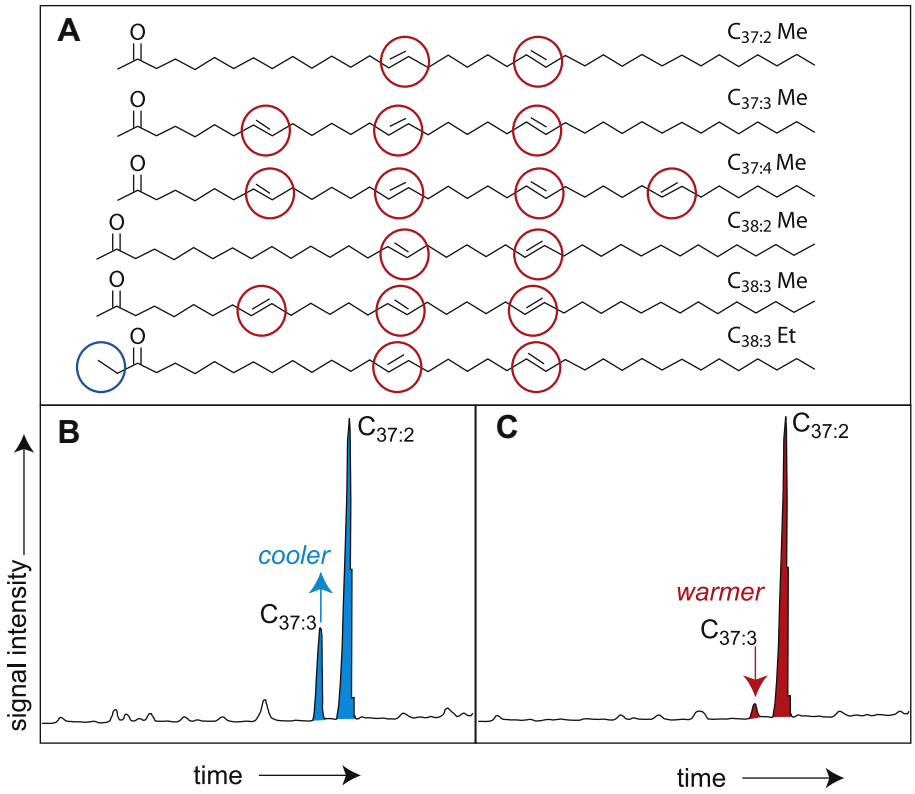

Fig. 2. A) Examples of structures of methyl (Me) and ethyl (Et; circled in blue) long-chain alkenones. These structures are somewhat similar but differ in the number of double bounds, which are indicated by the red circles. B) and C) Illustration of the $U^{k'}_{37}$ SST proxy. As temperature increases, the relative proportion of the $C_{37:3}$ alkenone decreases. Panel B illustrates the GC chromatogram of a sample with a relatively cold signal and C illustrates a sample with a relatively warm signal. Note that the uppermost limit of the $U^{k'}_{37}$ SST proxy is at ~28 °C (e.g. $U^{k'}_{37} = 1$, the corresponding temperature varies slightly depending on the calibration used), which is the point where no $C_{37:3}$ alkenone remains, or where its abundance is too low to quantify.

unsaturated ketone in the paleotemperature equation and the $U^{k'}_{37}$ Index (Table 1) was suggested (Prahl and Wakeham, 1987) and has been widely adopted. $U^{k'}_{37}$ ratios vary positively with growth temperature: as temperature increases, the relative proportion of the tri-unsaturated ketone decreases (Fig. 2). In marine environments, LCAs are mainly produced by two widely distributed species of haptophyte algae, *Emiliania huxleyi* (de Leeuw et al., 1979) and *Gephyrocapsa oceanica* (Conte et al., 1994; Volkman et al., 1995) and have also been reported in the coastal species *Isochrysis galbana* and *Chrysotila lamellosa* (Marlowe et al., 1984). These organisms are all haptophyte algae of the class Prymnesiophyceae, which require sunlight for photosynthesis and generally reside in the upper photic zone (Herbert, 2003 and references therein). LCAs also have been reported from brackish and freshwater environments. Lacustrine LCAs were first reported from the English Lakes district in 1985 (Cranwell, 1985) but more recent studies have revealed

Table 1
Lacustrine U^{k}_{37}, $U^{k'}_{37}$, U^{k}_{3738} and U^{k}_{38} calibrations and formulas.

Calibration equation	n	r^2	Calibrated to	Geographical location	Reference
$U^{k'}_{37} = 0.02T - 0.121$	9	0.89	Summer lake temp	Germany	Zink et al. (2001)
$U^{k}_{37} = 0.0211T - 0.725$	9	0.68	Summer lake temp	Germany	Zink et al. (2001)
$U^{k'}_{37} = 0.0328T + 0.126$	38	0.83	Mean annual air temp	China	Chu et al. (2005)
$U^{k'}_{37} = 0.037T + 0.108$	14	0.9	Mean annual air temp	China: fresh-brackish lakes	Chu et al. (2005)
$U^{k'}_{37} = 0.025T + 0.153$	24	0.67	Mean annual air temp	China: saline lakes	Chu et al. (2005)
$U^{k'}_{37} = 0.0011T^2 - 0.0157T + 0.1057$	14	0.99	Growth temp (10–22 °C)	China: *C. lamellosa* culture	Sun et al. (2007)
$U^{k'}_{37} = 0.0257T - 0.2608$	9	0.97	Growth temp (14–22 °C)	China: *C. lamellosa* culture (linear fit)	Sun et al. (2007)
$U^{k}_{3738} = 0.0464T - 0.867$	13	0.8	Mean autumn temp	Spain	Pearson E.J. et al. (2008)
$U^{k}_{38} = -0.753 + 0.0412T$	12	0.71	Mean autumn temp	Spain	Pearson E.J. et al. (2008)
$T = 39.9U^{k}_{37} + 36.418$	21	0.75	*in-situ* water temp	Lake George, North Dakota (USA)	Toney et al. (2010)
$T = 40.8U^{k}_{37} + 31.8$	34	0.96	*in-situ* water temp*	Braya Sø (Greenland)	D'Andrea et al. (2011)
$U^{k'}_{37} = 0.033T + 0.044$	370	0.98	Annual mean SST	Global marine	Müller et al. (1998)

$U^{k}_{37} = (C_{37:2} - C_{37:4})/(C_{37:2} + C_{37:3} + C_{37:4})$.
$U^{k'}_{37} = (C_{37:2})/(C_{37:2} + C_{37:3})$.
$U^{k}_{38} = (C_{38:2} - C_{38:4})/(C_{38:2} + C_{38:3} + C_{38:4})$.
$U^{k'}_{38} = (C_{38:2})/(C_{38:2} + C_{38:3})$.
$U^{k}_{3738} = (C_{38:2} - C_{38:4} + C_{37:2} - C_{37:4})/(C_{38:2} + C_{38:3} + C_{38:4} + C_{37:2} + C_{37:3} + C_{37:4})$.
*The calibration of D'Andrea et al. (2011) combines water filters from Braya Sø with the core top U^{k}_{37} calibration of Zink et al. (2001).

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

their presence in the water columns or sediments of lakes from around the world including Antarctica (Volkman et al., 1988; Coolen et al., 2004b; Jaraula et al., 2010), Europe (Cranwell, 1985; Thiel et al., 1997; Innes et al., 1998; Zink et al., 2001; Pearson E.J. et al., 2007, 2008), Asia (Li et al., 1996; Wang and Zheng, 1998; Sheng et al., 1999; Zink et al., 2001; Chu et al., 2005; Sun et al., 2007; Liu et al., 2008), North America (Zink et al., 2001; Toney et al., 2010), Africa (Kristen et al., 2010), South America (Theissen et al., 2005) and Greenland (D'Andrea and Huang, 2005; D'Andrea et al., 2011).

2.1. Lacustrine alkenone producers

Understanding the ecology of a particular organism, or group of organisms, is essential for interpretation of its associated molecular signature. In contrast to marine environments where the dominant alkenone producers are well known (*E. huxleyi* and *G. oceanica*), the organism(s) responsible for producing lacustrine alkenones are currently poorly understood although genetic studies provide some insights. Coolen et al. (2004b) examined preserved 18S rDNA in Holocene anoxic sediments from Ace Lake (Antarctica) and found six novel phylotypes related to known alkenone-biosynthesizing haptophytes, with the species *I. galbana* UIO 102 as their closest relative (98.3–99.5‰ sequence similarity). D'Andrea et al. (2006) also examined 18S rDNA in water filtrate, surface and Late-Holocene sediment samples from lakes in West Greenland. Their results suggest alkenones in these lakes are synthesized by a distinct phylotype, differing from both marine haptophytes and those from Ace Lake. Sun et al. (2007) isolated *C. lamellosa* Anand from a cultured mixture of phytoplankton (grown using filtered natural lake water with a Na^+ concentration of 8.78 g/L) collected from saline Lake Xiarinur (Inner Mongolia, China). DNA analysis of water column samples of Lake Fryxell (Antarctica) indicated 18S rDNA sequences closely related to *Isochrysis* spp., *C. lamellosa* and the haptophyte sequences previously reported from the west Greenland lakes and Ace Lake (Jaraula et al., 2010). Theroux et al. (2010) examined 18S rDNA from 15 alkenone-containing lake surface sediments from diverse geographical locations. They found that all haptophyte sequences grouped within the order Isochrysidales and none of the sequences branched directly with the marine species *E. huxleyi* or *G. oceanica*. An especially important finding of this study is that individual lakes contained DNA from multiple haptophyte species (Theroux et al., 2010). Clearly, the main alkenone producers vary from lake to lake, which in combination with the observation that multiple haptophyte species may exist in individual lakes, likely explains some of the variability noted in lacustrine LCA distributions and relationships observed with temperature or salinity (discussed in Sections 2.3 and 2.4).

2.2. Lacustrine LCA homologue distributions

Early work suggested that a characteristic feature of lacustrine LCA distributions was relatively high amounts of the $C_{37:4}$ Me ketone (Fig. 2) (Thiel et al., 1997). In contrast, marine environments are generally characterized by abundant di- and tri-unsaturated compounds ($C_{37:2}$ and $C_{37:3}$) whereas the $C_{37:4}$ homologues are typically present in minor abundances or are absent, except for more polar environments. Indeed, the presence of the $C_{37:4}$ Me ketone has been noted in nearly all lacustrine sediments from which compositional data is reported and in many cases, $C_{37:4}$ is the dominant homologue (Cranwell, 1985; Volkman et al., 1988; Li et al., 1996; Thiel et al., 1997; Wang and Zheng, 1998; Sun et al., 2004; Coolen et al., 2004b; Chu et al., 2005; D'Andrea and Huang, 2005; Liu et al., 2006b, 2008; Toney et al., in press). However, the $C_{37:4}$ homologue was not detected in many Spanish lakes (Pearson E.J. et al., 2008) or in lakes of the Nebraska Sand Hills (Toney et al., 2010) containing LCAs and is a minor component in Lake Tswaing, South Africa (Kristen et al., 2010). Thus, elevated abundances of the $C_{37:4}$ homologue appear to be a characteristic feature of many, but not all, lacustrine alkenone distributions. It has also been suggested that dominance of C_{38} homologues, and in particular of the $C_{38:3}$ homologue, possibly can be used as an indicator of alkaline, evaporitic or saline settings based on observations from several sites (Pearson E.J. et al., 2008; Kristen et al., 2010).

2.3. Relationships between lacustrine LCAs and salinity

It has been noted that the *occurrence* of lacustrine LCAs appears to be related to salinity as LCAs have been reported from many lakes in evaporative settings (e.g. Li et al., 1996; Thiel et al., 1997; Wang and Zheng, 1998; Sun et al., 2004, 2007; Chu et al., 2005; D'Andrea and Huang, 2005; Theissen et al., 2005; Liu et al., 2008; Pearson E.J. et al., 2008). Additionally, high concentrations of LCAs have been reported from both sulphate (Sun et al., 2004; Pearson E.J. et al., 2008; Toney et al., 2010, in press) and carbonate-dominated lakes (Chu et al., 2005; D'Andrea and Huang, 2005; Toney et al., 2010). In west Greenland lakes, unusually high LCA concentrations are found in carbonate-dominated oligosaline lakes but LCAs are absent in nearby freshwater lakes (D'Andrea and Huang, 2005). Similarly, 12 of 13 LCA-containing lakes of the Northern Great Plains (5 lakes, all sulphate-dominated) and Nebraska Sand Hills (8 lakes, 6 carbonate-dominated, one sulfate-dominated and one lacking anion chemistry data) are characterized by elevated salinity (Toney et al., 2010). LCAs are also present in prairie lakes of interior Canada with salinities >1.5 g/L (Toney et al., in press). Pearson E.J. et al. (2008) note that LCA occurrence in Spanish lakes seems to be restricted to brackish-hypersaline sites and that LCAs are more abundant in sulphate-dominated lakes. However, LCAs have also been reported from some freshwater lakes (Zink et al., 2001; Toney et al., 2010) indicating that elevated salinity itself is not a strict requirement for LCA occurrence. *Vice versa*, LCAs also are not detected in all lakes with elevated salinity (Pearson E.J. et al., 2008; Toney et al., in press).

Several studies have reported relationships between salinity and the percentage of the $C_{37:4}$ alkenone ($\%C_{37:4}$) as a proportion of the total C_{37} alkenones. Initially a correlation ($r^2 = 0.78$) between $C_{37:4}$ production and salinity was reported from the North Atlantic and Nordic Seas (Rosell-Melé, 1998; Rosell-Melé et al., 2002; Sicre et al., 2002). However, applying the marine calibrations (Rosell-Melé et al., 2002; Sicre et al., 2002) to West Greenland lakes produced salinity values an order of magnitude larger than the measured salinity values (D'Andrea and Huang, 2005) and subsequent marine research suggested that the $\%C_{37:4}$ salinity relationship was complicated by co-varying environmental factors (Bendle et al., 2005). Nevertheless, a study of Lake Qinghai (China) and its surrounding lakes, where large changes in surface salinity occur, suggests that $\%C_{37:4}$ can qualitatively indicate regional salinity changes (Liu et al., 2008, 2011). Here, it was found that $\%C_{37:4}$ increases with decreasing surface salinity (Liu et al., 2008, 2011) while $U^{K'}_{37}$ values do not change significantly across the large salinity range. The authors hypothesize that at a local or regional scale the LCA-biosynthesizing species may be the same allowing for the use of $C_{37:4}$ as a salinity indicator. However, this remains to be tested. The study of Theroux et al. (2010), which examined 15 lakes from diverse geographical regions (many of these lakes were previously examined in the studies referenced above), also does not support a linear relationship between $\%C_{37:4}$ and salinity across multiple lakes and species. The data of Toney et al. (2010) indicate no clear relationship between salinity and $C_{37:4}$ presence or absence but instead suggest that the sulfate:carbonate ratio of the

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

lake water may be related to the presence/absence of $C_{37:4}$. Lakes of the Northern Great Plains and Nebraska Sand Hills lacking the $C_{37:4}$ homologue were found to have significantly lower sulfate:carbonate ratios (0.01–2.59) compared to lakes containing abundant $C_{37:4}$ (15–117) (Toney et al., 2010). Although high sulfate:carbonate ratios >3.5 also are noted in Canadian prairie lakes where the $C_{37:4}$ homologue is present (Toney et al., in press), this relationship needs to be examined at other locations. Thus, at this point, it seems the relative abundance of $C_{37:4}$ may, at best, be a qualitative indicator for salinity provided that a regional calibration is made.

2.4. Relationships between lacustrine LCAs and temperature

Relationships between water temperature and the U^{k}_{37} or $U^{k'}_{37}$ Index have been reported for many of the LCA-containing lakes and several studies have provided calibrations (Table 1; Fig. 3) providing a method for reconstructing past lake surface temperature. Marine calibrations cannot be applied to lacustrine settings since predominance of $C_{37:4}$ over $C_{37:2}$ in many lakes results in unrealistically low temperature estimates (Zink et al., 2001). Zink et al. (2001) examined surface sediments of lakes in Germany and found the best correlation between the $U^{k'}_{37}$ Index and the summer average lake surface temperature ($r^2 = 0.90$; Table 1). Chu et al. (2005) also examined surface sediments of lakes in China and found a good correlation between $U^{k'}_{37}$ and mean annual air temperature (MAAT) ($r^2 = 0.83$), which generally correlates well with annual mean lake surface temperature (Fig. 3). Chu et al. (2005) also separated the China lakes into two groups, fresh-brackish and saline (salinity >3.0 g/L), and note the best correlation between $U^{k'}_{37}$ in fresh-brackish lakes and mean annual air temperature ($r^2 = 90$). Interestingly, the correlation for saline lakes is considerably lower ($r^2 = 0.67$). Pearson E.J. et al. (2008) were unable to calculate the U^{k}_{37} and $U^{k'}_{37}$ Indices for surface sediments in of many lakes in Spain due to low concentrations of the C_{37} homologues. Instead they substitute C_{38} compounds, which are abundant, into the U^{k}_{37} and $U^{k'}_{37}$ Indices (see Table 1 for equations) and find a significant relationship between U^{k}_{38} and mean autumn air temperature ($r^2 = 0.71$). They also calculated a combination of the C_{37} and C_{38} indices (U^{k}_{3738}; Table 1) and find the strongest relationship between U^{k}_{3738} and mean autumn air temperature ($r^2 = 0.8$). Sun et al. (2007) examined U^{k}_{37} and $U^{k'}_{37}$ values from a cultivated strain of *C. lamellosa* isolated from a lake in China. They found that $U^{k'}_{37}$ values were strongly correlated with growth temperature varying from 10 to 22 °C. A second order polynomial regression of the $U^{k'}_{37}$ index vs. water temperature produced the best correlation ($r^2 = 0.99$; Table 1) but a linear regression also results in a similar correlation ($r^2 = 0.97$). Interestingly, the slopes and intercepts of the calibration equations for the lacustrine *C. lamellosa* culture are considerably different from the calibration of a marine *C. lamellosa* species (Fig. 3). Toney et al. (2010) provide an *in-situ* calibration for U^{k}_{37} for Lake George, ND covering a temperature range from 2 to 22 °C based on filtered water samples. They found a significant relationship between the U^{k}_{37} Index and water temperature ($r^2 = 0.75$; Table 1) but in contrast to other studies, they found no relationship between $U^{k'}_{37}$ and water temperature ($r^2 = 0.14$). Toney et al. (2010) also note that the proportion of the $C_{37:4}$ alkenone, which is dominant in Lake George, is also linearly correlated to temperature ($r^2 = 0.73$). D'Andrea et al. (2011) created a U^{k}_{37} calibration for lake Braya Sø (Greenland) by combining data from filtered water samples with the core top U^{k}_{37} calibration of Zink et al. (2001) ($r^2 = 0.96$; Table 1). Thus, at this point there is no uniform calibration of U^{k}_{37} or $U^{k'}_{37}$ against lake surface temperature, which is likely related to the presence of different haptophyte producers at different sites. The presence of multiple haptophyte species within a lake is also a concern for lacustrine LCA calibrations; however, it has been suggested that if the haptophyte species are closely related, a single U^{k}_{37} or $U^{k'}_{37}$ calibration can be used for paleoclimate reconstructions if an *in-situ* or culture calibration is available (Theroux et al., 2010).

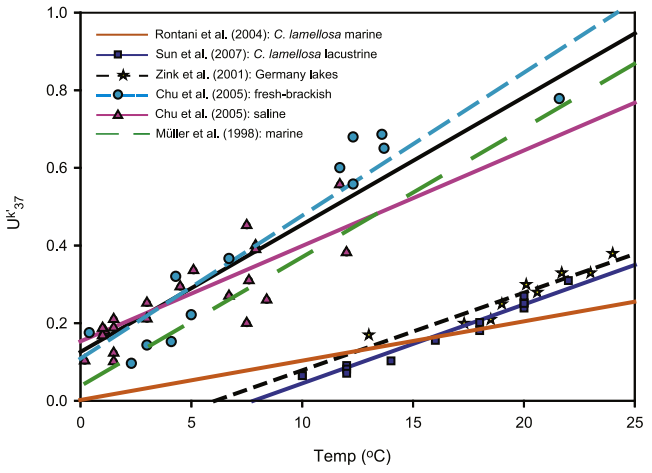

Fig. 3. Comparison of lacustrine alkenone calibration equations for the $U^{k'}_{37}$ Index. The marine calibrations of *E. huxleyi* (Prahl and Wakeham, 1987) and *C. lamellosa* (Conte et al., 1994) are shown for comparison. Lacustrine $U^{k'}_{37}$ calibrations include a calibration developed for surface sediments of lakes in China (solid black line; Chu et al., 2005), the same set of lakes divided into fresh-brackish and saline lakes (Chu et al., 2005), the calibration for Lake Braya Sø, Greenland (Theroux et al., 2010 and references therein), the calibration for lakes in Germany (Zink et al., 2001) and a calibration (linear and polynomial fit) for a cultivated strain of *C. lamellosa* isolated from a lake in China (Sun et al., 2007).

In addition to variability resulting from different haptophyte producers, a number of other factors are known to influence the relationship between U^{k}_{37} or $U^{k'}_{37}$ and temperature in marine environments (see Herbert, 2003 for a review), which likely also affect lacustrine environments. For example, seasonality may influence temperature reconstructions based on LCAs due to a seasonal production maximum for LCA-producing organisms. Sun et al. (2007) note the presence of *C. lamellosa* in phytoplankton samples collected from Lake Xiarinur (China) in spring and autumn whereas water column filtering of Lake George, ND, reveals alkenone production after ice out in the early spring (Toney et al., 2010). Similarly, alkenone fluxes to sediment traps in a Greenland lake indicates the haptophyte bloom occurring between June and mid-July (D'Andrea et al., 2011). Indeed, some of the available lacustrine LCA calibrations also report the best correlation with a seasonal temperature rather than with MAAT (Zink et al., 2001; Pearson E.J. et al., 2008). Thus, seasonal influences on temperature reconstructions from lacustrine alkenones are likely and should be evaluated for individual sites.

Non-thermal physiological growth factors including nutrient and light limitation are known to lead to significant variations in $U^{k'}_{37}$ values independent of temperature, and have been observed in culture experiments and in marine sediments (e.g. Prahl et al., 2006; Placencia et al., 2010). Batch culture experiments with *E. huxleyi* show that $U^{k'}_{37}$ values decrease under nutrient stress conditions and increase under prolonged dark stress conditions (Prahl et al., 2006). By changing nitrate and phosphate concentrations from 83.1 and 11.5 μM to 0.0 and 0.5 μM, respectively, Prahl et al. (2006) observed that $U^{k'}_{37}$ values decreased from 0.579 to 0.493, equivalent to a temperature change of 3 °C using the calibration of Müller et al. (1998). In the dark stress experiment at 15 °C a sample grown under a 12:12 light:dark cycle was compared to samples grown under 24 h of darkness, and it was found that $U^{k'}_{37}$ values increased by up to 0.042, equivalent to a temperature change of 1.3 °C (Prahl et al., 2006). Placencia et al. (2010) found

anomalously cold $U^{k'}_{37}$ values along the Peru-Chile margin where permanent upwelling and complete nutrient utilization by phytoplankton results in low surface nitrate (<2 μM) and chlorophyll *a* (<1 mg m^{-3}) concentrations. Thus, it seems likely that nutrient concentrations and upwelling can also influence lacustrine alkenone distributions while light limitation may be especially important to ice-covered lakes. These processes probably account for some of the scatter seen in lacustrine alkenone calibrations.

Finally, several marine and laboratory studies suggest diagenesis, and in particular, oxic degradation may influence $U^{k'}_{37}$ records, with preferential degradation of the $C_{37:3}$ ketone occurring, resulting in slightly warmer temperatures. For a review of these issues we refer to reader to Herbert (2003) as, to our knowledge, these issues have not yet been specifically examined for lacustrine environments.

2.5. Paleoclimate reconstructions based on lacustrine LCAs

There is particular interest in utilizing lacustrine LCAs for paleotemperature reconstructions, and indeed, several studies have utilized this approach. For example, Liu et al. (2006b) utilized LCAs to examine both temperature and salinity changes in Late-Holocene sediments of Lake Qinghai (China). $U^{k'}_{37}$ values revealed fluctuating periods of warmer and cooler temperatures that could be related to known climate events including warming during the 20th century, the Little Ice Age, the Medieval Warm Period, the Dark Ages Cold Period, and the Roman Warm Period (Fig. 4a). Fluctuations in $\%C_{37:4}$ provided evidence of salinity changes, which were found to be coupled to temperature changes, with fresher lake waters noted during warm periods. The authors related this pattern to the Asian monsoon exerting a large influence on the climate of the Lake Qinghai region (Liu et al., 2006b) (Fig. 4a).

D'Andrea et al. (2011) created U^{k}_{37} records for two lakes (Braya Sø and Lake E) in West Greenland after developing an in-situ temperature calibration from Braya Sø (Fig. 4b,c). They found the U^{k}_{37} records of both lakes to be in close agreement, displaying temperature changes of up to 5.5 °C over the past 5600 years and an overall pattern similar to that of the GISP2 ice core. Interestingly, major and abrupt temperature changes, occurring within decades, were found to coincide with archaeological records indicating the settlement and abandonment of Saqqaq, Dorset and Norse cultures (Fig. 4b). D'Andrea et al. (2011) hypothesize that these significant temperature variations may be associated with the North Atlantic Oscillation.

2.6. Outlook on the application of lacustrine LCAs to Quaternary studies

Despite the fact that LCAs have been reported from globally distributed lakes, to date, relatively few studies have utilized lacustrine LCAs for paleoclimate reconstructions and to our knowledge, no studies have yet used alkenone concentrations and an indicator of past haptophyte productivity although this is commonly done in marine settings. There are several reasons for the small number of paleoclimate reconstructions based on lacustrine LCAs. First, alkenone unsaturation ratios correspond

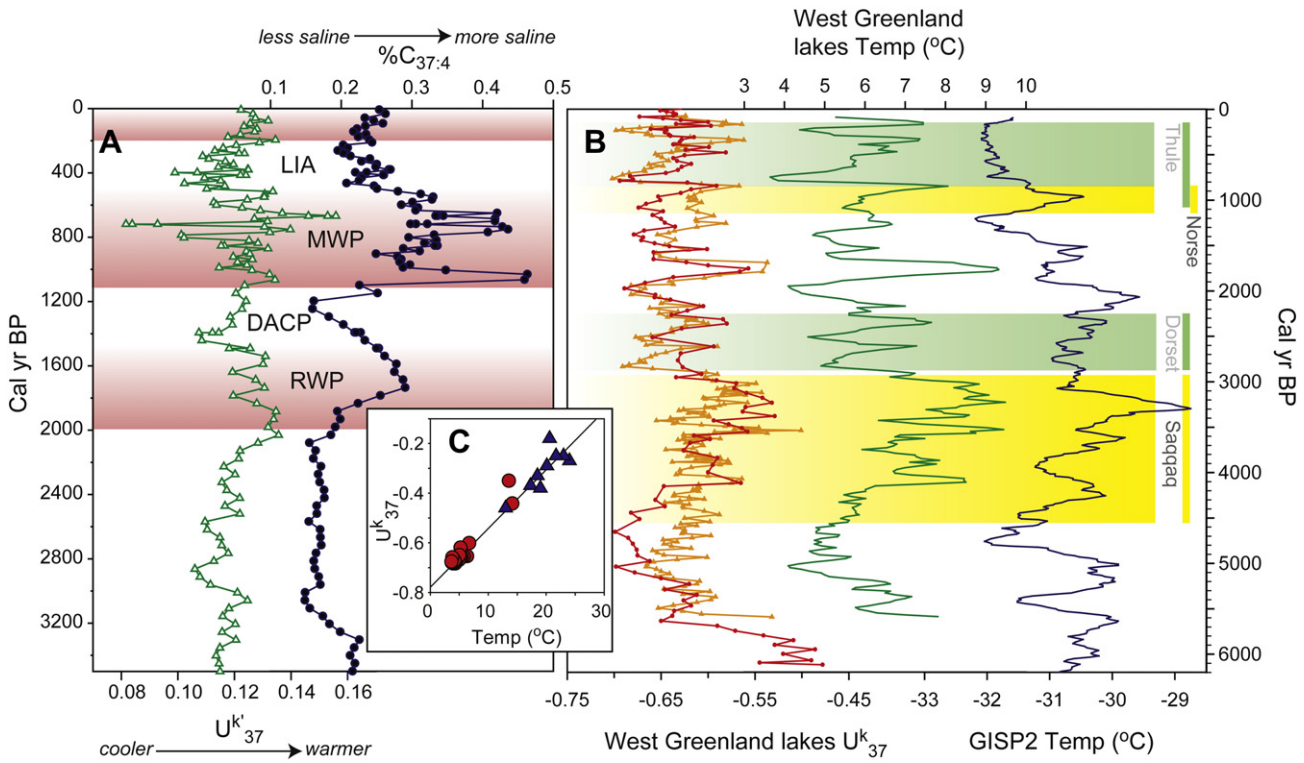

Fig. 4. Examples of lacustrine alkenone records. A) $U^{k'}_{37}$ and $\%C_{37:4}$ records of Lake Qinghai, China (data from Liu et al., 2006b). These records reveal a climate response to known climate events including 20th century warming, the Little Ice Age (LIA), the Medieval Warm Period (MWP), the Dark Ages Cold Period (DACP), and the Roman Warm Period (RWP). Warmer temperatures are found in association with fresher lake waters and is likely related to the influence of the Asian monsoon on the climate of Lake Qinghai. B) U^{k}_{37} temperature records of lakes in West Greenland (data from D'Andrea et al., 2011). The plot on the left shows U^{k}_{37} values for Braya Sø (red circles) and Lake E (orange triangles) in the Kangerlussaq region of West Greenland. The middle plot (green line) shows the stacked U^{k}_{37} records for these lakes, converted to temperature using a calibration developed by the authors (shown in C). The plot on the right (dark blue) shows a temperature reconstruction for the GISP2 Ice Core (Alley, 2004). The presence of the Saqqaq, Dorset Norse and Thule cultures is indicated by the yellow and green shading. C) U^{k}_{37} temperature calibration for Greenland lake Braya Sø ($r^2 = 0.96$), which was created by combining data from filtered water samples (red circles) with the core top U^{k}_{37} calibration of Zink et al. (2001) (blue triangles). Data from D'Andrea et al. (2011).

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

with temperature in only a small subset of LCA-containing lakes. Second, the occurrence of LCAs is episodic in some lakes and thus cannot be used to generate continuous climate records (Zink et al., 2001; Theissen et al., 2005). Furthermore, there is no generally applicable correlation of LST with alkenone distribution and one has to rely on regional calibrations. Nevertheless, several studies have generated paleoclimate records based on LCAs and for sites lacking calibrations, either U^{k}_{37} or $U^{k'}_{37}$ values have been used to examine *relative* temperature changes (Thiel et al., 1997; e.g. Wang and Zheng, 1998; Theissen et al., 2005; Liu et al., 2006b). Studies such as that of D'Andrea et al. (2011) demonstrate that high quality temperature records can be produced from lacustrine LCA distributions, providing important insights into past continental temperature variability. However, it is important to recognize that before these temperature reconstructions could be made, extensive background research was conducted on the Greenland lakes including filtering water column samples over multiple years to develop a temperature calibration (D'Andrea et al., 2011) and genetic studies to demine the main alkenone producing organism (D'Andrea et al., 2006). Such studies are essential for examining relationships between lacustrine LCA distributions and temperature (or salinity) and similar studies need to be conducted in a wider variety of locations. Additionally, identifying the main alkenone producers in other lakes where LCAs have been reported, and isolating and bringing them into culture, likely would facilitate utilizing these compounds as paleoenvironmental proxies.

3. Reconstructing temperature and soil organic matter input from glycerol dialkyl glycerol tetraethers (GDGTs)

Isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs) are membrane lipids diagnostic for certain groups within the Archaea. These GDGTs consist of an isoprenoid carbon skeleton ether bonded to a glycerol-moiety containing 0–3 cyclopentane rings (GDGTs I–III) (Fig. 5) and are of interest since they provide proxies for reconstructing marine and lake surface temperatures, and for examining inputs of soil organic matter to marine or lacustrine environments. A large number of phylogenetic groups within the domain Archaea synthesize isoprenoid GDGTs (Schouten et al., 2007b and references therein). Archaeal 16S rRNA sequences are also ubiquitous in normal marine waters and are comprised mainly of Thaumarchaeota (formerly Group I Crenarchaeota; see Brochier-Armanet et al., 2008; Spang et al., 2010) and Group 2 Euryarchaeota (DeLong, 1992; Fuhrman et al., 1992; Karner et al., 2001; Lipp et al., 2008). The GDGT "crenarchaeol" (GDGT IV), which contains four cyclopentane moieties and a cyclohexane moiety (Fig. 5), is suggested to be specific to the Thaumarchaeota (Pitcher et al., 2011 and references therein). 16S rRNA gene sequences related to the marine Thaumarchaeota have also been reported in lakes (e.g. Keough et al., 2003; Sinninghe Damsté et al., 2009) in agreement with the finding of crenarchaeol and GDGTs 0–III in the water columns and sediments of lakes (e.g. Powers et al., 2004, 2010; Tierney et al., 2008; Blaga et al., 2009; Sinninghe Damsté et al., 2009).

Another group of GDGTs, the branched GDGTs, contain methyl-substituted C_{28} *n*-alkyl side chains that contain 4, 5 of 6 methyl substitutes (Fig. 5) (Sinninghe Damsté et al., 2000) and are of interest since these compounds provide proxies for reconstructing mean annual soil temperature and soil pH (Weijers et al., 2007b). Branched GDGTs were first identified in peats (Sinninghe Damsté et al., 2000) and were later found to be ubiquitous and dominant in soils (Weijers et al., 2006b). In contrast to the isoprenoid GDGTs that are produced by Archaea, it is thought that branched GDGTs are biosynthesized by anaerobic soil bacteria (Weijers et al., 2006a; Sinninghe Damsté et al., 2011) although branched GDGTs have not yet been identified as the main membrane lipids in cultures and the exact source organism(s) remains unknown.

GDGTs provide good biomarkers as they are found in sediment back until at least the late Jurassic (Carillo-Hernandez et al., 2003). The various proxies based on isoprenoid and branched GDGTs (discussed in Sections 3.1–3.3) are all relatively new, beginning with the study of Schouten et al. (2002), and therefore much remains to be learned. However, these proxies have proven to be important indicators of past climate and thus have been widely applied to both marine and lacustrine sediments. Here, we examine application of these proxies to lacustrine environments.

3.1. The BIT Index as a soil organic matter tracer

The Branched and Isoprenoid Tetraether (BIT) index provides a proxy for aquatic vs. soil organic matter input and is based on relative abundances of soil derived (branched) GDGTs vs. crenarchaeol (a biomarker for aquatic Thaumarchaeota) (Fig. 5; Table 2) (Hopmans et al., 2004). BIT values range from 0 to 1, with a value of 0 indicating a purely marine (or aquatic) source in which only crenarchaeol is present, while a value of 1 represents pure soil OM source, consisting of only the branched GDGTs (Hopmans et al., 2004). However, since small to moderate amounts of crenarchaeol also may be present in soils and peat, soil OM is generally characterized by BIT values of >0.9 (Weijers et al., 2006b). In marine settings, high BIT values are noted near river mouths and decrease offshore while low BIT values are observed in open marine settings (Hopmans et al., 2004; Kim et al., 2010a). Thus, the BIT index can be useful for examining the delivery of soil organic matter to marine or lacustrine systems. Branched GDGTs are transported from terrestrial to aquatic environments by riverine input or surface runoff and are present in low abundance in open marine settings due to small amounts of *in-situ* production (Peterse et al., 2009). To date, branched GDGTs have not been detected in dust samples (Hopmans et al., 2004). It is important to note that in contrast to other terrestrial proxies (e.g. $\delta^{13}C_{org}$, C/N ratios), the BIT Index does not carry a large imprint of vegetation (Huguet et al., 2007; Walsh et al., 2008; Belicka and Harvey, 2009; Smith et al., 2010) as branched GDGTs are not produced by plants. Therefore, examining the BIT index in combination with other terrestrial proxies or biomarkers provides opportunities for examining the transport of soil organic matter and vegetation to marine or lacustrine environments.

Many lakes, especially smaller lakes, are generally characterized by a large watershed relative to the surface area of the lake. Thus, it is not surprising that many lakes are characterized by high BIT Index values. In a global survey of GDGTs in lakes (Powers et al., 2010) and a survey of GDGTs in European lakes (Blaga et al., 2009), it was found that >75% had high BIT values (>0.5). However, in lakes, high BIT values may also result from *in-situ* production of branched GDGTs in the water column. Several studies of lakes in East Africa (Sinninghe Damsté et al., 2009; Tierney et al., 2010b), Indonesia (Tierney and Russell, 2009); New Zealand (Zink et al., 2010) and Europe (Blaga et al., 2009; Bechtel et al., 2010) have concluded that *in-situ* production of branched GDGTs likely occurs in lakes, suggesting that they are biosynthesized by a source in addition to anaerobic soil bacteria. Branched GDGTs have been found in the water columns of both oxic and anoxic lakes (Sinninghe Damsté et al., 2009; Bechtel et al., 2010) and in oligotrophic and eutrophic lakes (Bechtel et al., 2010). As it appears that *in-situ* production of branched GDGTs is widespread in lakes, the BIT Index may not solely reflect soil organic matter input to all lakes, and in many lakes it is currently not clear what the signal represents.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

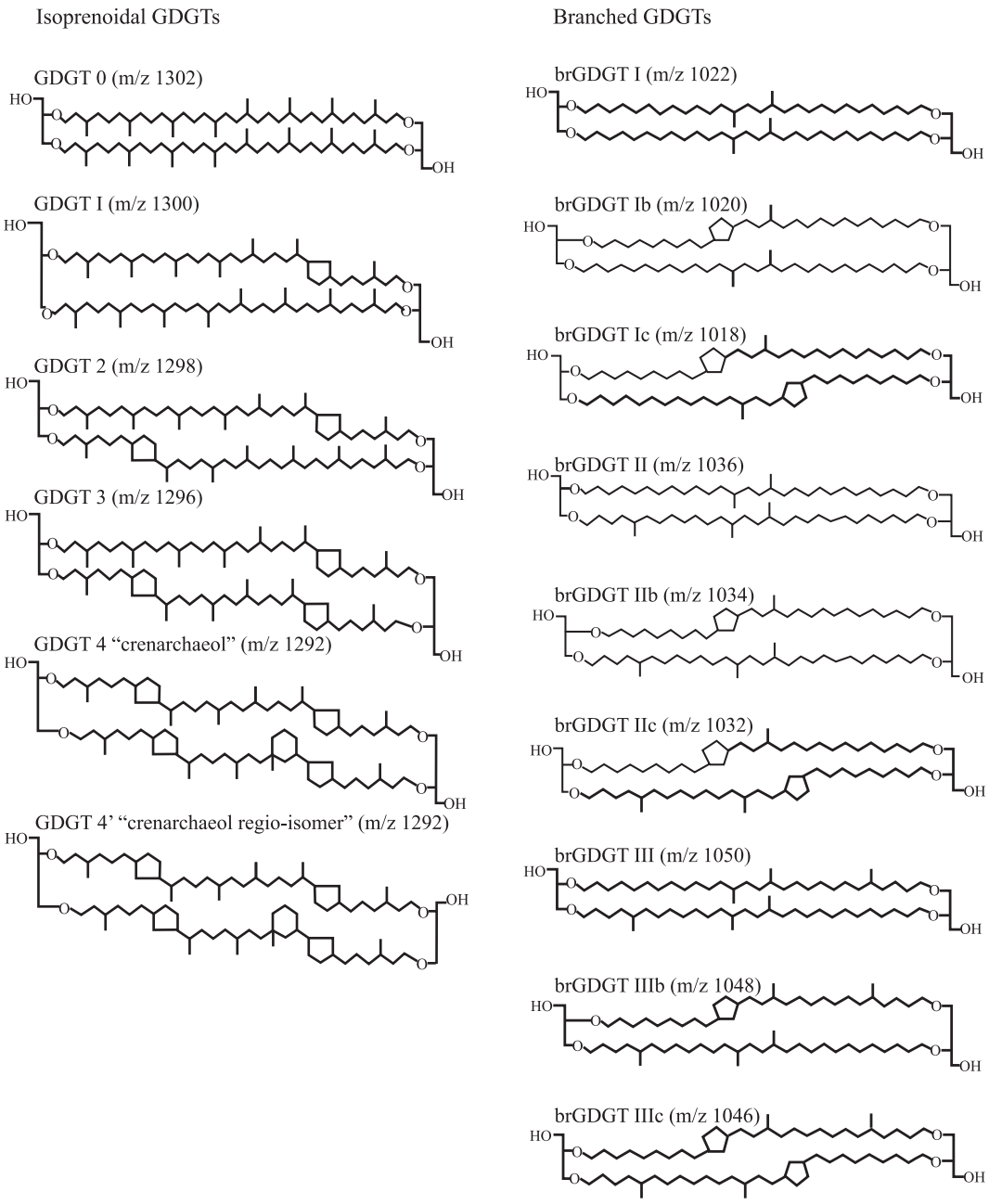

Fig. 5. Structures of the isoprenoid and branched glycerol dialkyl glycerol tetraethers (GDGTs) used for calculating TEX_{86}, the BIT Index, and MBT/CBT.

Table 2
Formulas for GDGT-based proxies including the BIT Index (Hopmans et al., 2004), TEX_{86} (Schouten et al., 2002), TEX_{86}^{H} and TEX_{86}^{L} (Kim et al., 2010b) and MBT and CBT (Weijers et al., 2007b).

$$BIT = \frac{[GDGT\ I + GDGT\ II + GDGT\ III]}{[crenarchaeol + GDGT\ I + GDG\ TII + GDGT\ III]}$$

$$TEX_{86} = \frac{[GDGT2 + GDGT3 + GDGT4']}{[GDGT1 + GDGT2 + GDGT3 + GDG4']}$$

$$TEX_{86}^{L} = \log \frac{[GDGT2]}{[GDGT1 + GDGT2 + GDGT3]}$$

$$TEX_{86}^{H} = \log \frac{[GDGT2 + GDGT3 + GDGT4']}{[GDGT1 + GDGT2 + GDGT3 + GDGT4']}$$

$$MBT = \frac{[GDGT\ I + GDGT\ Ib + GDGT\ Ic]}{[\sum \text{all branched GDGTs}]}$$

$$CBT = \frac{[GDGT\ Ib = GDGT\ IIb]}{[GDGT\ I + GDGT\ II]}$$

A study from Lake Challa (Kenya) in which water column, sediment trap and surface sediment samples were analyzed for GDGTs offers some insights into processes influencing the distribution of GDGTs in lakes. In Lake Challa, the major settling flux of branched GDGTs coincides with the period of maximum precipitation and it was also observed that surface sediments located near the periphery of the lake had higher BIT values than surface sediments located in the middle of the lake (Sinninghe Damsté et al., 2009). Both of these observations support the hypothesis that delivery of branched GDGTs to this lake occurs though erosion of soils in the lake catchment (Sinninghe Damsté et al., 2009). However, it was also found that concentrations of branched GDGTs were 1–2 orders of magnitude higher in the deep waters of Lake Challa compared to the surface waters. The authors conclude that sediment resuspension is unlikely and thus either *in-situ* production occurs in the anoxic lower water column or branched GDGTs

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

are delivered to the deep waters of the lake via groundwater inputs (Sinninghe Damsté et al., 2009).

Verschuren et al. (2009) used the BIT Index record as a proxy of rainfall-induced surface runoff at Lake Challa. They argue that because the lake is a steep-sided crater basin, even major fluctuations in lake level do not significantly change the catchment area and thus variations in the BIT Index mainly reflect changes in surface runoff. Variations in the BIT record, complemented by evidence from seismic-reflection stratigraphy, were found to be in agreement with lake-level changes noted at other lakes in the region. Thus, the authors suggest that on longer time scales BIT Index values are proportional to rainfall over the Lake Challa drainage basin. The Lake Challa records indicate that monsoonal rainfall in East Africa varied at half-percessional intervals, which were in phase with orbitally controlled insolation forcing (Verschuren et al., 2009).

When interpreting BIT Index records, it is important to note that variability in crenarchaeol concentrations may also drive changes in the BIT Index rather than the influx of branched GDGTs. This has been noted at some marine (Castañeda et al., 2010; Smith et al., 2010) and lacustrine (Tierney et al., 2010b) sites where BIT values were found to mainly reflect crenarchaeol production rather than the branched GDGT flux. Therefore, in order to utilize the BIT index to examine soil organic matter input to marine or lacustrine environments it is essential to determine absolute concentrations of GDGTs (Huguet et al., 2006b). Furthermore, one should be aware that *in-situ* contributions of branched GDGTs may complicate interpretation of past BIT variations, especially when branched GDGT concentrations are low.

3.2. MBT and CBT as proxies for air temperature and soil pH

In addition to the BIT Index, two more recently developed proxies also based on branched GDGTs (Fig. 5) are the Cyclisation of Branched Tetraethers (CBT) and the Methylation of Branched Tetraethers (MBT) (Table 2) (Weijers et al., 2007b). CBT provides a proxy for soil pH and is based on the observation that the relative number of cyclopentane moieties of branched GDGTs is exponentially negatively correlated with soil pH (Weijers et al., 2007b). MBT is primarily positively correlated with mean annual soil temperature, which in many cases is similar to mean annual air temperature (MAAT), but, to a lesser extent, is also negatively correlated with soil pH (Weijers et al., 2007b). To reconstruct MAAT, soil pH is first obtained from the CBT equation and then this value is used to correct the MBT equation (Tables 2 and 3) for the influence of soil pH (Weijers et al., 2007b).

The MBT/CBT calibrations are based on a dataset of globally distributed soils consisting of 134 samples from 90 different locations (Weijers et al., 2007b). The uncertainties with reconstructing soil pH from CBT are $\sim\pm1$ pH unit and ~5 °C for calculating absolute MAAT from MBT/CBT. However, it has been noted that local or regional calibrations may be necessary for reconstructing absolute MAATs (Weijers et al., 2007b; Sinninghe Damsté et al., 2008). It is also worth noting that a number of factors are currently poorly constrained with the MBT/CBT proxy. The relatively large uncertainties in the calibration equations suggest that other factors besides temperature and soil pH are affecting the distribution of branched GDGTs. Indeed, Weijers et al. (2007b) noted a weak correlation ($r^2 = 0.47$) between MBT and precipitation.

Initially, application of the MBT/CBT proxies in lake sediments to reconstruct continental MAAT appeared particularly promising in small lakes with high BIT values where TEX_{86} could not be applied. However, recent research demonstrated that *in-situ* production of branched GDGTs from within the water column of lakes also affects MBT/CBT, as it does the BIT Index (Sinninghe Damsté et al., 2009; Tierney and Russell, 2009; Bechtel et al., 2010; Blaga et al., 2010). Tierney and Russell (2009) investigated branched GDGT distributions in Lake Towuti, Indonesia, and in soils from its watershed. They found that CBT-inferred pH values appeared to reflect the pH of the lake water rather than the surrounding soils, predicted temperatures from MBT/CBT were significantly colder than MAAT, and that concentrations of branched GDGTs were an order of magnitude higher in the lake sediments than the surrounding soils. Based on these observations, they suggested that branched GDGTs are produced *in-situ* in lakes, similar to the results of Peterse et al. (2009) who noted *in-situ* production of branched GDGTs in a Svalbard fjord. Blaga et al. (2009) investigated branched GDGT distributions in the surface sediments of 82 globally distributed lakes of variable water depth and size and conclude that branched GDGTs in lakes are derived from mixed (soil and *in-situ*) sources. Tyler et al. (2010) examined MBT/CBT in Lake Lochnagar (Scotland) and found that CBT-inferred pH was in good agreement with diatom-inferred pH but that MBT/CBT significantly underestimated MAAT by ~5 °C. Bechtel et al. (2010) examined GDGTs in eutrophic Lake Lugano and oligotrophic Lake Brienz, Switzerland, in cores covering the interval from ~1900 AD to the present. They found that branched GDGTs at Lake Brienz appear to be mainly soil derived and that reconstructed MAAT was comparable to nearby weather station data. In contrast, at Lake Lugano, where the branched GDGTs appear to be at least partially *in-situ* produced, MBT/CBT significantly underestimates MAAT (by up to ~10 °C) but instead resembles the temperature of the deep lake quite well (Bechtel et al., 2010).

Despite the fact that *in-situ* production of branched GDGTs likely occurs in variable amounts in different lakes, several lacustrine studies suggest that it is still possible to reconstruct MAAT using the MBT/CBT proxies. Zink et al. (2010) examined branched GDGT distributions in eleven New Zealand lakes ranging from 101 to 2000 m above sea level. Interestingly, they found that in these lakes, where *in-situ* production of branched GDGTs appears significant, the CBT Index was mainly controlled by temperature, rather than pH, and that both MBT and CBT Indices indicated relationships with MAAT. They used their data to produce new calibration equations for MBT ($n = 10$, $r^2 = 0.74$) and CBT ($n = 9$, $r^2 = 0.72$; Table 3) and found that reconstructed MAATs show a clear covariance with altitude, in general agreement with weather station data and chironomid-based temperature reconstructions. Zink et al. (2010) also applied their MBT calibration to sediments of Alpine Lake to examine temperature changes during the past

Table 3
MBT and CBT calibrations for New Zealand and East African lakes compared to the global soils calibration dataset of Weijers et al. (2007).

Calibration equation	n	r^2	Geographical location	Reference
$MAAT = 55.01 \times MBT - 6.055$	10	0.74	New Zealand	Zink et al. (2010)
$MAAT = -6.567 \times CBT + 12.228$	9	0.72	New Zealand	Zink et al. (2010)
$MAAT = 50.47 - 74.18 \times (f\text{GDGT III}) - 31.60 \times (f\text{GDGT II}) - 34.69 \times (f\text{GDGT I})$[a]	38	0.94	East Africa	Tierney et al. (2010b)
$CBT = 3.33 - 0.38 \times pH$	134	0.70	Global soils	Weijers et al. (2007b)
$MBT = 0.122 + 0.187 \times CBT + 0.020 \times MAAT$	134	0.77	Global soils	Weijers et al. (2007b)

[a] Note that "*f*" denotes the fractional abundances of the branched GDGTs relative to the *total* branched GDGTs (includes GDGTs I, Ia, Ib, II, IIa, IIb, III, IIIa, IIIb).

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

29,000 years and found their results were similar to a chironomid-based temperature reconstruction from a nearby lake. Tierney et al. (2010b) examined branched GDGTs in 46 East African lakes. They noted that applying the global soils calibration to the East African lake sediments produced cooler than expected MAATs and thus present a different type of calibration, i.e. by using weighing factors for different GDGTs, for these lakes ($n = 38$, $r^2 = 0.94$; Table 3). Tierney et al. (2010b) find that temperature and pH are the main factors that can be related to variations in the distribution of branched GDGTs and suggest that despite being from mixed sources, branched GDGTs can be used to examine MAAT in the East African lakes.

Although uncertainties exist regarding the origin of branched GDGTs in lakes, at some sites there is strong evidence that the MBT/CBT paleothermometer indeed reflects MAAT. Fawcett et al. (2011) conducted a multi-proxy study of a lacustrine sediment core from Valles Caldera (New Mexico) and used MBT/CBT to examine MAAT and soil pH during Marine Isotope Stages (MIS) 10–14 (~368–552 Kyr). They found that the glacial stages were characterized by millennial-scale temperature variations of up to 7 °C. Stadials were characteracterized by cooler temperatures and increased percentages of boreal *Picea* + *Abies* pollen while interstadials were marked by warmer temperatures and increased percentages of *Quercus* and *Juniperus* pollen (Fig. 6). In addition, CBT reconstructions of soil pH indicate that arid conditions occurred during warm intervals (MIS 11 and 13) while calcium counts from core scanning XRF indicate closed-basin conditions at these times (Fig. 6). The Valles Caldera records display remarkable agreement between branched GDGT, pollen and core scanning data, and show that extended "dust-bowl-like" megadroughts, lasting for centuries to millennia, occurred in the southwestern United States during MIS 11 and 13 (Fawcett et al., 2011).

3.2.1. Outlook for lacustrine MBT/CBT reconstructions

Overall, many uncertainties currently exist regarding sources of branched GDGTs to lakes and thus the application of the MBT/CBT paleothermometer to lakes. Studies such as Zink et al. (2010) and Tierney et al. (2010b) are promising as they suggest that branched GDGTs can be used to reconstruct MAAT, using local calibrations. A key factor in determining whether MBT/CBT is applicable for reconstructing MAAT in lakes may be the relative proportion of soil- and lacustrine-derived GDGTs. Although branched GDGTs in lakes reflect mixed sources (Blaga et al., 2010; Tierney et al., 2010b) lakes where either soil- or lacustrine-derived GDGTs dominate may be particularly suitable for reconstructing MAAT or water column temperatures, respectively. However, lake water temperatures are often strongly correlated with MAAT (Livingstone and Lotter, 1998) and thus lakes with mixed sources of branched GDGTs may also be suitable for reconstructing MAAT, depending on the geographical location of lake or the water depth of maximum GDGT production. Tropical lakes may be better suited for MBT/CBT temperature reconstructions because surface water temperatures are generally similar to MAAT and also smaller differences exist between surface and bottom water temperatures. In subtropical or temperate lakes, where the temperature difference between surface and bottom waters is greater, larger differences between MBT/CBT-inferred

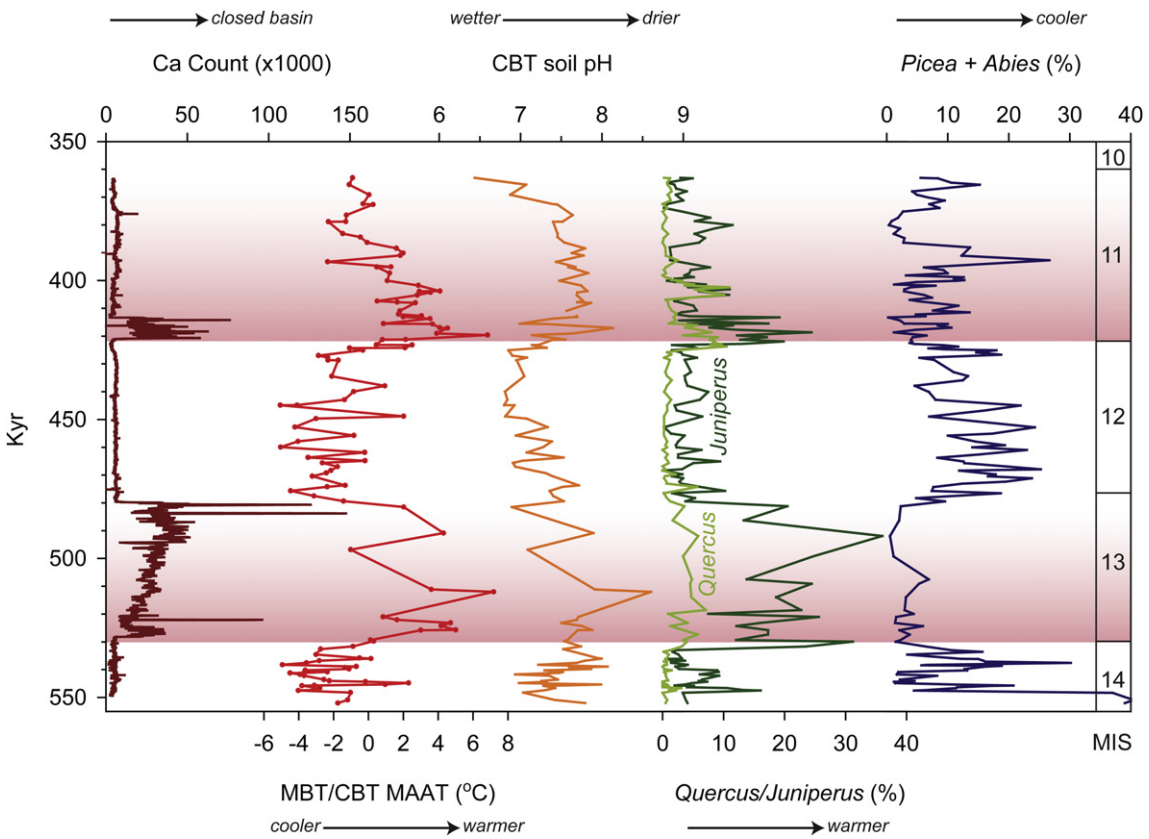

Fig. 6. Multi-proxy data from Valles Caldera, New Mexico (Fawcett et al., 2011). Calcium counts from core scanning XRF are plotted in dark red. MBT/CBT reconstructions of mean annual air temperature (MAAT) are plotted in red, CBT reconstructions of soil pH are plotted in orange. Percent *Quercus* and *Juniperus* pollen are plotted in light and dark green, respectively, while boreal pollen (*Picea* + *Abies*) is plotted in dark blue. Marine Isotope Stages (MIS) 10–14 are indicated on the right side of the graph and interstadials are highlighted in red. High calcium concentrations indicate periods of closed-basin conditions during MIS 11 and 13 and coincide with warmer MAAT, elevated soil pH (indicating arid conditions) and increased percentages of *Quercus* and *Juniperus* (warm) pollen. In contrast, boreal pollen displays increased percentages during the stadials (MIS 12 and 14).

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

temperature and MAAT may exist, depending on the location of branched GDGT productivity within the water column. It is also likely that seasonal variations in GDGT production could exist for some lakes and may influence MAAT reconstructions. Given that these proxies are only a few years old (Weijers et al., 2007b), a number of outstanding questions exist that remain to be answered by future studies. Clearly, the applicability of the MBT/CBT proxies needs to be assessed for individual sites but may be useful for temperature reconstructions in some lakes.

We note that when evaluating MBT/CBT records, it is important to consider that the age of the branched GDGTs may differ in comparison to marine (or lacustrine) derived components. Branched GDGTs are formed on land and thus may arrive in the marine (or lacustrine) realm with a significant time lag, although Weijers et al. (2007a) did not note a substantial time lag for Late Quaternary marine sediments collected from the Congo River fan. A related issue is that the sources of soil OM to marine (or lacustrine) sediments may have changed over time. This has been noted by an MBT/CBT study of the Amazon River fan, in which warmer MBT/CBT MAATs were noted during the LGM compared to the present and attributed to a change in source region from the Amazon flood plain to the Andes mountains (Bendle et al., 2010). Therefore, the transport pathways of branched GDGTs to marine or lacustrine settings should be evaluated for individual sites.

3.3. The TEX_{86} paleothermometer

The TEX_{86} (TetraEther index with 86 carbon atoms) (Schouten et al., 2002) temperature proxy is based on the relative abundance of isoprenoidal GDGTs, which are mainly biosynthesized by Thaumarchaeota (Fig. 5). The basic premise behind the TEX_{86} is that the number of cyclopentane moieties increases with increasing growth temperature (Fig. 7). The two most abundant isoprenoidal GDGTs, GDGT-0 and crenarchaeol (Fig. 5), are excluded from the TEX_{86} to avoid their overpowering influence on the index since their abundances are generally much higher compared to the other GDGTs (Schouten et al., 2002). In addition, GDGT-0 is known to be produced by other types of Archaea, including methanogenic and methanotrophic Euryarchaeota, such as those living in anoxic sedimentary environments (Schouten et al., 2007b).

3.3.1. TEX_{86} temperature calibrations

The most recent marine calibration for TEX_{86} is based on a dataset of 426 core top samples and utilizes a log calibration (Kim et al., 2010b). Since it appears that the crenarchaeol regio-isomer is insensitive to temperature changes in the polar oceans, two calibration equations were developed for TEX_{86} for application in low (<15 °C; TEX_{86}^{L}) and high (>15 °C; TEX_{86}^{H}) temperature marine settings (Table 4; Kim et al., 2010b). TEX_{86} has also been shown to work in some lakes (e.g. Powers et al., 2004, 2010; Tierney et al., 2008; Blaga et al., 2009). In contrast to the relatively large dataset for the marine calibration, the present linear calibration of TEX_{86} in lakes is based on a much smaller dataset (Table 4). Powers et al. (2004) first investigated application of TEX_{86} in four lakes and found that the samples fit on the initial marine calibration of Schouten et al. (2002) and reflected mean annual lake surface temperature. More recently, Powers et al. (2010) generated a TEX_{86} calibration for lakes based on 12 samples (Fig. 8), which derive mostly from medium to large lakes ($r^2 = 0.86$; Table 4). Tierney et al. (2010a) added five additional samples, all with temperatures >23 °C, to the calibration of Powers et al. (2010) and removed samples with temperatures <10 °C to produce a lacustrine TEX_{86} calibration covering a temperature range from 11 to 30 °C ($n = 13$, $r^2 = 0.92$; Table 4). Combining all lakes used in the calibrations of Powers et al. (2010) and Tierney et al. (2010a) also yields a temperature calibration with a good correlation ($n = 19$, $r^2 = 0.89$; Fig. 8). The root mean square error for the different TEX_{86} calibrations ranges from 1.7 to 4.0 °C (Table 4) while TEX_{86} measurements

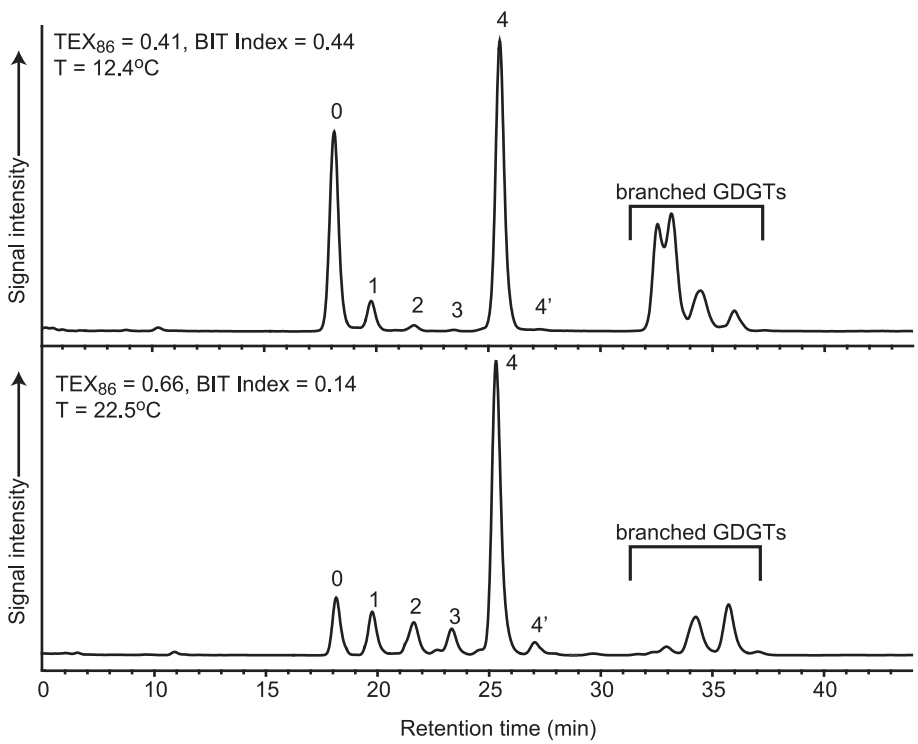

Fig. 7. HPLC chromatogram of the GDGT distribution of a cold sample from Lake Superior with a BIT Index value of 0.44 (shown in the upper panel) and a warm sample from Lake Turkana with a low BIT Index value of 0.14 (shown in the bottom panel). Applying the Powers et al. (2010) lacustrine TEX_{86} calibration, the Lake Superior sample yields a temperature of 8.7 °C and the Lake Turkana a temperature of 22.5 °C.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Table 4
Marine and lacustrine TEX_{86} calibrations. The formulas for calculating TEX_{86}, TEX_{86}^{H} and TEX_{86}^{L} values are provided in Table 2. See Fig. 8 for details on the combined calibration.

Calibration equation	n	r^2	Range (°C)	Error (°C)	Geographical location	Reference
$TEX_{86} = 0.15T + 28$	44	0.92	0–30	±2.0	Global marine surface sediments	Schouten et al. (2002)
$T = -10.78 + 56.2 \times TEX_{86}$	223	0.94	8–30	±1.7	Global marine surface sediments	Kim et al. (2008)
$T = 67.5 \times TEX_{86}^{L} + 46.9$	396	0.86	−3–30	±4.0	Global marine surface sediments	Kim et al. (2010b)
$T = 68.4 \times TEX_{86}^{H} + 38.6$	225	0.87	5–30	±2.5	Global marine surface sediments	Kim et al. (2010b)
$T = 55.231 \times TEX_{86} - 13.955$	12	0.86	5–30	±3.62	Global lake surface sediments; BIT < 0.5	Powers et al. (2010)
$T = TEX_{86} \times 38.874 - 3.4992$	13	0.92	11–30	±2.1	Global lake surface sediments with $T > 10$ °C; BIT < 0.6	Tierney et al. (2010a)
$T = 54.889 \times TEX_{86} - 13.363$	19	0.89	5–30	±3.1	Global lake surface sediments	Combined calibration

can be determined with a reproducibility of ±0.004, equivalent to ±0.3 °C (Schouten et al., 2007a).

3.3.2. *Factors potentially influencing TEX_{86} temperature reconstructions*

Although the current lakes calibrations for TEX_{86} are based on a relatively small number of samples, surface sediments of a considerably larger number of lakes have been analyzed for TEX_{86}. For example, Powers et al. (2010) examined 46 lakes while Blaga et al. (2009) examined 47 lakes for GDGTs. However, several factors complicate application of the TEX_{86} in many lakes. Both Powers et al. (2010) and Blaga et al. (2009) note that not all lakes contain the full suite of GDGTs needed to calculate a TEX_{86} value. Second, some of the isoprenoid GDGTs used to calculate TEX_{86} are also found in small amounts in soils, which are produced not only by soil Thaumarchaeota but also likely by other Archaea (Weijers et al., 2006b), and can be transported to oceans or lakes. The presence of soil-derived isoprenoid GDGTs may lead to either a warm or a cold bias in TEX_{86} temperatures, and the direction of the bias is not predictable. In sediments with high BIT Index values, it is likely that crenarchaeol and the other isoprenoid GDGTs are partially derived from soils (Weijers et al., 2006b). Thus, it has been suggested for marine environments that TEX_{86} only be applied where the BIT Index is ~<0.3 (Weijers et al., 2006b). However, due to potential *in-situ* production of branched GDGTs (Section 3.1), the BIT index may not accurately reflect soil organic matter input to lakes. It is also worth noting that in some cases, samples with relatively high BIT Index values can produce reliable TEX_{86} estimates since TEX_{86} temperatures have been found to agree closely with other temperature proxies such as the $U^{K'}_{37}$ Index (Castañeda et al., 2010). The degree of bias is dependent on the 'TEX_{86}' value of GDGTs brought in from soils to the lakes: if this value is similar to that of the TEX_{86} produced in the lake then high input of soil organic matter (and thus high BIT values) will not have a large impact. The most appropriate testing may be to check for coinciding changes of BIT with TEX_{86}: in these cases care should be taken in interpreting TEX_{86} temperature estimates.

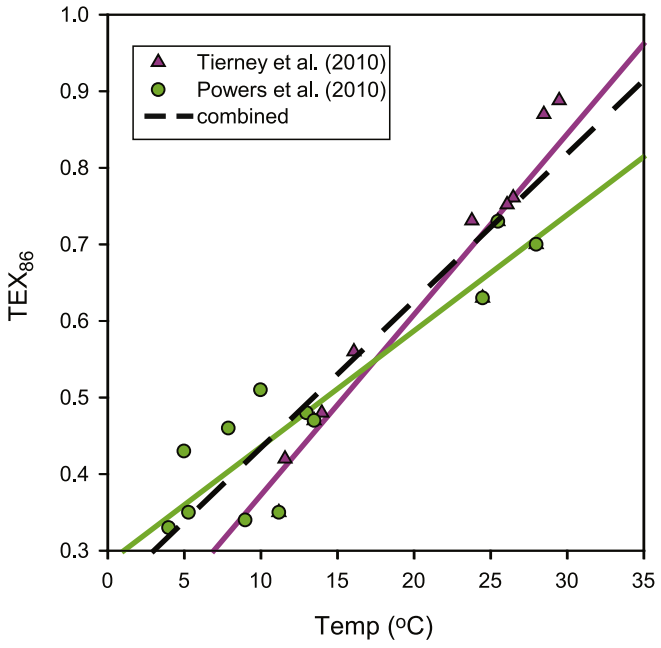

Fig. 8. Lacustrine TEX_{86} calibrations. Data points used for the calibrations of Powers et al. (2010) and Tierney et al. (2010a) are shown by the green circles and pink triangles, respectively, while the solid lines of the same colors represent the linear fit. The black line represents the linear fit of all data points used in both the calibrations of Powers et al. (2010) and Tierney et al., (2010a). See Table 4 for equations and correlation coefficients of these calibrations.

A third factor that can influence TEX_{86} values is additional contribution of isoprenoid GDGTs from groups other than Thaumarchaeota, such as methanogenic Euryarchaeota (Blaga et al., 2009). GDGT-0, a common Archaeal membrane lipid, is found in thermophilic Crenarchaeota and Euryarchaeota, methanogenic Euryarchaeota (Koga et al., 1993) and Euryarchaeota mediating the anaerobic oxidation of methane (Pancost et al., 2001; Blumenberg et al., 2004) in addition to Thaumarchaeota (Sinninghe Damsté et al., 2002a). In lakes, the most likely sources of GDGT-0 are from methanogenic Euryarchaeota and Thaumarchaeota (Blaga et al., 2009). It has been proposed that the ratio of GDGT-0 to crenarchaeol can be used to assess contributions from methanogenic Euryarchaeota because GDGT-0 and crenarchaeol are produced both by Thaumarchaeota and methanogenic Euryarchaeota whereas methanogenic Euryarchaeota produce GDGT-0 but lack crenarchaeol (Blaga et al., 2009). If the GDGT-0/crenarchaeol ratio is >2, a substantial methanogenic origin for GDGT-0 is likely (Blaga et al., 2009). Anoxic conditions are required for methanogenesis and thus the process can occur in sediments as well as in anoxic water columns. Indeed, many lake sediment and water column samples have been observed with GDGT-0/crenarchaeol values >2, which is perhaps not surprising given that methanogenesis is the dominant anaerobic mineralization process in lake sediments. Interestingly, Blaga et al. (2009) note that some samples from aerobic part of the water column were also characterized by GDGT-0/crenarchaeol ratios >2, suggesting an additional, possibly allochthonous, source of GDGT-0 in some settings.

A fourth factor that can influence TEX_{86} values is the seasonal timing of the Thaumarchaeota bloom. In marine systems it has been noted that marine Thaumarchaeota are generally abundant in surface waters at times of the year when the majority of phytoplankton are not blooming (e.g. Murray et al., 1999; Wuchter et al., 2006a) and thus, TEX_{86} temperatures may reflect this period in the seasonal cycle. Because most of the Thaumarchaeota seem to be nitrifiers (Francis et al., 2005; Könneke et al., 2005; Wuchter et al., 2006a) their growth rates are likely related to ammonium availability, derived from the decay of organic matter from primary producers. Indeed, it has been noted at several marine sites that TEX_{86} reflects either summer or winter SST (Herfort et al., 2006; Menzel et al., 2006; Wuchter et al., 2006a; Castañeda et al., 2010;

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Leider et al., 2010; Richey et al., 2011), which is likely the cause of some of the scatter in the TEX_{86} core top calibration (Kim et al., 2010b). Similar seasonal influences have also been noted in lakes. At Lake Lucerne (Switzerland) the highest concentrations of isoprenoid GDGTs in suspended particulate material from surface waters (2 m) is observed in January–February (Blaga, 2010). Maximum fluxes of isoprenoid GDGTs occurs during the winter at Lake Challa (Sinninghe Damsté et al., 2009). Similarly, at Lake Superior fluxes of isoprenoid GDGTs towards the sediment mainly occurs in winter and late spring/early summer and particle transport initiates during overturning conditions (Woltering et al., 2010). Powers et al. (2010) also note a statistically significant difference between TEX_{86} and winter surface temperature ($r^2 = 0.84$) in comparison to summer surface temperature ($r^2 = 0.71$). While presently limited to a few studies, it appears seasonal variability in Thaumarchaeota production likely exerts an influence on lacustrine TEX_{86} values.

Sub-surface production by Thaumarchaeota is a fifth factor that can influence TEX_{86} values. Thaumarchaeota are likely chemoautotrophs and therefore are not required to reside within the photic zone (Karner et al., 2001; Sinninghe Damsté et al., 2002a). In fact, Thaumarchaeota are distributed throughout the marine (Murray et al., 1999; Karner et al., 2001; Herndl et al., 2005) and lacustrine (Woltering et al., 2010) water columns yet studies of TEX_{86} in sinking particle fractions in marine systems indicate that GDGTs mostly derive from the upper water column and that Thaumarchaeota living in deeper waters do not contribute substantially to the GDGT flux and thus the TEX_{86} signal (Wuchter et al., 2005, 2006b). In some locations, Thaumarchaeota appear to reside in the upper water column but at greater depths than the sea surface. Indeed, TEX_{86} has been reported to reflect sub-surface temperatures in several locations including the Benguela upwelling system (>40 m depth) (Lee et al., 2008), the Santa Barbara Basin (100–150 m depth) (Huguet et al., 2007), offshore NW Africa (~30 m depth) (Lopes dos Santos et al., 2010) and possibly in the Pigmy Basin, Gulf of Mexico (Richey et al., 2011). Sub-surface production has also been noted in lakes. Woltering et al. (2010) examined Archaeal 16S rRNA genes and GDGTs in sediment trap and filtered samples from the water column of Lake Superior over three annual cycles. They found that both GDGTs and Archaeal 16S rRNA genes are concentrated around the hypolimnion when Lake Superior is thermally stratified but are distributed throughout the water column during overturning periods. Woltering et al. (2010) also note that TEX_{86} derived temperatures of the settling particles appear to represent the water temperature of the hypolimnion. Similarly, in Lake Lucerne (Switzerland) maximum production of isoprenoid GDGTs occurs within the aphotic zone, at ~50 m depth (Blaga, 2010). Interestingly, in a Lake Lucerne sediment core, an offset to higher temperatures is noted prior to ~1960 AD and is hypothesized to be related to the recent eutrophication of the lake, which likely resulted in migration of the Thaumarchaeota to a deeper ecological niche (Blaga, 2010).

Another factor which may need particular consideration is pH, which can be highly variable in lakes. In marine environments, the potential effects of pH on GDGT distributions are likely minor due to relatively small pH variations, even on geologic time scales. However, lakes display a wide range of pH values. For example, the volcanic crater lake Kawah Ijen (Indonesia) is extremely acidic with a pH < 0.3 (Lohr et al., 2005) while alkaline Lake Magadi (Kenya), which is recharged mainly by saline hot springs, has a pH of 10 (Jones et al., 1977). Even within individual lakes, some are known to have experienced large pH variations in the past. Pearson A. et al. (2008) found that GDGT distributions in hot springs displayed a good correlation with pH. Although hot springs contain a wide variety of (thermophilic) archaea with different GDGT distributions, it is possible that pH may influence TEX_{86} values. Culture experiments with thermophilic Euryarchaeota also show a decrease in cyclopentane moieties with decreasing pH (Shimada et al., 2008). Therefore, pH variations may be a potential concern for application of TEX_{86} to lacustrine environments and there is a need for future studies to further investigate the potential effects of pH on GDGT distributions.

The impact of diagenesis on TEX_{86} is not well-constrained although the few studies that have investigated the effects of oxic degradation suggest no substantial effect. Schouten et al. (2004) examined Arabian Sea sediments that were deposited in contrasting redox conditions but did not find a significant effect on TEX_{86} values. Similarly, Kim et al. (2009) conducted a water column degradation experiment over a one year and did not find a significant effect of oxic degradation on TEX_{86}. Huguet et al. (2006a) also found no significant effect of herbivory on TEX_{86} values. Thus, at this point it appears that diagenesis does not have a significant effect on TEX_{86}; however, differences in BIT Index (Section 3.1) values have been noted. Huguet et al. (2008) examined BIT Index values across the oxidation fronts of deep-sea turbidites (~127 Ka to 14 Ma) deposited at the Madeira Abyssal Plain. They note increasing BIT values on long-term exposure to oxygen and attribute this pattern to the enhanced preservation of soil organic matter due to sorptive protection, rather than to differences in degradation kinetics for the branched and isoprenoid GDGTs. We note that the impact of diagenesis on the MBT/CBT proxies (Section 3.2) have not yet been investigated and additional studies are needed to further examine the impacts of diagenesis on both branched and isoprenoid GDGTs and their associated proxies.

Finally, different populations of Thamuarchaeota may reside in different lakes, requiring local calibrations for TEX_{86}. In the high salinity and temperature environment of the Red Sea, Trommer et al. (2009) found that TEX_{86} in surface sediments from the northern basin has a very different relationship between TEX_{86} and temperature when compared to the global marine calibration. They speculated that this is due to a different population of Thamuarchaeota residing in this region. Indeed, Ionescu et al. (2009) found that Thamuarchaeota in the Gulf of Aqaba, northern Red Sea, were genetically distinct from those of the open ocean. It is possible that regional calibrations are necessary for increased accuracy of temperature predictions using TEX_{86} in lakes, similar to the $U^{k'}_{37}$ index.

3.3.3. *Lacustrine TEX_{86} temperature reconstructions and outlook*

Despite the many uncertainties with applying TEX_{86} in lakes, the proxy has been applied to several lakes and importantly, has provided a method to examine continental paleotemperature history. TEX_{86} has proven particularly successful in the large lakes of the East African Rift Valley, where isoprenoidal GDGTs are particularly abundant, and to date, LST records have been generated from Lake Malawi (Powers et al., 2005, 2011; Woltering et al., 2011), Lake Tanganyika (Tierney et al., 2008, 2010a) and Lake Turkana and Lake Victoria (Berke et al., 2009, 2010). The temperature records of these lakes exhibit several common features indicating a regional, rather than a local, response to climate variability. These include a Last Glacial Maximum (LGM) present-day temperature difference of 3.5–4 °C, early warming following the LGM (Powers et al., 2005; Tierney et al., 2008; Woltering et al., 2011), a mid-Holocene warming centred at ~5 kyr (Powers et al., 2005; Tierney et al., 2008; Berke et al., 2009) and a recent warming on the order of ~2.5 °C occurring within the past 100 years (Tierney et al., 2010a; Powers et al., 2011) (Fig. 9). Thus, TEX_{86} provides a useful tool for reconstructing past LST and for examining continental paleoclimate; however, its applicability to lakes needs to be assessed using the constraints outlined above.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

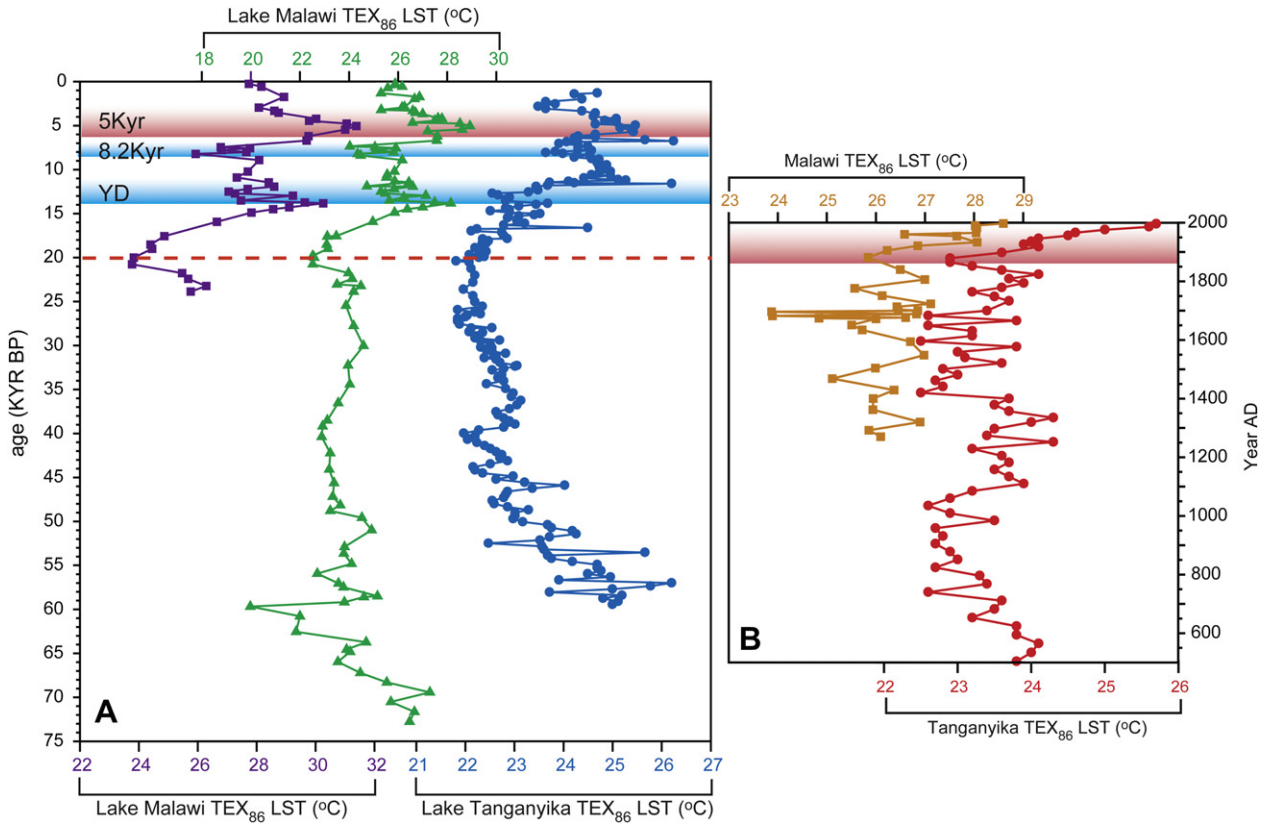

Fig. 9. TEX_{86} lake surface temperature (LST) reconstructions from East Africa. In panel A, TEX_{86} data from Lake Malawi core M98-1P (Powers et al., 2005) is shown with the TEX_{86} data from Lake Malawi core MAL05-2A (Woltering et al., 2011) and the Lake Tanganyika TEX_{86} record (Tierney et al., 2008). A continuous record from Lake Tanganyika was generated from cores NP04-KH04-3A-1K and NP04-KH04-4A-1K (Tierney et al., 2008). All TEX_{86} records indicate early warming initiating at ~20,000 years (indicated by the dashed red line) followed by a period of generally increasing temperatures until ~14,000 years. Variable and cooler conditions are noted until ~12,000 years, spanning the interval of the Younger Dryas (YD) (blue shading). A minor cooling in noted in all records around 8000 years (blue shading), and may be related to the 8.2 Kyr cold event. An interesting feature of these records is a mid-Holocene warm period, centred at approximately 5000 years (red shading). Panel B shows two recent TEX_{86} records: the record of cores M98-11MC and M98-2PG from Lake Malawi (Powers et al., 2011) and Lake Tanganyika cores KH1 and MC1 from Lake Tanganyika (Tierney et al., 2010a). Both of these records indicate a substantial >2.5 °C warming since ~1900 AD (red shading).

4. Reconstructing C_3 vs. C_4 vegetation and primary productivity using compound-specific isotopes ($\delta^{13}C$)

The *n*-alkanes, *n*-alkanols and *n*-alkanoic acids are straight-chain hydrocarbons produced by many organisms and the dominant chain lengths, carbon number distributions and isotopic compositions vary depending on the source organism. In many organisms the *n*-alkanes exhibit strong odd over even carbon number predominance whereas the *n*-alkanols and *n*-alkanoic acids exhibit strong even over odd carbon number predominance. The long-chain (C_{27}–C_{35}) *n*-alkanes (and the C_{26}–C_{36} *n*-alkanols and *n*-alkanoic acids) are a main component of the epicuticular waxes of higher plants (Eglinton and Hamilton, 1967). In contrast, aquatic algae are dominated by shorter-chain homologues (C_{17}–C_{21} *n*-alkanes) (Giger et al., 1980; Cranwell et al., 1987) while the mid-chain homologues (C_{23}–C_{25} *n*-alkanes) are a dominant component of submerged aquatic macrophytes (Ficken et al., 2000). The *n*-alkanes (*n*-alkanols and *n*-alkanoic acids) are generally well preserved in sediments and plant leaf waxes are transported to marine or lacustrine sediments via water or wind erosion. These compounds are identified and quantified by GC and GC/MS, while their isotopic composition is determined by GC-IRMS. The carbon and deuterium isotopic composition of both plant leaf waxes and algal lipids can provide important paleo-environmental information, which is discussed in detail below and in Section 5.

Ratios based on *n*-alkanes of differing chain lengths have been used to examine relative inputs of aquatic macrophytes or terrestrial organic matter into lake sediments. For example, the P_{aq} ratio is the abundance of mid-chain *n*-alkanes over the total sum of the abundances of the mid plus long-chain *n*-alkanes and is used to discriminate sources of submersed and emersed vegetation (Ficken et al., 2000). The ratio of the long chain ($C_{27} + C_{29} + C_{31}$) to short-chain ($C_{15} + C_{17} + C_{19}$) *n*-alkanes can be used to assess terrestrial vs. aquatic sources of organic matter (Meyers, 1997). In addition to being able to differentiate between source organisms, the distribution patterns of *n*-alkanes can sometimes be used to distinguish between different vegetation types (e.g. Schwark et al., 2002; Hanisch et al., 2003). The C_{31} *n*-alkane tends to be dominant in grasses while the C_{27} and C_{29} *n*-alkanes are dominant in deciduous trees (Cranwell, 1973). Additionally, the carbon preference index (CPI) (Bray and Evans, 1961) of *n*-alkanes is used to examine the odd over even carbon number predominance, which can be used to distinguish terrestrial plant from bacterial or petroleum sources, while the average chain length (ACL) of *n*-alkanes has been observed to increase with increasing aridity or temperature at some, but not all, locations (e.g. Peltzer and Gagosian, 1989; Rommerskirchen et al., 2003).

Although longer-chain lengths are *generally* produced by higher plants and the shorter-chain lengths by aquatic algae, some notable exceptions have been observed. For example, it was found that *Betula* (birch) leaves contain significant amounts of the C_{23} *n*-

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

alkane (Sachse et al., 2006) while long-chain C_{27} and C_{29} *n*-alkanes have been reported from emersed aquatic macrophytes (Aichner et al., 2010b). Mid-chain *n*-alkanes have also been detected in *Sphagnum* species (Baas et al., 2000). Certain types of algae such as *Botryococcus braunii* may also be a source of long-chain *n*-alkanes in sediments (Lichtfouse et al., 1994) while some algae also produce unsaturated alkanes (e.g. C_{27} and C_{29} *n*-alkenes in *Rhizosolenoid* diatoms (Sinninghe Damsté et al., 1999a)). Thus, care should be taken when examining *n*-alkane distributions and when assigning sources to particular homologues.

4.1. Reconstructing C_3 vs. C_4 vegetation using plant leaf wax $\delta^{13}C$

The carbon isotopic composition ($\delta^{13}C$) of the long-chain *n*-alkanes (or other compounds derived from higher plants, such as lignin phenols) can be used to distinguish between vegetation utilizing different photosynthetic pathways. Plants utilizing the C_3 (Calvin–Benson) photosynthetic pathway tend to have average *n*-alkane carbon isotopic compositions of −34.7‰ for the C_{29} *n*-alkane (−35.2‰ for the C_{31} *n*-alkane), while plants utilizing the C_4 (Hatch-Slack) photosynthetic pathway are isotopically enriched with average *n*-alkane carbon isotopic compositions of around −21.4‰ for the C_{29} *n*-alkane (−21.7‰ for the C_{31} *n*-alkane) (Fig. 8) (Castañeda et al., 2009a and references therein). A third photosynthetic carbon-fixation pathway, the Crassulacean Acid Metabolism (CAM) pathway, has isotopic values intermediate between those of C_3 and C_4 plants (Deines, 1980). Thus, the $\delta^{13}C$ of plant leaf waxes preserved in sediments can be used to examine past vegetation type, which in turn can be related to climatic conditions such as temperature, aridity and atmospheric carbon dioxide (pCO_2) concentrations (Cerling et al., 1993; Collatz et al., 1998; Kuypers et al., 1999; Pagani et al., 1999; Huang et al., 2001). These endmember values for C_3 and C_4 plants can be used to create a binary mixing model for examining the percentage of C_4 plants present in past vegetation assemblages (e.g. Schefuss et al., 2003; Castañeda et al., 2007; Collins et al., 2011).

A recent study of bulk leaf carbon isotopes of 334 species of globally distributed C_3 trees and shrubs reports wide range of values from −34.9‰ to −21‰ (Diefendorf et al., 2010). Although *n*-alkane $\delta^{13}C$ was not examined, this study suggests that within the C_3 plants a wide range in *n*-alkane $\delta^{13}C$ values may also occur, and if so, assigning an endmember value for C_3 plants for use in a binary mixing model becomes difficult. Thus, the wide range in leaf $\delta^{13}C$ values noted in the relatively large dataset of Diefendorf et al. (2010) suggests that the error associated with converting *n*-alkane $\delta^{13}C$ values to $\%C_4$ vegetation may be larger than the currently estimated error of ±20% (Castañeda et al., 2009a), which is reflects uncertainty in the endmember values reported from approximately 50 samples each for C_3 and C_4 plants. However, additional surveys of *n*-alkane $\delta^{13}C$ values in modern vegetation are needed in order to constrain this uncertainty. Furthermore, it may be the case that a smaller range in endmember $\delta^{13}C$ values exists for particular ecosystems or biomes but this would require regional surveys of local biomes. Nevertheless, these uncertainties do not affect interpretation of the overall trends where relatively enriched (depleted) *n*-alkane $\delta^{13}C$ values indicate increased (decreased) inputs from C_4 plants (Fig. 10).

A number of lacustrine studies have utilized compound-specific $\delta^{13}C$ to examine past vegetation change and these studies have provided important insights into past environmental conditions (StreetPerrott et al., 1997; Ficken et al., 1998; Brincat et al., 2000; Huang et al., 2001; Boom et al., 2002; Castañeda et al., 2007, 2009a; Feakins et al., 2007; Tierney et al., 2010c). For example, Huang et al. (2006) examined the $\delta^{13}C$ of long-chain *n*-alkanes and

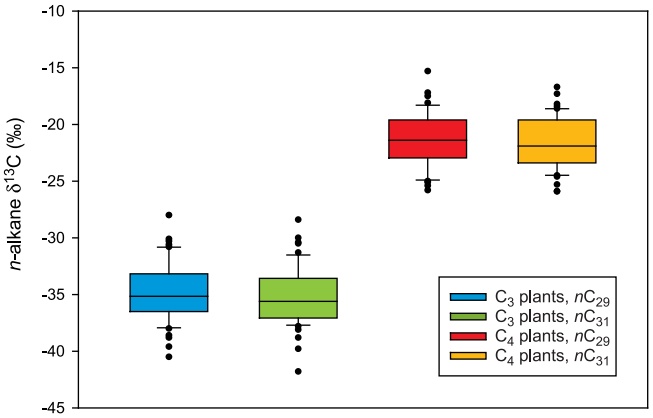

Fig. 10. Carbon isotopic composition ($\delta^{13}C$) of C_{29} and C_{31} *n*-alkanes in C_3 and C_4 plants. The box and whisker plots show the 25th (bottom of the box) and 75th (top of the box) percentile (the lower and upper quartiles) while the line in the middle of the boxes represents the median (the 50th percentile). The whiskers (error bars) above and below the box indicate the 90th and 10th percentiles, respectively. The black dots represent outliers. Each of these boxes represents approximately 50 samples of modern day vegetation and the data was compiled from values reported from the literature (see supplementary dataset of (Castañeda et al., 2009a)).

n-acids in a ~62,000 year sedimentary record from Lake Tulane (Florida) and compared the results to existing pollen data for the same lake. Instead of using a binary mixing model to reconstruct $\%C_4$ vegetation, they created a three endmember mixing model because Lake Tulane receives inputs from pines and oaks. Although both pine and oak are C_3 plants, leaf waxes from pine (or other evergreens) are 4–5‰ enriched compared to oak (or other angiosperm) leaf waxes (Huang et al., 2006 and references therein). Therefore, Huang et al. (2006) used the fraction of pine pollen as an input parameter and estimated the input of C_3 and C_4 plants while taking into consideration the differing $\delta^{13}C$ values of evergreen and deciduous trees. They found that the stable carbon isotope values of the long-chain *n*-alkanes and *n*-acids were in good agreement with the pollen record showing the highest $\%C_4$ input during the LGM (Fig. 11), which they attributed to more arid conditions and lower pCO_2 levels. Despite low pCO_2 levels during the deglacial period, an increase in pine pollen was noted and accompanied by a shift to lower $\%C_4$ values, which resulted from increased precipitation. Small changes of ~5‰ are noted during the Holocene and are attributed to changes in the relative abundance of pine and oak, rather than changes in C_3 and C_4 vegetation, supported by the pollen data (Huang et al., 2006). This study demonstrates the power of combining both plant leaf wax $\delta^{13}C$ and pollen data; however, it also should be noted that in some cases these proxies may not yield similar results since *n*-alkane inputs to lake sediments have been mainly attributed to local (within the watershed) sources while pollen may reflect more regional conditions due to long-distance atmospheric transport (e.g. Zheng et al., 2009). Conversely, long-distance atmospheric transport of *n*-alkanes can also occur and thus sources of *n*-alkanes and pollen need to be examined for individual sites. Some types of plant do not produce pollen and this may also lead to differences between *n*-alkane and pollen records.

4.2. Examining primary productivity using the $\delta^{13}C$ of short-chain *n*-alkanes (*n*-acids, *n*-alcohols)

The carbon isotopic composition of bulk organic matter ($\delta^{13}C_{OM}$) is widely used as a proxy for aquatic productivity in lakes (Meyers, 2003; Eglinton and Eglinton, 2008), with enriched $\delta^{13}C_{OM}$ values generally indicating increased productivity (Hollander and

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

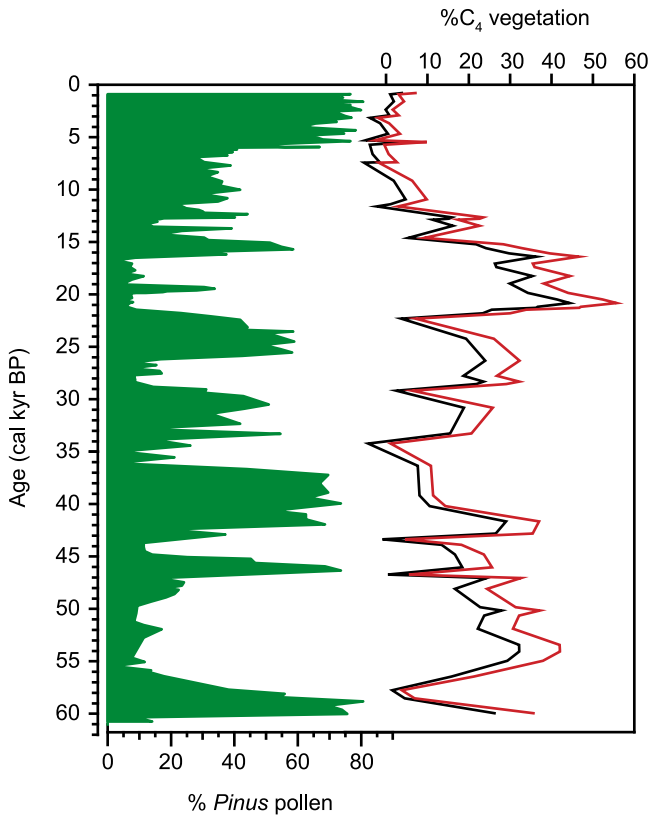

Fig. 11. Vegetation reconstruction from Lake Tulane, Florida. Percent *Pinus* pollen (C_3 plant) and the percent C_4 vegetation estimated from *n*-alkane $\delta^{13}C$ values. The percentage input from C_4 plants was calculated with two different isotopic endmember assumptions. The black line is the percentage C_4 input using endmember values of $\delta C_4 = -20‰$, and $\delta_p = -33‰$, and $\delta C_3 = -38‰$, where δC_4, δ_p, and δC_3 are endmember $\delta^{13}C$ values for leaf waxes C_4 plants, pine, and C_3 plants (excluding pine, including oak and other C_3 trees and grasses), respectively. The red line represents endmember values of $\delta C_4 = -23‰$, $\delta_p = -33‰$, and $\delta C_3 = -39‰$. Data from Huang et al. (2006).

McKenzie, 1991; e.g. Eglinton and Eglinton, 2008). However, bulk organic matter reflects contributions from terrestrial, aquatic and bacterial sources and a variety of processes can influence $\delta^{13}C_{OM}$ values. For example, enriched $\delta^{13}C_{OM}$ values can be produced by bacterial processing of terrestrially derived C_4 organic matter (Hedges et al., 1997). When dissolved CO_2 is limited in lakes, many organisms utilize dissolved bicarbonate (HCO_3^-) as the carbonate source, leading to enriched isotopic compositions that can be heavier than those of land plants (Meyers, 2003). In anoxic systems, anaerobic respiration of organic matter produces ^{13}C-depleted methane and respired CO_2 (Woltemate et al., 1984; Whiticar et al., 1986), which can be incorporated into surface waters during upwelling events and produce phytoplankton that are ^{13}C-depleted during a time of enhanced productivity (Hollander and Smith, 2001). Other environmental factors including pH, temperature, salinity, growth rate, nitrogen limitation, eutrophication and physical diffusion barriers (such as ice cover) can also influence phytoplankton $\delta^{13}C$ values (e.g. Beardall et al., 1982; Takahashi et al., 1990; Schelske and Hodell, 1991, 1995; Fogel and Cifuentes, 1993; Hinga et al., 1994; Laws et al., 1995). In lakes that receive significant terrestrial inputs the $\delta^{13}C_{OM}$ record may mainly reflect vegetation changes in the watershed rather than changes in primary productivity. Examining the carbon isotopic composition of both terrestrial and aquatic biomarkers may help shed light on these processes.

Many lacustrine studies have examined the $\delta^{13}C$ of aquatic biomarkers, such as short-chain *n*-alkanes, to examine past changes in primary productivity or shifts in the dominant carbon source (e.g. Ostrom et al., 1998; Huang et al., 1999a; Filley et al., 2001; Castañeda et al., 2009b; Aichner et al., 2010a). In some cases, aquatic biomarker $\delta^{13}C$ records have been found to differ considerably from bulk $\delta^{13}C_{OM}$ records, which is not surprising given the various factors and processes that can influence bulk isotopic composition, as outlined above. For example, in Mud Lake (Florida) distinct $\delta^{13}C$ depth relationships are observed for the short-, mid- and long-chain *n*-alkanes, which differ from that of the bulk $\delta^{13}C_{OM}$ (Filley et al., 2001). In Lake Malawi it was found that $\delta^{13}C_{OM}$ mainly reflects changes in C_3 vs. C_4 vegetation in its watershed rather than changes in aquatic productivity (Castañeda et al., 2009b). However, compounds such as the short or mid-chain *n*-alkanes, while more source specific than bulk organic matter, likely still represent inputs from multiple source organisms and thus shifts in their carbon isotopic signatures can be quite difficult to interpret.

To date, only a few studies have examined the $\delta^{13}C$ of other, more source specific, algal lipids (e.g. sterols, long-chain *n*-alkyl diols or botryococcenes). Huang et al. (1999b) examined the $\delta^{13}C$ of multiple compounds (short-, mid- and long-chain *n*-alkanes, *n*-alcohols, *n*-acids and botryococcenes produced by the green alga *B. braunii*) from Sacred Lake, Kenya. They conclude that during the LGM, the relative contribution of biogenic CO_2 to carbon pool of Sacred Lake decreased, the ^{13}C content of the lake increased due to a shift to C_4 vegetation dominance in the catchment, and lower ambient atmospheric carbon dioxide concentrations were prevalent. The combination of these factors likely led to severe inorganic carbon limitation, thus producing algal biomass highly-enriched in ^{13}C. Huang et al. (1999b) also conclude that *B. braunii* must have used biocarbonate as its main carbon source. Although the authors were able to gain important insights into past carbon cycling at Sacred Lake, their study also illustrates the multitude of processes influencing $\delta^{13}C$ signatures, which can interfere with using $\delta^{13}C$ as a primary productivity proxy.

Aichner et al. (2010a) examined $\delta^{13}C$ values of total organic carbon ($\delta^{13}C_{TOC}$), total inorganic carbon ($\delta^{13}C_{TIC}$) and of a variety of biomarkers in a sediment core from Lake Koucha (Tibetan Plateau), a shallow lake densely populated by aquatic macrophytes that preserves carbonates. They found that the ^{13}C values of mid-chain *n*-alkanes derived from aquatic macrophytes tracked carbon limitation in the lake. They suggest that due to considerable variation in the isotopic composition of the carbon source, rather than examining shifts in the $\delta^{13}C$ of the C_{23} *n*-alkane alone, the offset between $\delta^{13}C$ values of the C_{23} *n*-alkane and TIC may provide a better indication of carbon limitation, and thus could provide an indicator of lake productivity (Aichner et al., 2010a). However, they caution that the main contributors to the sedimentary organic carbon pool must be known in order to interpret offsets between biomarker $\delta^{13}C$ and TIC (Aichner et al., 2010a).

Overall, deciphering lipid biomarker $\delta^{13}C$ records is very complex in many settings due to the numerous processes influencing $\delta^{13}C$ values (Huang et al., 1999b; Castañeda et al., 2009b; Kristen et al., 2010; Aichner et al., 2010a). For this reason, some studies of compound-specific $\delta^{13}C$ have led to inconclusive results (Russell et al., 2009; e.g. Castañeda et al., 2009b). Studies that have combined examining biomarker concentrations in conjunction with $\delta^{13}C$ records (of both aquatic and terrestrial sources) appear to be the most successful for assessing shifts in the dominant carbon source and primary productivity. However, in many cases, as outlined above, compound-specific $\delta^{13}C$ records cannot be used to specifically examine past changes in primary productivity.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

5. Examining hydrological variability using compound-specific isotopes (δD)

5.1. Reconstructing hydrological variability using plant leaf wax δD

The deuterium isotopic composition (δD) of long-chain plant leaf waxes (e.g. *n*-alkanes or *n*-alkanoic acids) is being increasingly utilized as a tool for examining changes in aridity and precipitation δD values. The isotopic composition of meteoric water, the hydrogen source for terrestrial plants (Gat, 1996), is geographically influenced, reflecting environmental parameters including temperature, the source and amount of precipitation, elevation, and distance from the ocean, and exhibits an overall trend of decreasing δD values in precipitation with increasing latitude (Craig and Gordon, 1965; Bowen and Revenaugh, 2003). Indeed, at continental and global scales, studies have shown that precipitation δD values are an important factor controlling the δD of plant leaf waxes (δD_{lw}; Fig. 12), reflecting the "latitude effect" (Bi et al., 2005; Sachse et al., 2006; Smith and Freeman, 2006; Hou et al., 2008; Liu and Yang, 2008; Polissar and Freeman, 2010). Shifts in δD_{lw} from a single site have been qualitatively interpreted as reflecting evapotranspiration (e.g. Schefuß et al., 2005) or a shift in precipitation δD (e.g. Liu and Yang, 2008) (e.g. a negative δD shift would indicate wetter conditions in both cases).

While the δD_{lw} is dependent on the δD of the source water, a number of other factors may influence δD_{lw} including an isotopic offset caused by fractionation during *n*-alkane biosynthesis, evapotranspiration from soil and leaf water, relative humidity, plant life form (e.g. tree, shrub, grass), and physiological differences such as differing photosynthetic pathways or water-use efficiencies (Craig and Gordon, 1965; Sessions et al., 1999; Smith and Freeman, 2006; Hou et al., 2008; Liu and Yang, 2008; McInerney et al., 2011). Furthermore, widely variable δD_{lw} values (up to 70‰) have been reported from the same site (Bi et al., 2005; Liu et al., 2006a; Hou et al., 2007c) and also in a single plant utilizing a water source with constant δD value where δD_{lw} values were found to vary throughout the different seasons (Sessions, 2006b). These factors complicate use of δD_{lw} as a paleohydrological proxy and must be considered before paleoclimatic interpretations can be made. Below we discuss these factors in more detail.

5.1.1. Influence of vegetation type on leaf wax dD

Quantitative reconstructions of the δD of meteoric water rely on the existence of a constant biosynthetic fractionation ("net fractionation" or "apparent fractionation") between meteoric water and δD_{lw} values. However, differences in the net fractionation between meteoric water and δD_{lw} are known to exist between plant species (Chikaraishi and Naraoka, 2003; Smith and Freeman, 2006; Hou et al., 2007c; Feakins and Sessions, 2010a) and the available evidence suggests that a constant fractionation factor is unlikely (Chikaraishi and Naraoka, 2003; Liu and Yang, 2008). Net fractionations ranging from −73‰ to −242‰ for grasses (average −156‰) and from −57‰ to −220‰ for woody species (average −120‰) are reported based on a compilation of data from globally distributed sites (Liu and Yang, 2008 and references therein). Additionally, somewhat smaller net fractionations (−90‰) between meteoric water and δD_{lw} have been noted in semi-arid to arid environments (Feakins and Sessions, 2010a). Despite these complications, it is thought that within watersheds these differences are integrated and thus might allow for a constant offset to be used for paleoenvironmental reconstructions (Sachse et al., 2006; Hou et al., 2008; Feakins and Sessions, 2010a).

Differences in δD_{lw} have been noted between plants utilizing the C_3 vs. C_4 photosynthetic pathways in several studies, although some of the results are contradictory. While most studies have shown that *n*-alkanes from C_4 grasses are slightly enriched in δD in comparison to *n*-alkanes from C_3 grasses (in the range of <35‰) (Smith and Freeman, 2006; Liu et al., 2006a; Liu and Yang, 2008; McInerney et al., 2011), in *n*-alkanes from Japan and Thailand the opposite was observed with C_4 plants having slightly lower δD_{lw} values compared to C_3 plants (Chikaraishi and Naraoka, 2003) whereas no significant differences in δD_{lw} were observed between C_3 and C_4 plants collected from South China (Bi et al., 2005). Liu et al. (2006a) and Liu and Yang (2008) suggest that plant ecological life forms (e.g. trees, shrub, grass) exert a greater influence on δD_{lw} rather than differences in photosynthetic pathway. These authors argue that the various ecological life forms utilize different source waters, which leads to variations in δD_{lw} on the order of 60–70‰, and find that grasses are more deuterium depleted compared to woody plants (trees and shrubs). Since trees and shrubs typically have longer and deeper roots they utilize water from deeper soil horizons (with potentially more enriched δD values) in comparison to grasses with short roots that use surface

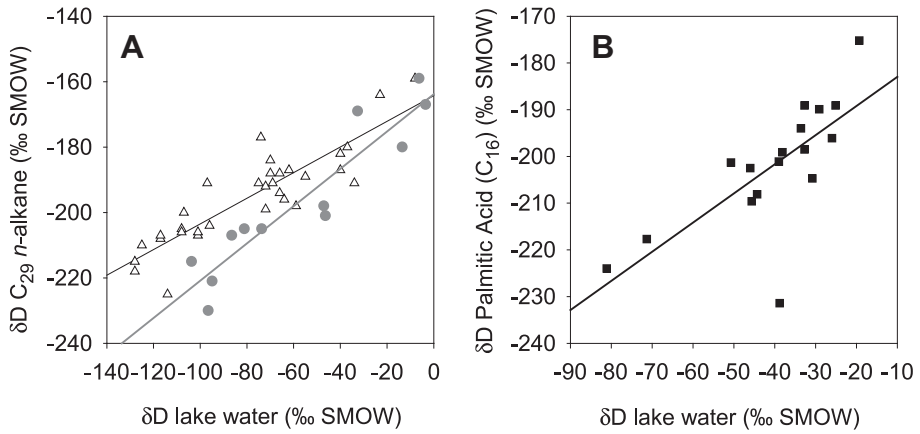

Fig. 12. Examples of relationships between δD of lipids and δD of lake water. A) The δD of the C_{29} *n*-alkane vs. δD of lake water from sites in South and North America (data from Polissar and Freeman, 2010) is indicated by the open triangles ($r^2 = 0.79$, $n = 31$). The gray circles indicate the δD of the C_{29} *n*-alkane vs. δD of lake water ($r^2 = 0.87$, $n = 12$) from a north–south transect of lakes in Europe (data from Sachse et al., 2004). Despite the fact that these lakes span a wide range of climatic conditions, elevations, and ecosystem types and structures, a significant relationship is noted between δD of lake water and *n*-alkane δD (combining the data for the American and European lakes yields a correlation with an $r^2 = 0.72$). B) The δD of palmitic acid (C_{16} *n*-acid) vs. the δD of lake water ($r^2 = 0.53$, $n = 17$) from and an east-west precipitation gradient in South Dakota and Minnesota (USA) (data from Shuman et al., 2006).

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

soil water (potentially more depleted δD values). Succulent plants using the crassulacean acid metabolism (CAM) photosynthetic pathway, which have the ability to switch between using the CAM and C_3 pathways (Osmond et al., 1989), were found to display a wide variability (~90‰) in δD_{lw} ranging from −193‰ to −107‰ even though environmental growth conditions were controlled (Feakins and Sessions, 2010b). Feakins and Sessions (2010b) suggest that coupled leaf wax $\delta^{13}C$ and δD data can be used to gain insights into the importance of CAM ecology in the past, in environments where it is possible to independently constrain the isotopic composition of meteoric waters. They note that with C_3 plants, leaf wax $\delta^{13}C$ and δD values are usually inversely correlated (Bi et al., 2005; Hou et al., 2007a) whereas they are positively correlated in CAM plants (Feakins and Sessions, 2010b).

5.1.2. Influence of transpiration on leaf wax δD

Relative humidity, via evaporative enrichment of soil and/or leaf water (transpiration), is another factor that can influence δD_{lw} values but its importance is currently debated. Hou et al. (2008) grew trees and grasses in humidity-controlled growth chambers and found that changing relative humidity from 80% to 40% produced only a ~7‰ increase in δD_{lw} relative to the source water. The authors concluded that most of the D-enrichment should occur through soil water evaporation. McInerney et al. (2011) conducted both growth chamber and field experiments of grasses, which produced contrasting results. In the growth chambers they did not find an effect of transpirational D-enrichment on δD_{lw} values; however the field samples provided clear evidence of D-enrichment, correlating with variations in relative humidity at the sites. Their observations, supported by a Craig–Gordon isotopic fractionation model, suggest that evaporation from soils and/or stems affects δD_{lw} but transpiration from leaves does not. McInerney et al. (2011) suggest that these observations can be explained by enrichment of the grass source water by evaporation from soils and/or stems for the field samples. In contrast, Feakins and Sessions (2010a) examined δD values of precipitation, groundwater, plant xylem water to examine their impact on δD_{lw} in an arid ecosystem. They found that leaf transpiration is the process responsible for most of the D-enrichment rather than soil water evaporation and observe that many species take up groundwater or precipitation without significant fractionation. Polissar and Freeman (2010) examined δD_{lw} in 28 watersheds spanning a range of precipitation δD, vegetation and climate types. They find that net fractionations between δD_{lw} and precipitation varies with ecosystem type and structure within the watershed and observe that δD_{lw} values from open grasslands are more sensitive to changes in aridity whereas those from closed, forested ecosystems are less sensitive due to reduced soil evaporation (Polissar and Freeman, 2010).

5.1.3. δD of leaf waxes: applications in paleoclimate reconstruction

Despite the apparent complications in interpreting the δD of plant waxes, they have been applied as a qualitative indicator for continental hydrology (e.g. Schefuß et al., 2005; Weijers et al., 2007a; Tierney et al., 2008, 2011). Tierney et al. (2008) examined δD_{lw} (the C_{28} *n*-alkanoic acid) and TEX_{86} (see Section 3.3) in a sediment core from Lake Tanganyika (East Africa), spanning the past ~60,000 years. They found that both temperature and hydrology in the Tanganyika basin were highly variable: δD_{lw} values spanning a range of ~50‰ and temperature changes of ~4 °C were noted, indicating that Lake Tanganyika experienced abrupt changes in both temperature and hydrology (Fig. 13). Interestingly, temperature and precipitation were found to co-vary on orbital time scales whereas millennial-scale arid intervals noted in the δD_{lw} record were not accompanied by cooler lake surface temperatures. Their results suggest that precipitation at Lake

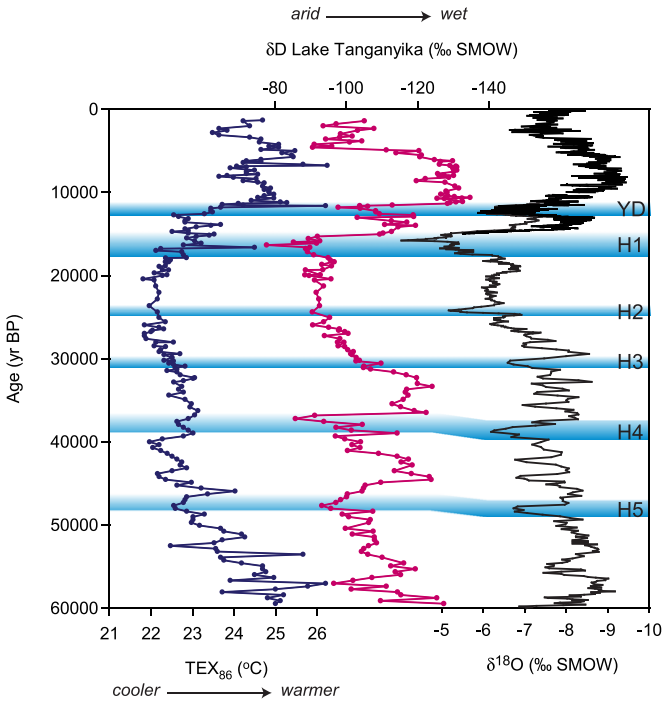

Fig. 13. Temperature and hydrologic history of Lake Tanganyika (East Africa) from TEX_{86} and leaf wax (C_{28} *n*-acid) δD analyses (Tierney et al., 2008). Oxygen isotope data from Hulu and Dongge Caves is shown for comparison (Wang et al., 2001; Dykoski et al., 2005). The blue shading indicates the arid intervals of the Younger Dryas (YD) and Heinrich Events H1–H5. Note that the TEX_{86} data of Tierney et al. (2008) was re-calibrated using the newer lacustrine calibration of Tierney et al. (2010a).

Tanganyika is mainly influenced by Indian Ocean sea surface temperatures and the winter Indian monsoon rather than by past migrations of the position of the Intertropical Convergence Zone (Tierney et al., 2008).

5.1.4. Outlook: leaf wax δD as a hydrological proxy

Overall, it is clear that many outstanding questions exist with regard to the biological processes controlling δD_{lw}. Yet despite these complexities, δD_{lw} is emerging as a powerful proxy for examining continental hydrological variability (e.g. Schefuß et al., 2005; Weijers et al., 2007a; Tierney et al., 2008, 2011), at least qualitatively. Although more studies are certainly needed to better understand controls on δD_{lw}, it is apparent that evaluating the influence of vegetation change on δD in conjunction with δD_{lw} data is essential, a point that has been stressed by many authors (e.g. Liu et al., 2006a; Hou et al., 2007c; Liu and Yang, 2008; Polissar and Freeman, 2010; Feakins and Sessions, 2010b; Pu and Weiguo, 2011). Sites where vegetation change can be constrained by leaf wax $\delta^{13}C$ and/or pollen data or where large vegetation/ecosystem changes have not occurred in the past may be better suited for applying δD_{lw} in paleohydrological reconstructions.

5.2. Reconstructing hydrologic variability using the δD of algal lipids

Similar to the long-chain plant leaf waxes, δD measurements of algal lipids is also used as a tool for examining past hydrological fluctuations. Algal lipids are particularly well-suited for δD studies because all hydrogen in algae is derived from water and algae do not transpire (Zhang and Sachs, 2007), a process that can overprint the δD signal in land plants (see Section 5.1.2). The sensitivity of algal lipids δD as a recorder of source water δD values has been

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

demonstrated by both culture and surface sediment studies. Studies of algal cultures have examined a variety of lipids including alkenones, *n*-alkanes, *n*-alkanoic acids, and bytrococcenes, and have demonstrated that the δD of algal lipids can closely track ($R^2 > 0.99$) water δD values (Englebrecht and Sachs, 2005; Zhang and Sachs, 2007). Studies of δD values of core top sediments also reveal a good correlation with the δD of the lake source water (Fig. 12; Sauer et al., 2001; Huang et al., 2004; Sachse et al., 2004). For these reasons, lipid biomarker δD is emerging as a potentially powerful paleoclimate proxy for lakes that do not preserve carbonates and where traditional paleolimnological proxies, such as oxygen isotope ratios of lacustrine carbonates, cannot be applied. In comparison to the oceans, lakes are much more sensitive to changes in precipitation/evaporation due to their smaller size and thus the δD of algal lipids can be a sensitive recorder of environmental conditions. While the δD of kerogen from bulk organic matter (e.g. Krishnamurthy et al., 1995; Tiljander et al., 2006; Lovan and Krishnamurthy, in press) or cellulose from aquatic plants (e.g. Edwards and Fritz, 1988; Edwards and Mcandrews, 1989; Wolfe et al., 2007) has been utilized for lacustrine paleoclimate studies, both can have significant allochthonous components possessing a different isotopic signature relative to the aquatic organic matter (Sauer et al., 2001). Therefore, δD measurements of bulk organic matter or cellulose should not be applied to sediments that receive large or varying inputs of allochthonous material. It also should be noted that in lakes where snowmelt is a major contributor to the lake water, the δD signal can be complicated by changing meltwater dynamics (e.g. Enders et al., 2008).

5.2.1. *Influence of biosynthetic fractionations and other environmental factors on δD of algal lipids*

Although culture and surface sediment studies have demonstrated that δD of various algal lipids exhibit good relationships with source water δD over large δD gradients, a key assumption to utilizing δD as a paleoclimatic proxy, like for plant leaf waxes, is a constant net apparent fractionation for each biomarker lipid. Thus, if the same lipid is analyzed for δD throughout a sediment core the biosynthetic fractionations will be similar and will not affect overall trends in δD. However, culture studies suggest this assumption is unlikely to be correct (Zhang and Sachs, 2007; Zhang et al., 2009). Zhang and Sachs (2007) examined hydrogen isotopic fractionation in five species of cultured freshwater green algae, including three strains of *B. braunii*, and demonstrated that algal lipid δD values reflect source water δD values but within a single species the hydrogen isotopic fractionation was found to vary systemically between lipids and lipid homologues. Importantly, they also note large differences (~90–100‰) in the hydrogen isotopic fractionation of a single lipid between families of green algae and also relatively small (10–15‰) differences between different species of green algae. They caution that if a non-source specific lipid is used to reconstruct water δD values, a shift in the dominant algal group could affect the lipid δD signature and be incorrectly interpreted as a shift in the δD of lake water (Zhang and Sachs, 2007). Given this, it is surprising that several studies have reported strong relationships between the δD of short-chain *n*-alkanes or *n*-alkanoic acids in surface sediments and source water δD (Huang et al., 2004; Sachse et al., 2004, 2006; Shuman et al., 2006; Hou et al., 2007b; Henderson et al., 2010) since these compounds are produced by multiple sources. However, Gao et al. (2011) examined D/H ratios in a wide range of plants in and around Blood Pond (MA) and created a mathematical model to quantitatively assess aquatic inputs of the mid-chain *n*-alkyl lipids to the lake sediments. They found that 97% of the total mid-chain *n*-alkyl lipids in Blood Pond derived from aquatic macrophytes. Thus, it appears that for some lakes a dominant source of the *n*-alkyl lipids exists, facilitating the use of their δD as a paleoenvironmental proxy.

Other environmental factors such as temperature, salinity, growth rate, nutrient availability and light levels can also influence D/H fractionation. Zhang et al. (2009) investigated the effects of temperature and cultured two species of freshwater green algae at 15 and 25 °C and found increased D/H fractionation (2–4‰ per °C) for all lipids analyzed at the higher temperature. They also investigated the effects of nitrogen limitation and found that fatty acids from both nitrogen replete and nitrogen-limiting cultures had similar δD values whereas sterols in the nitrogen-limiting culture were enriched in δD by 37‰ compared to the nitrogen replete culture. These results suggest that growth rate likely does not influence D/H fraction in acetogenic lipids and thus *n*-alkanes, fatty acids, alkenones, alkadienes and other linear lipids may be good targets for δD analysis (Zhang et al., 2009).

A study of surface sediments from 28 saline and hypersaline lakes on Christmas Island (central Pacific Ocean), where cyanobacteria are the major source of the organic matter, indicates that salinity also can induce a large effect on D/H fractionation. Sachse and Sachs (2008) examined δD values of a variety of lipids and found that as salinity increased, the lipids became increasingly deuterium enriched. They note that lipid δD values span a range of 100‰ whereas the δD of the source waters exhibited relatively little variability, spanning a range of 12‰. Thus, the net D/H fractionation between the lipids and the source water decreases with increasing salinity, by a factor of approximately 0.8‰–1.1‰ for every 1-unit increase in salinity (Sachse and Sachs, 2008). Schouten et al. (2006) reported a somewhat larger D/H fractionation of 4–5‰ for every 1 unit of salinity for long-chain alkenones produced by *E. huxleyi* and *G. oceanica*. These studies suggest that δD might be used to develop a paleosalinity proxy if it is possible to make additional constraints on the source water δD. Given the observed effects of temperature and salinity on lipid D/H fractionation, it is probably best to target lakes that have not undergone significant temperature or salinity variations in the past for δD reconstructions.

5.2.2. *δD as a proxy for evapotranspiration or lake water balance*

It has been suggested that the difference between long- and short-chain *n*-alkane δD may serve as a proxy for evapotranspiration or water balance in some lakes. Sachse et al. (2004) examined a north–south transect of small, groundwater fed lakes in Europe and noted that long-chain *n*-alkanes recorded the δD value of meteoric water but were enriched by ~30‰ compared to the C_{17} *n*-alkane, reflecting evapotranspiration processes in plant leaves. They suggested that the difference between δD values of aquatically and terrestrially derived *n*-alkanes could serve as an evapotranspiration proxy in small, closed lake systems that are fed by meteoric water (Sachse et al., 2004, 2006). However, an important assumption to this proxy is that the water source remains constant. Subsequent research by Mügler et al. (2008) examined both lacustrine and higher plant *n*-alkanes of sediments in semi-arid to arid lakes in Tibet (Lakes Nam Co and Co Jiana) and of a humid lake in Germany (Lake Holzmaar). At humid Lake Holzmaar they found that terrestrial *n*-alkanes (C_{29}) were isotopically enriched in δD by ~30‰ compared to aquatic *n*-alkanes (C_{23}) in agreement with the results of Sachse et al. (2004). In contrast, in the semi-arid to arid Tibetan lake sediments terrestrial *n*-alkanes were isotopically depleted in comparison to aquatic *n*-alkanes, with an enrichment of ~60‰ observed for the aquatic *n*-alkanes. Mügler et al. (2008) note that the lake water, precipitation and inflow water are in isotopic equilibrium at humid Lake Holzmaar whereas lake water at the Tibetan sites is enriched by 30–50‰ compared to the inflow water, reflecting evaporation. The authors suggest that a positive C_{29}–C_{23} δD difference can potentially indicate humid environments

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

whereas semi-arid and arid conditions are reflected by a negative C_{29}–C_{23} δD difference. They further suggest that the C_{29}–C_{23} δD difference can be used to estimate evaporation to inflow (E/I) ratios and to reconstruct the lakes past water balance.

Aichner et al. (2010b) further tested using the δD difference between terrestrial and aquatic *n*-alkanes as a proxy to reconstruct past lake water balance. They examined surface sediment samples from a number of sites on the Tibetan Plateau and a sediment core from Koucha Lake, in the NE Tibetan Plateau. In contrast to the results of Mügler et al. (2008), it was found that most of the surface sediment samples did not display a significant offset between δD values of aquatic and terrestrially derived *n*-alkanes. A similar result was found in the downcore record, where only minor offsets between δD values of aquatic and terrestrially derived *n*-alkanes were observed. They note that in arid environments evapotranspiration alters the hydrogen isotope signal of leaf and soil water, in addition to evaporation enriching lake water δD. Thus this paleoaridity proxy may not be applicable to all settings since for it to work δD-enrichment of soil and leaf water must be outweighed by lake water evaporation (Aichner et al., 2010b).

5.2.3. Outlook: δD of algal lipids as hydrologic proxy

From the above discussion it is clear that more studies are needed to investigate the effects of biosynthetic fractionations and other environmental parameters including salinity, temperature, growth rate, nutrient availability and light limitation on lipid D/H fractionation in a wider variety of algal species and over a wider range of environmental conditions. Nevertheless, several studies have demonstrated that the δD of algal lipids can be used to examine past hydrologic variability from lake sediment, at least qualitatively, and have provided important paleoenvironmental information (Shuman et al., 2006; Hou et al., 2007b; Mügler et al., 2008; Henderson et al., 2010; Aichner et al., 2010b).

Considering the observation that large difference in hydrogen isotopic fractionation exist between single lipids produced by different algae (Zhang and Sachs, 2007), and the fact that many lipids have multiple source organisms, the choice of a lipid to analyze for δD reconstructions is an important one. Lipids that have been identified as being the most promising for δD reconstructions include C_{34} botryococcene, which produced solely by the B race of *B. braunii* (Zhang and Sachs, 2007), and lacustrine alkenones, which derive from haptophyte algae and provide a lake water signal (D'Andrea and Huang, 2005). Unfortunately, in many lakes these lipids are either not present or their abundances are too low to allow for δD analysis (Sachse et al., 2004; Castañeda et al., 2009b). Huang et al. (2004) suggested that the δD of palmitic acid, a C_{16} fatty acid that is abundant in many lake sediments, also captures the δD signals of lake water. From a north–south transect of lake surface sediments from eastern North America, Huang et al. (2002) demonstrated a strong correlation between lake water δD and the δD of palmitic acid. They also found that downcore δD values from Crooked Pond (MA) exhibited the same trends as pollen-inferred temperature data. Similarly, Hou et al. (2007c) examined δD of behenic acid (C_{22} *n*-acid) in a sediment core from Blood Pond (MA) and showed that the δD record displays a remarkable similarity with Greenland ice core records and also a pollen-inferred temperature record from Blood Pond as well as a carbonate $\delta^{18}O$ record from a nearby lake (Fig. 14). However, the results of Zhang and Sachs (2007) strongly argue against using palmitic acid, or any compound that derives from multiple sources, for δD reconstructions.

Clearly, there is a need to identify a suitable aquatic freshwater biomarker for δD reconstructions that is both widespread and abundant in lakes. We suggest that the long-chain (C_{28}–C_{32}) 1,15 *n*-alkyl diols (discussed in section 8.4), biomarkers for eustigmatophyte algae (Volkman et al., 1992; Versteegh et al., 1997), may offer possibilities for lacustrine δD reconstructions these compounds appear to be both very abundant and widespread in lake sediments (Xu et al., 2007; Xu and Jaffé, 2008; Castañeda et al., 2009c; Shimokawara et al., 2010). Another potential candidate would be the δD of ether-bound isoprenoid from archaeal membranes using chemical degradation and GC/pyrolysis/IRMS (Kaneko et al., 2011). This approach, although time consuming, allows for the determination of δD of biphytane moieties of GDGTs (Kaneko et al., 2011). Since crenarchaeol is very abundant in some lakes, it may provide a suitable biomarker for δD reconstructions in lakes that receive little terrestrial input (i.e. where BIT index values are low).

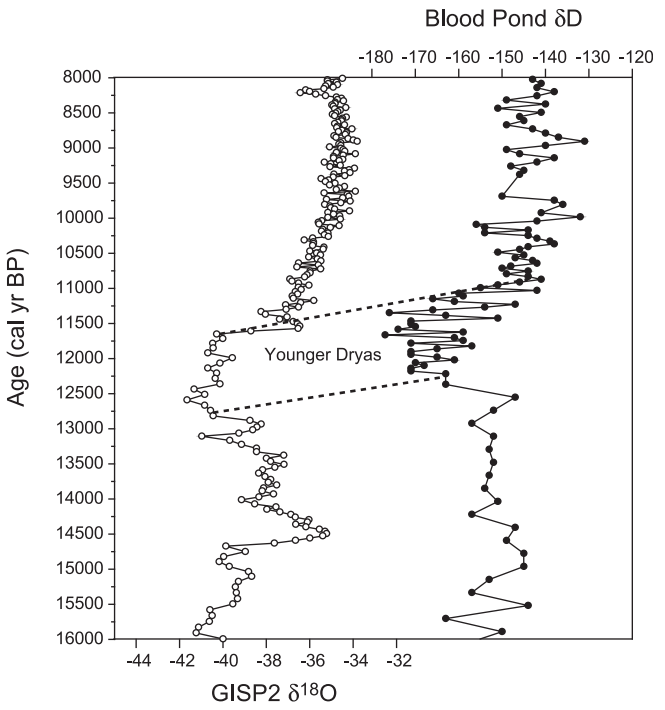

Fig. 14. Deuterium isotope (δD) reconstruction from Blood Pond, MA. Data from Hou et al. (2007b). The δD of behenic acid (C_{22} *n*-acid) is shown next to the oxygen isotope ($\delta^{18}O$) record from Greenland Ice Sheet Project 2 (GISP2) for comparison. The dashed lines indicate excursions noted during the interval of the Younger Dryas cold period in both records.

6. Investigating aquatic microbial community composition and UV radiation using sedimentary pigments

Pigments such as chlorophylls, carotenoids and their derivatives, preserved in sediments have long been utilized for paleolimnological studies (e.g. Fox, 1944; Vallentyne, 1954, 1956, 1957). Algae, microbes and higher plants synthesize a variety of pigments for use in photosynthesis and while some are broadly-distributed (e.g. chlorophyll *a*, β-carotene, pheophytin *a*), others provide a high degree of taxonomic specificity. Sedimentary pigments have been used to address a wide range of research questions including changes in algal and bacterial community composition, changes in trophic status, food–web interactions, lake acidification, and anthropogenic impacts on aquatic ecosystems (Table 5) (Sanger, 1988; Leavitt, 1993; Millie et al., 1993; Leavitt and Hodgson, 2001). In lakes, the main pigment sources are planktonic and benthic algal and microbial communities, aquatic macrophytes, and higher plant materials from the surrounding catchment. Chlorophyll *a* is the most common pigment and has been used to estimate

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Table 5
Common sedimentary pigments and some of the environmental parameters they can be used to reconstruct. Table modified from Leavitt and Hodgson (2001). The main sources of each pigment are indicated: planktonic (P), littoral (L), terrestrial (T) or sedimentary (S; post-depositional derivatives). Derivatives of chlorophylls and carotenoids can provide important environmental information regarding water column and sedimentary processes that transform pigments including grazing, anoxia, stratification, and light intensity. Other proxies, such as the ratio of absorbance at 430 and 410 nm provides information on the extent of chlorophyll to pheopigments, and has been used as proxy for lake acidification (Guilizzoni et al., 1992).

Pigment	Source	Affinity	Potential for proxy reconstruction
Carotenoids			
β, β-carotene	P, L, T	Higher plants, algae, some phototrophic bacteria	Total algal abundance
β, α-carotene	P, L	Cryptophytes, chrysophytes, dinoflagellates, some chlorophytes	Total algal abundance
Alloxanthin	P	Cryptophytes	Cryptophyte productivity
Fucoxanthin	P, L	Diatoms, chrysophytes, some dinoflagellates,	Siliceous algae and dinoflagellate abundance
Diatoxanthin	P, L, S	Diatoms, dinoflagellates, chrysophytes	Algal abundance
Diadinoxanthin	P, L, S	Diatoms, dinoflagellates, chrysophytes, cryptophytes	Algal abundance
Dinoxanthin	P	Dinoflagellates	Dinoflagellate abundance
Peridinin	P	Dinoflagellates	Very labile compound, rarely recovered from sediments
Echinenone	P, L	Cyanobacteria	Cyanobacteria abundance
Zeaxanthin	P, L	Cyanobacteria	Cyanobacteria abundance
Canthaxanthin	P, L	Colonial cyanobacteria, herbivore tissues	Cyanobacteria abundance
Myxoxanthophyll	P, L	Colonial cyanobacteria	Cyanobacteria abundance
Oscillaxanthin	P, L	Cyanobacteria (Oscillatoriaceae)	Cyanobacteria abundance
Aphanizophyll	P, L	N_2-fixing cyanobacteria (Nostocales)	Cyanobacteria abundance
Lutein	P, L, T	Green algae, euglenophytes, higher plants	Algal abundance
Neoxanthin	L	Green algae, euglenophytes, higher plants	Algal abundance; very labile compound
Violaxanthin	L	Green algae, euglenophytes, higher plants	Algal abundance; very labile compound
Okenone	P	Purple sulphur bacteria	Photic zone anoxia, water column stratification
β—isorenieratene	P	Chlorobiaceae (green sulphur bacteria)	Photic zone anoxia, water column stratification
Isorenieratene	P	Chlorobiaceae (brown varieties)	Photic zone anoxia, water column stratification
Chlorobactene	P	Chlorobiaceae (green sulphur bacteria)	Photic zone anoxia, water column stratification
Astaxanthin	P, L	Invertebrates, N-limited Chlorophyta	Indicator of herbivory (grazing); labile compound
Scytonemin	P, L	Colonial cyanobacteria	Past UV radiation environments
Total carotenoids	P, L, T, S	All of the above	Total phosphorus concentrations in lake water
Mycosporine-like amino acids	P	Diatoms, cyanobacteria, haptophytes, dinoflagellates	Past UV radiation environments
Chlorophylls			
Chlorophyll *a*	P, L	Photosynthetic algae, higher plants	Total algal abundance
Chlorophyll *b*	P, L	Green algae, euglenophytes, higher plants	Chlorophyte abundance
Chlorophyll *c*	P, L	Dinoflagellates, diatoms, chrysophytes	Total algal abundance; very labile compound
Chlorophyll degradation products			
Chlorophyll *a*′	P, L, T, S	chl *a* derivative, forms as an artefact of extraction	Total algal abundance
Chlorophyllide *a*	P, L, T, S	chl *a* derivative	Algal abundance; product of senescence
Chlorophyllone *a*	P	chl *a* derivative	Indicator of zooplankton herbivory (grazing)
Chlorophyll *a* allomers	P, L, T, S	chl *a* derivative, produced by autoxidation reaction	Grazing, photoxidation
Pheophytin *a*	P, L, T, S	chl *a* derivative (general)	Total algal abundance
Pheophytin *b*	P, L, T, S	chl *b* derivative (general)	Chlorophyte abundance
Pheophorbide *a*	P, L, S	chl *a* derivative (grazing, senescent diatoms)	Indicator of zooplankton herbivory (grazing)
Pyro-pheo(pigments)	L, S	Derivatives of *a* and *b*-phorbins	
Deoxophylloerythroetioporphyrin (DPEP)	S	Defunctionalized product of chl *a*	
Purpurin-18 phytol ester	P	chl *a* derivative	Oxidative transformations associated with senescence or particle sinking
Sterol chlorin esters (SCEs)	S	Sterol group originates from zooplankton or phytoplankton	Indicator of zooplankton herbivory (grazing); formed by biological reaction at the time of deposition
Bacteriochlorophylls			
Bacteriochlorophyll *a*	P	Purple photosynthetic bacteria	Photic zone anoxia, water column stratification
Bacteriochlorophyll *b*	P	Purple photosynthetic bacteria	Photic zone anoxia, water column stratification
Bacteriochlorophyll *c*	P	Green sulphur bacteria	Anoxygenic photosynthesis, photic zone anoxia
Bacteriochlorophyll c_s	P	Green non-sulphur bacteria (Chloroflexi)	Oxic conditions
Bacteriochlorophyll *d*	P	Green sulphur bacteria	Anoxygenic photosynthesis, photic zone anoxia
Bacteriochlorophyll *e*	P	Green sulphur bacteria	Anoxygenic photosynthesis, photic zone anoxia
Bacteriochlorophyll *g*	T	Heliobacteria	Anoxic conditions
Bacteriochlorophyll degradation products			
Me Et maleimides	P	Phytoplanktonic chlorophyll	
Me n-Pr maleimides	P	Bacteriochlorophylls *c*, *d*, and *e*	Anoxygenic photosynthesis, photic zone anoxia
Me i-Bu maleimides	P	Bacteriochlorophylls *c*, *d*, and *e*	Anoxygenic photosynthesis, photic zone anoxia

phytoplankton biomass in the water column (e.g. Steele, 1962; Cullen, 1982). Aquatic organisms produce carotenoid compounds for photosynthesis and a number of different carotenoids (e.g. alloxanthin, lutein, echinenone, fucoxanthin, peridinin) can be used to examine changes in specific algal classes (Leavitt and Hodgson, 2001 and references therein). Certain benthic algae produce unique pigments when exposed to ultraviolet (UV) radiation and these pigments can be used to examine past changes in UV

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

radiation in lakes (Leavitt et al., 1997, 1999). Specific pigments and bacteriochlorophylls derived from photosynthetic green and purple sulphur bacteria provide reliable biomarkers for water column anoxia since they require both light and sulphide. For example, purple sulphur bacteria produce bacteriochlorophyll *a* or bacteriochlorophyll *b* as well as several characteristic carotenoids including okenone, which is highly specific to this group (Sinninghe Damsté and Schouten, 2006 and references therein). Green sulphur bacteria produce bacteriochlorophyll *c*, *d* or *e* as well as the aromatic carotenoids chlorobactene and isorenieratene (Koopmans et al., 1996; Sinninghe Damsté and Schouten, 2006 and references therein). The presence of these compounds in ancient lake sediments has been used as an indicator of stratified conditions (e.g. Ariztegui et al., 2001; Hanisch et al., 2003; Itoh et al., 2003; Mallorquí et al., 2005).

Although it is well-known that most pigments are degraded within the water column and surface sediments (e.g. Furlong and Carpenter, 1988) where they undergo a series of transformation reactions, in many cases the diagenetic and catagenetic products retain enough specificity for them to be used as environmental indicators (Summons and Powell, 1987; Koopmans et al., 1996; Sinninghe Damsté et al., 2001a). Sedimentary pigments have thus been used to examine past phytoplankton dynamics and water column anoxia by countless studies, which are too numerous to review here. We note that sedimentary pigments have been previously reviewed (Sanger, 1988; Leavitt, 1993; Millie et al., 1993; Leavitt and Hodgson, 2001; Sinninghe Damsté and Schouten, 2006) and that they continue to be utilized for many paleolimnological investigations (e.g. Squier et al., 2002; Waters et al., 2005; Soma et al., 2007; Romero-Viana et al., 2009; Guilizzoni et al., in press; Hobbs et al., 2010; Aichner et al., 2010b). Here, we briefly highlight a couple of recent research developments.

6.1. Scytonemin and mycosporine-like amino acids as indicators of past UV receipt

Certain types of photoautotrophs produce ultraviolet (UV)-absorbing pigments to protect against cellular damage from UV radiation, and these compounds have the potential to serve as proxies for examining past solar irradiance (Leavitt et al., 1997; Sinha et al., 1998; Quesada et al., 1999; Squier et al., 2004; Hodgson et al., 2005). Scytonemin (Fig. 15) is a sheath pigment produced by certain types of cyanobacteria and variations in its abundance have been used to examine past UV variations because cyanobacteria increase extra-cellular concentrations of photoprotective compounds when exposed to elevated UV radiation (Hodgson et al., 2005). Although absolute intensities of UV radiation cannot be reconstructed from scytonemin concentrations, relative changes can be examined. For example, Hodgson et al. (2005) examined the ratio of total scytonemin to total sedimentary carotenoids in Lake Reid, East Antarctica, and concluded that during the last glacial benthic cyanobacteria were exposed to significantly higher levels of UV radiation (more than three times higher) than during the Holocene. Similarly, Verleyen et al. (2005) examined scytonemin in a sedimentary record spanning the past ~2000 years from a shallow lake, Pup Lagoon, in the Larsemann Hills of East Antarctica. The authors used the ratio of total scytonemin concentrations to the total cyanobacterial carotenoid concentration as a proxy for light intensity in the UV radiation wavelengths. This ratio excludes influences from changes in the abundances of cyanobacteria and other co-dominant algal groups (Verleyen et al., 2005). They found that several reconstructed periods of high UV radiation coincide with solar minima noted in historical records. Antarctic lakes are particularly well-suited for analysis of photoprotective compounds since dissolved organic matter (DOM), which absorbs UV radiation, is generally absent (Hodgson et al., 2005). In other Arctic and high-latitude lakes, fluctuations in DOM inputs from vegetation and soils have been related to significant variations in UV radiation receipt (Leavitt et al., 2003).

Another group of UV-screening compounds, the mycosporine-like amino acids (MAAs), are known from over 380 species of marine organisms (including bacteria, algae, corals, and fish) and also in freshwater organisms including cyanobacteria, microalgae and zooplankton (Helbling et al., 2002; Tartarotti et al., 2004 and references therein). MAAs reported from marine phytoplankton occur predominately in members of Dinophyceae (dinoflagellates), Bacillariophyceae (diatoms), and Haptophyceae (Sinha et al., 1998). Interestingly, MAAs provide protection against UV radiation to both organisms that produce these compounds, as well as to their primary and secondary consumers (Sinha et al., 1998 and references therein; Helbling et al., 2002). Over 20 different types of MAAs have been described but typically a glycine subunit is found at the third carbon atom of the ring system (Sinha et al., 1998). It should be noted that while higher concentrations of MAAs are noted in organisms exposed to intense solar radiation (e.g. Tartarotti et al., 2004) it is thought that MAAs may also play other roles in cellular metabolism (Sinha et al., 1998 and references therein), which may influence MAA concentrations.

MAAs have been discovered embedded in the frustules of marine diatoms from the Southern Ocean in both plankton and sediment samples, which appears to protect them from chemical degradation (Ingalls et al., 2010). These MAAs are stable when associated with the diatom frustules and after being released by HF digestion they can be quantified by HPLC-MS techniques. Ingalls et al. (2010) suggest that it might be possible to develop an MAA-based indicator of past solar irradiance, assuming that there is a reliable relationship between frustule-bound MAA concentrations and irradiance. As diatoms are a major contributor to primary productivity in many lakes, frustule-bound MAAs may be useful for paleolimnological studies of past solar irradiance. Ingalls et al. (2010) also suggest that MAAs are well-suited for paleoenvironmental reconstructions based on compound-specific nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$ and $\Delta^{14}C$) isotopes.

6.2. Sedimentary pigments as a proxy for past phosphorous concentration in lakes

Recently, it has been proposed that sedimentary pigments can be used to infer past phosphorous concentration in lakes. Guilizzoni et al. (2011) spectrophotometrically measured total carotenoids (TC) in sediment samples from 28 Italian lakes and found a significant positive relationship ($r = 0.78$; $p < 0.001$) between TC concentrations (relative to organic matter content) and total phosphorous (TP) concentrations of lake water measured at overturn. They developed a transfer function from this dataset and then used TC concentrations in sediment cores to estimate past TP concentrations. At Lake Maggiore, where two other diatom-based reconstructions of TP were available in addition to measured TP values during recent times, the pigment and diatom-based TP estimates were in good agreement (Fig. 16) and it was found that the TC method provided the best approximation of the measured TP values (Guilizzoni et al., 2011). The lakes they examined are characterized by a variety of climate conditions, morphologies, and nutrient conditions but despite this, it found that the pigment model correctly estimated TP in all lakes except for those rich in submerged aquatic macrophytes and epiphytes, which were outliers in the TP vs. TC relationship. Thus, the approach of using sedimentary pigments to examine past TP concentrations appears promising but requires additional testing in a wider variety of geographical locations.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

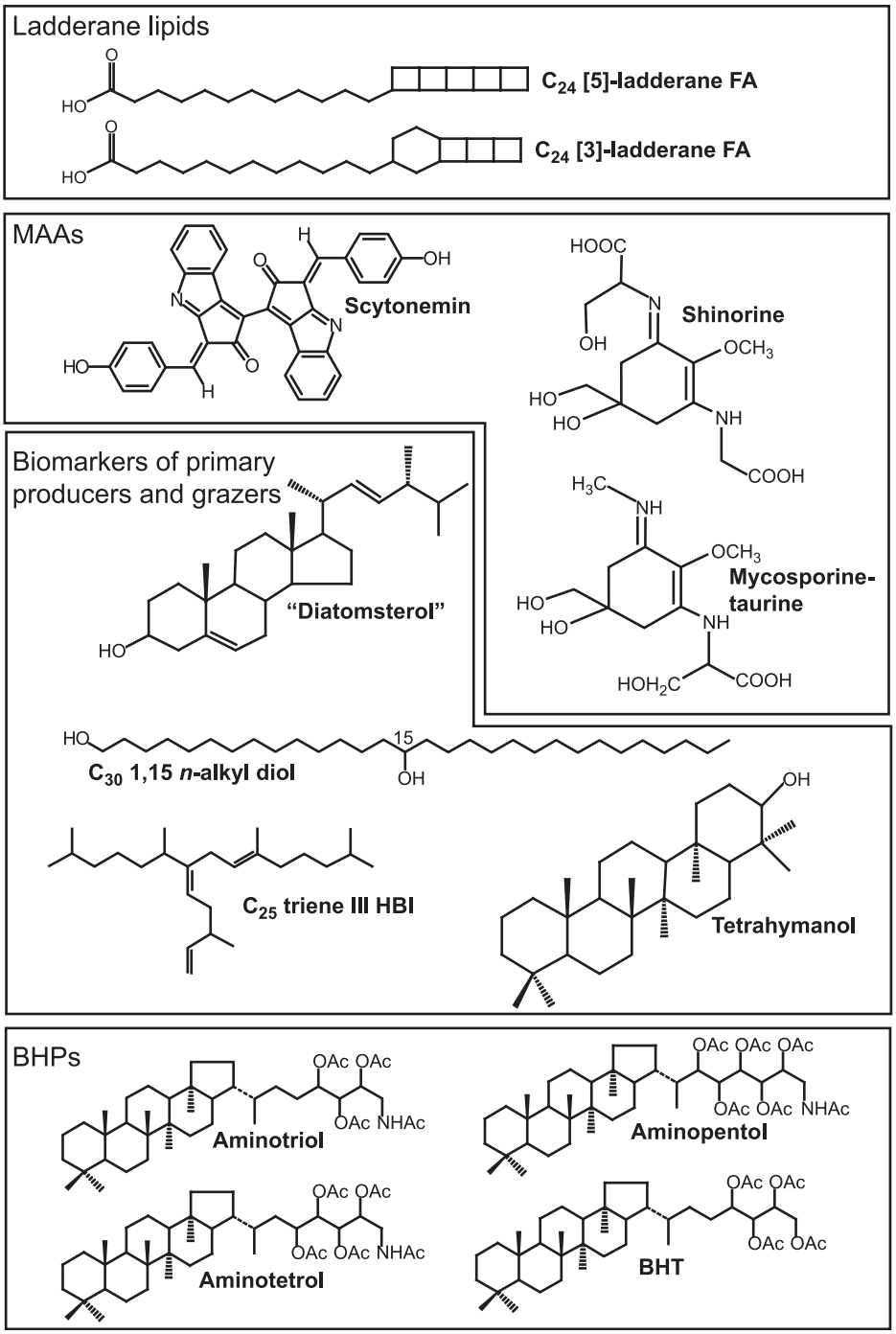

Fig. 15. Structures of selected biomarkers discussed in the text. Structures shown include the C_{24} [5]-ladderane fatty acid (FA) and the C_{24} [3]-ladderane FA; the compound scytonemin; examples of the mycosporine-like amino acids (MAAs) including scytonemin, shinorine and mycosporine-taurine; the C_{30} 1,15 *n*-alkyl diol, BHPs including aminotriol, aminopentol, aminotetrol and bacteriohopane-32,33,34,35-tetrol (BHT); a highly branched isoprenoid (HBI) alkane, C_{25} triene III; and, tetrahymanol.

7. Exploring soil, cyanobacteria and methanotrophic bacteria inputs and processes using bacteriohopanepolyols

Intact bacteriohopanepolyols (BHPs) are pentacyclic triterpenoids (Fig. 15) that comprise a diverse group of membrane lipids produced by many (but not all) bacteria including α-, β-, and γ-proteobacteria, cyanobacteria and planctomycetes (Talbot and Farrimond, 2007; e.g. Cooke et al., 2009; Welander et al., 2010). BHPs are also the major precursors of sedimentary geohopanoids (e.g. hopanes, hopenes, hopanoic acids, hopanols) (e.g. Ourisson and Albrecht, 1992). A wide variety of BHP structures are known, which vary in the number, position and nature of the functional groups on the side chain (Talbot and Farrimond, 2007). The most common BHP in soils and sediments is bacteriohopane-32,33,34,35-tetrol (BHT), which is known to be produced by a diverse suite of organisms (Talbot and Farrimond, 2007) and has been reported in sediments up to 50 Ma (van Dongen et al., 2006). While some BHPs are produced by numerous organisms, others are more specific and can be related to groups of organisms or environments and thus provide biomarkers for examining bacterial

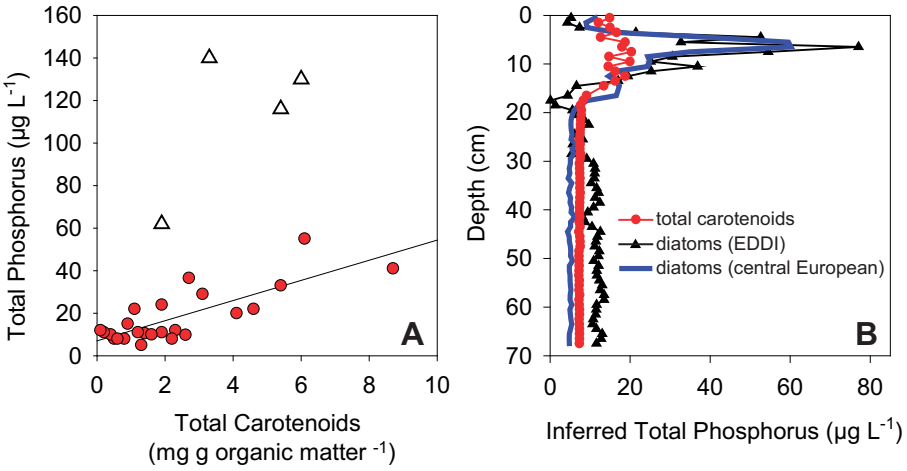

Fig. 16. Total carotenoids as a proxy for total phosphorus concentration in lake water. A) Correlation between total phosphorus of water samples with total sedimentary carotenoid concentrations ($r^2 = 0.78$, $n = 24$) in lakes from Italy (data from Guilizzoni et al., 2011). Four shallow lakes were outliers (indicated by the open triangles) and were not included in the correlation. B) Inferred total phosphorus reconstructions from a Lake Maggiore sediment core (data from Guilizzoni et al., 2011). The total phosphorus reconstruction based on total carotenoids is indicated by the red circles while two models based on diatoms remains for the European Diatom Database (EDDI) (Battarbee et al., 2000) and a regional central-European dataset (Wunsam and Schmidt, 1995) are shown by the black triangles and the solid blue line, respectively.

populations and processes in modern and ancient environments (e.g. Talbot et al., 2003c; Talbot and Farrimond, 2007; Cooke et al., 2009; Handley et al., 2010). Although sedimentary geohopanoids, analyzed by GC–MS techniques, are widely recognized (e.g. Ourisson and Albrecht, 1992) the investigation of intact BHP structures by APCI LC-MS^n is relatively new (Talbot et al., 2003a,b). Thus, the diversity of BHP structures and their potential as microbial markers is just beginning to be elucidated. Here, we highlight a few intact BHPs that seem potentially useful to (paleo)limnological studies but note that the reader should refer to Talbot and Farrimond (2007) for a detailed overview of the diversity of BHP structures and related source organisms.

7.1. Adenosylhopane, a tracer of soil OM to aquatic environments

Adenosylhopane (Fig. 1), 2-methyladenosylhopane and structurally related compounds have been proposed as being synthesized solely by soil bacteria (Cooke et al., 2008a). Thus far, adenosylhopane has been identified in two proteobacteria, the nitrogen-fixing bacterium *Bradyrhizobium japonicum* and the ammonia oxidizing bacterium *Nitrosomonas europea* while 2-methyladenosylhopane has been identified in *B. japonicum* (Talbot and Farrimond, 2007; Cooke et al., 2009 and references therein). Adenosylhopane, 2-methyladenosylhopane and structurally related compounds have been found to be abundant in soils from a widely distributed geographical locations (Talbot and Farrimond, 2007, and references therein) and thus can serve as tracers of soil organic matter input to aquatic environments (Talbot and Farrimond, 2007; Cooke et al., 2008b, 2009; Handley et al., 2010; Kim et al., 2011), similar to the BIT Index (see Section 3.1). However, recently adenosylhopane has been identified as the first intermediate in hopanoid side chain synthesis in *Methylobacterium* (Bradley et al., 2010). The authors suggest that adenosylhopane may also occur as an intermediate in all hopanoid-producing bacteria, which, if proven correct, may limit its use as marker specifically for soil bacteria.

Adenosylhopane, 2-methyladenosylhopane and structurally related compounds also have been reported from a few lacustrine environments including Lake Windermere (UK), Lake Nkunga (Kenya) and Loch Ness (UK) (Talbot and Farrimond, 2007). High terrestrial inputs occur at both Lake Nkunga and Loch Ness (Ficken et al., 1998; Talbot and Farrimond, 2007) and thus these compounds may be present in other lakes with similarly high terrestrial inputs. However, Talbot and Farrimond (2007) re-analyzed 24 lacustrine sediments with multistage MS that they had previously analyzed using single stage MS (Talbot et al., 2003c) but did not find adenosylhopane or 2-methyladenosylhopane at other lacustrine sites. Therefore, these BHPs can potentially serve as a tracer for soil organic matter to lacustrine environments but it remains to be seen whether these compounds are common in lacustrine sediments.

To date, the diagenetic alteration of intact BHPs has not been systematically investigated. Although many of the intact BHPs appear to be well preserved on long time scales (e.g. the presence of BHT in 50 Myr old sediments) (van Dongen et al., 2006), it has been noted that other intact BHPs are likely influenced by diagenesis and some also may be diagenetically produced. For example, in their 1.2 Ma record from the Congo deep-sea fan, Handley et al. (2010) found that the ratio of BHT to (BHT plus adenosylhopane) increased gradually with depth suggesting a potential diagenetic source. In a 70 Kyr sedimentary record from the Benguela Upwelling System, a decoupling between BHPs and geohopanoids is noted (Blumenberg et al., 2010). Here, it appears that the geohopanoids likely reflect laterally-transported fossil organic matter whereas the source of BHPs is from the water column thereby demonstrating that sedimentation processes can complicate using geohopanoids and BHPs for paleoenvironmental reconstructions (Blumenberg et al., 2010).

7.2. BHP markers for cyanobacteria

Cyanobacteria are important primary producers in many lacustrine systems and some types produce BHPs. Methylation at C-2 is a well-known structural feature of cyanobacterial BHPs (e.g. Summons et al., 1999; Talbot et al., 2008) and species producing C-2 methylated structures occur in all five divisions of cyanobacteria (Chroococcales, Pluerocapsales, Oscillatoriales, Nostocales and Stigonematales) (Talbot et al., 2008). However, C-2 methylated structures are not produced by all cyanobacteria. A study of 58 strains of cyanobacteria found that while most (49 strains) produce BHPs including BHT and aminotriol (discussed in Section 7.3), the C-2 methylated BHPs are not as widespread and are noted in only 21 strains (Talbot et al., 2008 and references therein). C-2 methylated structures also can be produced by other organisms including facultative methylotrophs and some nitrogen-fixing bacteria and

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

a purple non-sulfur bacteria grown anaerobically (Summons et al., 1999 and references therein; Rashby et al., 2007; Talbot et al., 2008; Welander et al., 2010). The hydrocarbon skeletons of BHPs are resistant to biodegradation and are extremely refractory, allowing for incorporation into kerogen or sulphur-linked macromolecules (Summons et al., 1999). Indeed, 2-methyl-BHP derivatives, the 2α-methylhopanes have been found to be abundant in organic-rich sediments up to 2500 Myr old, where they were used as biomarkers for cyanobacterial oxygenic photosynthesis (Summons et al., 1999). However, more recently Welander et al. (2010) identified the protein responsible for hopanoid methylation at C-2 (S-adenosylmethionine (SAM) methylase encoded by *hpn*P) in cyanobacteria but also in acidobacteria and a subclade of the rhizobiales within α-proteobacteria. Thus, the findings of Welander et al. (2010), that *hpn*P is found in many modern bacteria that do not utilize oxygenic photosynthesis, argues against using 2-methylhopanoids as biomarkers for this process.

In addition to methylation at C-2, a number of other side chain structures have been reported for cyanobacteria (Talbot et al., 2008) and some of these structures seem to be unique to cyanobacteria. For example, specific cyanobacterial biomarkers may be provided by a 2-methyl cyclitol ether, which is currently only reported from the cyanobacterium *Anacystis montana*, and bacteriohopanepentol (BHpentol), which has only been reported to occur in *Nostoc muscorum* and *Nostoc* sp. (Talbot et al., 2008 and references therein). Other side-chain structures that are only known from cyanobacteria include an irregular pentol, an alternative tetrol glycoside, and *O*-β-3,5-anhydrogalacturonopyranosyl tetrol (Talbot et al., 2008). Additionally, novel structures have been identified in *O. amphigranulata*, *Calothrix* sp. and in an enrichment culture of *Gloeocapsa* (see Talbot et al., 2008 for structures). Some of these cyanobacterial BHPs have been reported from lacustrine sediments. For example, 2-methyl cyclitol ether was found in Loch Ness (UK) and in La Piscina de Yuririah (Mexico) while BHpentol was found in Lake Druzhby (Antarctica) and also in Loch Ness (Talbot and Farrimond, 2007).

7.3. BHP markers for methanotrophs

Methanotrophs are subdivided into two types depending on their carbon assimilation pathway; Type 1 methanotrophs are members of the γ-proteobacteria and utilize the ribulose monophosphate pathway whereas Type II methanotrophs are members of the α-proteobacteria and utilize the serine pathway (Hanson and Hanson, 1996; Talbot et al., 2003c). In aquatic settings methane consumption occurs by either anaerobic oxidation of methane (AOM) or aerobic methanotrophy (e.g. Zhu et al., 2010 and references therein). To date relatively few studies have conducted organic geochemical investigations of aerobic methanotrophy in lacustrine environments; however, this can be investigated by examining BHPs. In particular, 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol), has been identified as a BHP specific for Type I methane oxidizing bacteria (Talbot and Farrimond, 2007 and references therein). Others BHPs, while somewhat less specific, can also be related to methane oxidizing bacteria. 35-aminobacteriohopane-31,32,33,34-tetrol (aminotetrol) is present in varying amounts in all methanotrophs (Talbot and Farrimond, 2007) but also in trace amounts in some species of sulfate reducing bacteria (Blumenberg et al., 2006). 35-Aminobacteriohopane-32,33,34-triol (aminotriol) is produced by all Type II methanotrophs, some Type 1 methanotrophs, as well as a diverse range of other microorganisms (Talbot and Farrimond, 2007 and references therein). Zhu et al. (2010) used these BHPs to trace aerobic methane oxidation across a large methane concentration gradient in surface sediments from the lower Yangtze River and the East China Sea.

The occurrence of aminopentol, aminotetrol, and aminotriol BHPs has also been noted in a number of lacustrine sediments. Talbot et al. (2003c) examined BHP distributions in a number of lakes including temperate, Antarctic, high-altitude, and saline lakes. The aminotriol BHP, presumably derived from methanotrophs, was found to be one of the major components in many of these sediments. The relative proportion of hexafunctionalized BHPs (such as aminopentol) has been observed to be high in small, stratified and highly productive lakes but low in marine settings (Farrimond et al., 2000; Watson and Farrimond, 2000; Talbot et al., 2003c). While sulphate reduction dominates over methanogenesis in marine sediments, methanogenesis is the dominant process in highly productive lakes and Type 1 methanotrophs, producers of hexafunctionalized BHPs, are known to occur in the water columns of these types of lakes (Talbot et al., 2003c).

7.4. Application of BHPs in an Antarctic lacustrine record

An interesting study of Ace Lake (Antarctica) examined both BHPs and 16S ribosomal RNA genes (16S rDNA) to help reveal sources for sedimentary BHPs and examine if changing environmental conditions are reflected in BHP distributions (Coolen et al., 2008). Ace Lake has a unique history; it was initially a meltwater filled freshwater lake but due to sea level rise following deglaciation, it was then connected to the ocean and became a stratified fjord with sulfidic bottom waters, and later, due to isostatic rebound, the lake was again re-isolated (Coolen et al., 2008 and references therein). Presently Ace Lake is saline with anoxic bottom waters that are characterized by high methane and sulphide concentrations (Coolen et al., 2008). Coolen et al. (2008) found that when Ace Lake was a fresh meltwater lake, the main BHPs present were aminotriol, aminotetrol and aminopentol BHPs (Fig. 17). Although aminotriol is produced by a wide range of organisms, compound-specific carbon isotope analysis of these lipids revealed a highly depleted ^{13}C content, confirming a methanotrophic origin for these BHPs (Jahnke et al., 1999; Coolen et al., 2008). In these sediments, phylotypes related to Type I methanotrophs of the genus *Methylomonas* and to Type II methanotrophs of the genus *Methylocystis* were detected (Coolen et al., 2008). When Ace Lake became a stratified fjord, a number of major changes are noted. Significantly lower levels of total BHPs are observed and 16s rDNA of methanotrophs comprises a smaller portion of the total bacterial 16S rDNA pool (Coolen et al., 2008). These observations are consistent with sulphate reduction likely dominating over methanogenesis at this time (Coolen et al., 2008). Subsequently, when Ace Lake returned to being an isolated lake, there is again evidence for an active methane cycle. Aminotetrol and aminotrol BHPs were found to be present in these sediments while aminopentol was absent (Fig. 17). While this distribution was previously considered a good indicator for Type II methanotrophs, the 16S rDNA data indicated that phylotypes related to Type II methanotrophs were not present (Coolen et al., 2008). Instead, there was evidence that a phylotype related to methanotrophic gill symbionts of deep-sea cold-seep mussels was the likely source of aminotetrol and aminotriol in these sediments. These phylotypes also produce ^{13}C-depleted 4-methylated sterols, compounds also found in methanotrophs isolated from Ace Lake (Schouten et al., 2001a).

7.5. Outlook: BHPs for lacustrine paleoenvironmental reconstructions

The use of BHPs such as aminopentol and 2-methyl cyclitol ether as biomarkers of methanotrophs and cyanobacteria, respectively, is of particular interest to lacustrine studies as these organisms are dominant in many lakes and their biomarkers may provide

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

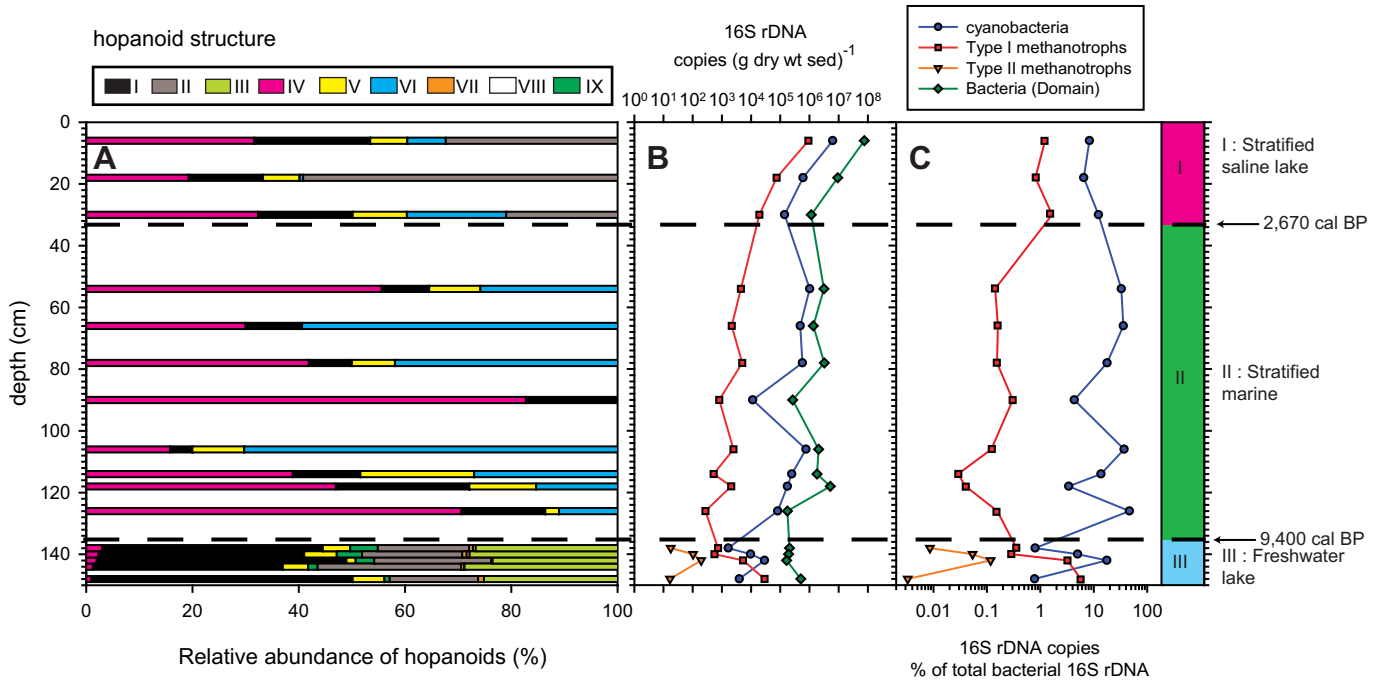

Fig. 17. BHP and 16S rDNA data from Ace Lake, Antarctica. Data from Coolen et al. (2008). A) The relative abundance of intact BHPs in Ace Lake sediments. BHPs structures indicate sources from: I (aminotriol), II (aminotetrol), III (Aminopentol), IV (BHT), V (bacteriohopanetetrol cyclito ether), VI (bacteriohopanetetrol glycoside, VII (bacteriohopanepentol cyclito ether), VIII (bacteriohopanepentol glycoside), IX (2-methylBHT) (see Coolen et al., 2008 for more details). B) Quantitative and C) relative distribution of sedimentary 16S rDNA of cyanobacteria, Type 1 methanotrophs, Type II methanotrophs, and bacteria (general). Shifts in the relative distribution of BHPs and 16S rDNA coincide with the depositional history of Ace Lake reflecting changes from a freshwater lake to stratified marine system, to a stratified saline lake.

opportunities for investigating past methane or nitrogen cycling. However, at present only a few studies have examined BHPs in lakes and thus more investigations are required to determine how widespread and abundant BHPs are in lacustrine sediments. In addition, further studies are certainly needed to better asses diagenetic and lateral transport effects on BHPs as well as the occurrence of BHPs (e.g. adenosylhopane) in other hopanoid producing bacteria (Bradley et al., 2010).

8. Lipid biomarker indicators of primary producers and grazers

Microalgae are generally the major sources of lipids in lacustrine environments and there are biomarkers for a number of different types microalgae. Above we already discussed the examples of alkenones as biomarkers for haptophyte algae, carotenoids for different types of photoautotrophs and BHPs for cyanobacteria. Here, we highlight a few examples of other biomarkers that can be used to examine primary productivity of selected algal classes in many lacustrine environments. We note that most of these microalgal biomarkers have been previously reviewed by Volkman et al. (1998) and Volkman (2003), and the reader should refer to these publications for detailed information on the wide variety of lipids present in microalgae. For a detailed review on the distribution of sterols in diatoms we refer the reader to the comprehensive study of Rampen et al. (2010). The algal lipids discussed in Sections 8.1–8.4 are generally analyzed by GC and GC/MS.

8.1. Dinosterol, a biomarker for dinoflagellates

Sterols are compounds that occur in all eukaryotes and are membrane rigidifiers, and the specificity of some of these compounds for different phytoplankton groups is well known (Volkman, 1986, 2003; Volkman et al., 1998). The compound dinosterol (4α,23,24-trimethyl-5α-cholest-22-en-3β-ol; Fig. 1) is found in many dinoflagellate (Pyrrophyta) species (Withers, 1983; Piretti et al., 1997) and is commonly used as a biomarker for these organisms (Boon et al., 1979; Robinson et al., 1984; Volkman, 2003). While many sterols are produced by both aquatic algae and terrestrial plants, dinosterol is not synthesized by higher plants and is thus recognized as a robust biomarker for dinoflagellates (Volkman et al., 1999). However, it should be noted that dinosterol it is not found in all dinoflagellate species (Kokke et al., 1981) and in fact a study by Leblond and Chapman (2002) only found it in about half of 43 dinoflagellate species examined. Dinosterol can also be produced by a few diatoms and haptophyte algae (Volkman et al., 1993, 1997). Nevertheless, dinoflagellates are an important primary producer in many lakes and since dinosterol is present in many lake sediments, it may be useful for examining past changes in dinoflagellate productivity in some systems (e.g. Castañeda et al., 2011).

8.2. Diatom biomarkers

A number of different sterols are often used as biomarkers for diatoms. For example, the compound 24-methylcholesta-5,22E-dien-3β-ol is known as “diatomsterol” (Fig. 15); however, this sterol and other common diatom sterols are produced by a large number of algal classes (Volkman, 2003) thus restricting their use as biomarkers for diatoms. In fact, a recent study that analyzed sterols in 106 diatom cultures revealed that all of the major sterols found in diatoms are also common sterols of other algal groups (Rampen et al., 2010). The most common sterols found in diatoms are 24-methylcholesta-5,24(28)-dien-3β-ol and the Δ^5 sterols, cholest-5-en-3β-ol (cholesterol), 24-methylcholest-5-en-3β-ol, and 24-ethylcholest-5-en-3β-ol (Rampen et al., 2010). Notably, “diatomsterol” was found to be absent in some diatoms and relatively high concentrations of this compound were only observed in pennate

diatoms (Rampen et al., 2010). Furthermore, some of the major sterols found in diatoms are also produced by higher plants (Nishimura and Koyama, 1977) thus restricting their utility as an aquatic biomarker in many systems. However, in lakes that receive little terrestrial input, a number of sterols could potentially serve as diatom biomarkers. In lakes where diatoms are one of the dominant primary producers, sterol distributions could provide information regarding the class of diatoms present (Rampen et al., 2010).

The compounds loliolide (Fig. 1) and isololiolide are the anoxic degradation products of the pigment fucoxanthin, the major carotenoid present in diatoms (Klok et al., 1984; Repeta, 1989), and can provide a diatom biomarker in some environments. When fucoxanthin undergoes anoxic degradation, loliolide (isololiolide) is produced on a mole-to-mole basis (Repeta, 1989) and this process can occur both in the water column and in the sediments. Although dinoflagellates and haptophyte algae can also contain fucoxanthin (Klok et al., 1984; Jeffrey and Vesk, 1997), loliolide and isololiolide can provide a reliable biomarker for diatoms in lakes where dinoflagellates are not a major contributor to primary productivity and where haptophyte algae are not present (e.g. Castañeda et al., 2011).

Highly branched isoprenoid alkanes (HBIs) (Fig. 15) are highly specific biomarkers for diatoms and are produced by four genera: *Haslea* (Volkman et al., 1994; Belt et al., 1996; Wraige et al., 1997, 1998; Allard et al., 2001; Sinninghe Damsté et al., 2004), *Rhizosolenia* (Volkman et al., 1994; Sinninghe Damsté et al., 1999b; Rowland et al., 2001; Massé et al., 2004; Sinninghe Damsté et al., 2004), *Pleurosigma* (Belt et al., 2000; Belt et al., 2001a; Grossi et al., 2004), and *Navicula* (Belt et al., 2001b; Sinninghe Damsté et al., 2004). While the majority of known HBI producers are marine (both benthic and planktonic species) diatoms, the freshwater diatom *Navicula sclesvicensis* produces a C_{25} HBI triene (Belt et al., 2001b). HBIs have been noted in sediments from several lakes including saline lake Small Meromictic Basin in Ellis Fjord, Antarctica (Sinninghe Damsté et al., 2007), and freshwater Mud Lake, Florida (Filley et al., 2001), Lake Koucha (Aichner et al., 2010a) and Lake Lugano (Bechtel and Schubert, 2009). In a sediment core from Lake Lugano (Switzerland) spanning the interval from 1900 AD to the present, increased concentrations of HBIs, in agreement with high 24-methylcholesta-5,22-dien-3b-ol (brassicasterol) concentrations, provided evidence for periods of increased input from diatoms (Bechtel and Schubert, 2009). In a 16 cal ka record from Lake Koucha (Tibetan Plateau), the appearance of an unsaturated C_{25} HBI at 4.7 cal ka BP is noted along with increased concentrations of other algal biomarkers since ~6.1 cal ka BP (Aichner et al., 2010a). Lake Koucha transitioned from a saline to a freshwater system at ~7.2 cal ka BP and after this time a number of phytoplankton biomarkers are observed whereas previously the lake had been dominated by aquatic macrophytes (Aichner et al., 2010a).

Overall, molecular biomarkers, and in particular the highly specific HBIs, can be useful for examining past diatom productivity, especially in lakes where silica dissolution has occurred. However, diatoms are often well preserved in many lacustrine sediments and thus highly specific species level information can be gained from examining diatom assemblages, which in many cases cannot be gained from lipid analysis. Nevertheless, for studies targeting past changes in diatom productivity it could be useful to examine diatom biomarkers in conjunction with biogenic silica or diatom assemblage data.

8.3. Tetrahymanol, a biomarker for bacterivorous ciliates

The compound tetrahymanol (gammaceran-3β-ol; Fig. 15) is abundant in many lake sediments (e.g. Hanisch et al., 2003; Castañeda et al., 2011) and is produced by bacterivorous ciliates, such as the freshwater ciliate Tetrahymena (Mallory et al., 1963; Harvey and McManus, 1991). More specifically, it is recognized that ciliates biosynthesize tetrahymanol only when their diet does not contain sterols (Harvey and McManus, 1991) and in modern stratified environments, ciliates feed on organisms found at or below the chemocline such as purple sulphur bacteria and sulphide-oxidizing bacteria (Sinninghe Damsté et al., 1995 and references therein). Tetrahymanol can also be produced by the anaerobic purple bacterium *Rhodopseudomonas palustris* (Kleemann et al., 1990), anaerobic rumen fungus (Kemp and Lander, 1984), and in small amounts by a fern (Zander et al., 1969). Sources from rumen fungus and ferns are unlikely in many lake sediments but anaerobic purple bacteria could be a potential source of tetrahymanol in some environments. However, in aquatic sediments tetrahymanol typically derives from ciliates (Harvey and McManus, 1991) and previous studies have attributed its occurrence to the presence of a stratified water column (e.g. Hanisch et al., 2003; Xu and Jaffé, 2008) since bacterivorous ciliates are typically found at the oxic–anoxic boundary where large bacterial populations are present (Sinninghe Damsté et al., 1995; Thiel et al., 1997). In a study of Lake Valencia (Venezuela), it was found that an abrupt increase in tetrahymanol concentration occurred at ~7260 cal BP whereas prior to this time its abundance was below the detection limit (Xu and Jaffé, 2008). The authors attributed the increase in tetrahymanol concentrations to the establishment of an oxic–anoxic boundary in the water column of Lake Valencia, supported by independent evidence for lake-level changes between the Late Pleistocene and early Holocene (Xu and Jaffé, 2008 and references therein). It also should be noted that the compound gammacerane, a C_{30} triterpane which has been found to be abundant in many lacustrine deposits, is produced from tetrahymanol by diagenesis and early catagenesis (ten Haven et al., 1989).

8.4. Long-chain diols as a biomarker for Eustigmatophyte algae

Long-chain (C_{28}–C_{32}) 1,15 *n*-alkyl diols (Fig. 11) are produced by Eustigmatophyte (yellow-green) algae (Volkman et al., 1992; Versteegh et al., 1997), a class that relatively little is known about (Ott and Oldham-Ott, 2003). Long-chain *n*-alkyl diols also have been noted in many lacustrine sediments, and often they are present in high abundances (Xu et al., 2007; Xu and Jaffé, 2008; Castañeda et al., 2009c; Shimokawara et al., 2010). Interestingly, long-chain *n*-alkyl diols have been reported from many lakes although eustigmatophyte algae have not yet been positively identified from any these lakes, to the best of our knowledge. Most species of eustigmatophytes are very small (2–4 mm) and can be easily confused with coccoid forms of Chlorophyceae or Xanthophyceae and thus this group may have been overlooked in algal surveys (Ott and Oldham-Ott, 2003). In addition, the class Eustigmatophyceae includes members that inhabit terrestrial soils (Ott and Oldham-Ott, 2003) and so terrestrial sources to lakes may be possible but previous studies point to aquatic sources for the long-chain *n*-alkyl diols (Xu et al., 2007; Xu and Jaffé, 2008; Castañeda et al., 2009c; Shimokawara et al., 2010). Furthermore, a study of the phytoplankton in Lake Tanganyika (East Africa) based on polymerase chain reaction-amplified 18S ribosomal DNA, provides evidence for the presence of eustigmatophytes possessing a sequence similar to marine and freshwater members of *Nannochloropsis* (De Wever, 2006). Alternatively, it has been suggested that cyanobacteria may be a source of the long-chain 1, 15 *n*-alkyl diols in lakes (Xu et al., 2007). At Lake Valencia (Venezuela), one of the most productive lakes in the world, primary productivity is dominated by cyanobacterial species, which comprise >90% of the biomass (Xu et al., 2007). The exceptionally high abundance of diols

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

in this lake, supported by similar $\delta^{13}C$ values of the diols and other cyanobacterial biomarkers, suggests that cyanobacteria may be a source of these compounds in Lake Valencia (Xu et al., 2007). Given widespread occurrence of the long-chain *n*-alkyl diols in lakes, and the fact that they are often present in high abundances, there is a need to identify the producer(s) of these lipids in freshwater environments.

8.5. Examining past changes in productivity from biomarkers of primary producers: an example from Lake Malawi

Examining changes in the abundance of several different aquatic biomarkers provides a method for examining past changes in primary productivity. While biomarker abundances cannot be directly correlated to biomass due to complications arising from degradation and variations in cellular lipid concentrations, changes in the relative abundances of microalgal lipids can be used to examine past trends in aquatic ecosystem structure and productivity (e.g. Holtvoeth et al., 2010; Kristen et al., 2010). For example, in a Lake Malawi sediment core spanning the past 700 years, Castañeda et al. (2011) utilized the accumulation rates of loliolide, dinosterol, long-chain *n*-alkyl diols, and tetrahymanol as productivity tracers of diatoms, dinoflagellates, eustigmatophyte algae and bactivorous ciliates, respectively (Fig. 18). In modern Lake Malawi, where dinoflagellates are a minor contributor to algal productivity and haptophyte algae are not present, it was found that accumulation rates of loliolide exhibited the same overall trends as biogenic silica, another proxy for diatom productivity. The biomarker records revealed several notable changes including an increase in dinoflagellate and bacterivorous ciliate biomarkers over the past few centuries, accompanied by a decrease in diatom lipids (Fig. 18). Independent evidence from Lake Malawi showed that a change in the dominant wind direction over the lake occurred at the end of the Little Ice Age (Brown and Johnson, 2005), with the northern end of Lake Malawi experiencing stronger or more frequent northerly winds prior to this time. Diatom productivity in the northern basin of Lake Malawi is sensitive to changes in wind strength and direction, which control upwelling. The decreased diatom productivity noted in Lake Malawi after ~1780 AD coincides with a shift to less frequent or weaker northerly winds over the lake. A change in the dominant wind regime may also explain the increased abundances of dinoflagellate biomarkers after this time since studies have suggested that dinoflagellate blooms are favoured by a stable water column with minimal mixing (Pollingher and Zemel, 1981). In contrast to diatoms, which rely on turbulent mixing to remain in the photic zone, turbulent mixing can destroy or damage dinoflagellate cells (Pollingher and Zemel, 1981). Observations from quantitative algal surveys of Lake Malawi also support the increased presence of dinoflagellates with recent blooms observed (Hecky et al., 1999).

9. Fossil DNA indicators of primary producers and grazers

Ancient DNA preserved in sediments (fossil DNA) is a relatively recent tool that can be used to reconstruct past ecosystems and has been used to examine environmental changes in specific marine, lacustrine and terrestrial settings (Coolen et al., 2004b, 2008; D'Andrea et al., 2006; Willerslev et al., 2007; Boere et al., 2009). While the majority of lipid biomarkers cannot be used to provide taxonomic differentiation at the species level, fossil DNA is perhaps the ultimate biomarker as it can be used to provide species level information from past environments and thus there is much interest in developing these techniques for application in Quaternary science. However, DNA is fragile and degradation of ancient DNA to shorter fragments occurs relatively rapidly after deposition, within the first several thousand years (Coolen and Overmann, 1998). Nevertheless, the shorter DNA fragments (less than 500 base pair-long (Coolen and Gibson, 2009)) can be analyzed using

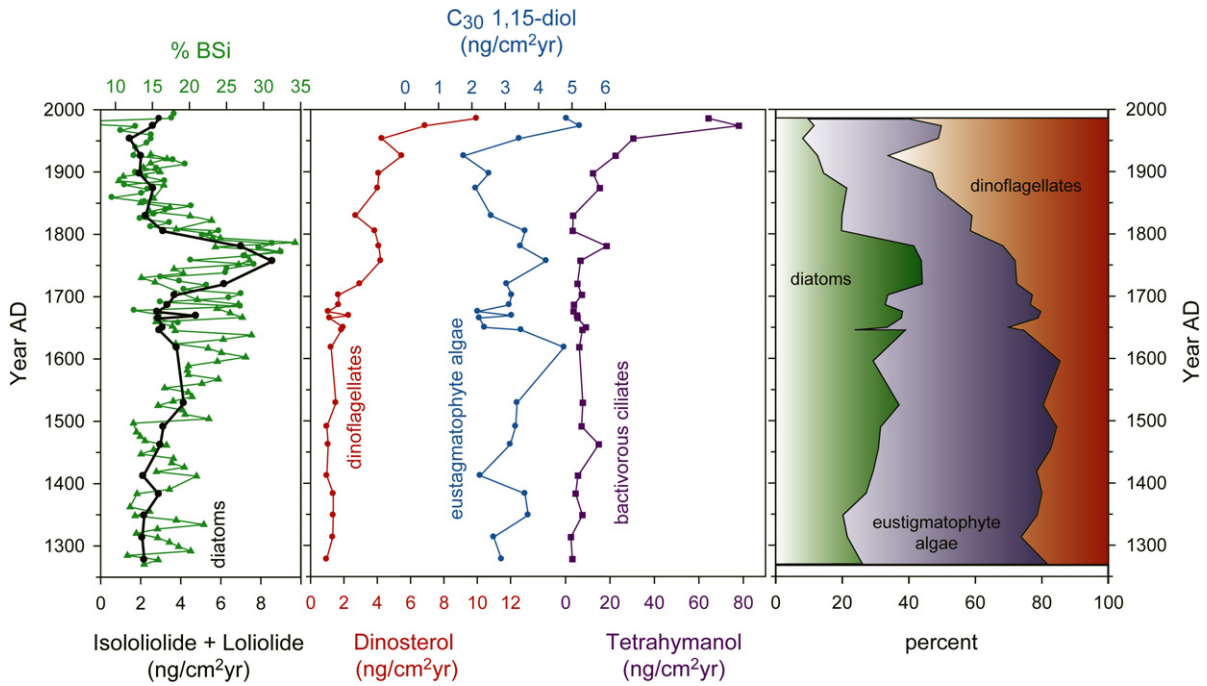

Fig. 18. Lake Malawi productivity biomarkers (data from Castañeda et al., 2011). Mass accumulation rates of isololiolide and loliolide, a diatom biomarker, are plotted with biogenic silica (data from Johnson et al., 2001), another diatom proxy. Mass accumulation rates of dinosterol (a biomarker of dinoflagellates), the C_{30}, 1,15 *n*-alkyl diol (a biomarker of eustigmatophyte algae) and tetrahymanol (a biomarker for bactivorous ciliates) are also shown. The panel on the far right is a relative percentage plot of the main aquatic biomarkers present in Lake Malawi sediments. One compound representative of each group (diatoms, eustigmatophyte algae and dinoflagellates) was chosen and abundances were normalized to 100%. An increase in dinoflagellates accompanied by a decrease in diatoms is noted since ~1800 AD.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

polymerase chain reaction (PCR) techniques to amplify DNA and produce billions of copies of a particular DNA sequence. Sedimentary conditions favourable to DNA preservation include cold, anoxic and light-free environments (Coolen et al., 2004b) and fossil DNA analysis has proven to be especially useful to Holocene studies of polar lakes (e.g. Coolen et al., 2004b, 2008). Another complicating factor with fossil DNA analysis is that metabolically active organisms in deep waters and sediments contribute to the DNA pool; however, species that express genes in deep waters and sediments at the time of sampling can be examined and excluded as paleoenvironmental proxies (Coolen and Gibson, 2009). Additionally, fossil DNA analysis can be conducted along with lipid biomarker analysis to further ground-truth fossil DNA data and also provide insights into lipid biomarker distributions (Coolen and Gibson, 2009). To date, fossil DNA has commonly been used to examine the diversity of past planktonic communities including unicellular aquatic organisms such as copepods (Bissett et al., 2005; Gibson and Bayly, 2007).

An interesting study by Boere et al. (2009) utilized a multi-proxy approach to examine fossil DNA, lipid biomarkers and palynomorphs of dinoflagellates from Holocene sediments of Small Meromictic Basin, Ellis Fjord (Antarctica), which is in the advanced stages of a transition from a fjord system to a meromictic saline lake. Their fossil 18S rDNA-based survey revealed at least nine different dinoflagellate species have lived in Ellis Fjord and they found that fossil DNA was preserved for ~2700 years in organic carbon-rich and sulfidic sediments of Small Meromictic Basin. At ~1850 cal yr BP a community shift is noted and the autotrophic sea-ice dinoflagellate *Polarella glacialis* was found to be the main precursor of fossil dinoflagellate biomarkers in the younger sediments. In contrast, abundances of dinosterol, the only dinoflagellate-diagnostic lipid present in the sediments, suggested decreasing contributions of dinoflagellates to sediments in the youngest portion of the core. However, they note that *P. glacialis* was found not to produce dinosterol in culture studies and thus studies using only dinosterol as a dinoflagellate biomarker may lead to biased interpretations of past changes in dinoflagellate abundance. Boere et al. (2009) were not able to relate specific palynomorph morphotypes to the 18S rDNA sequences but they note that rare species that were present as cysts were not detected with the phylogenetic analysis. Thus, these three approaches provide complimentary information regarding past dinoflagellate succession in Small Meromictic Basin.

Overall, fossil DNA analysis is proving to be an extremely powerful approach for examining past species composition in polar lakes and also for examining biological sources of lipid biomarkers. However, many outstanding questions presently exist regarding the factors and conditions that control DNA preservation, which need to be addressed before fossil DNA techniques can be more broadly applied (Coolen and Gibson, 2009). Distinguishing DNA signals from living and fossil populations of microorganisms, as well as contamination, also continues to be a challenge and care must be taken when utilizing fossil DNA for paleoenvironmental studies.

10. New biomarkers and techniques potentially useful for lacustrine studies

New biomarkers and organic geochemical proxies are continually being discovered and developed. In this section we highlight a few recently discovered biomarkers and research developments that will likely be useful for lacustrine studies but that, to our knowledge, have not yet been widely applied to paleolimnological investigations. Several new biomarkers can be related to nitrogen or methane cycling and thus are of much interest for Quaternary studies. Nitrogen is often a limiting element for primary productivity and therefore plays a major role in both ocean and lake biogeochemistry. Likewise, methane is an important greenhouse gas and biological production by methanogens (anaerobic members of the Archaea) is the source of approximately 70% of global methane (Schimel, 2004). In addition to these new biomarkers, we also discuss recent developments in using compound-specific radiocarbon analysis as a tool for improving lacustrine sediment chronologies.

10.1. Tracing past N_2 fixation

In addition to the BHPs discussed in Section 7.2, long-chain glycolipids (Fig. 1) have been recently reported as biomarkers of cyanobacteria, specifically for N_2-fixing heterocyst cyanobacteria. Two intact glycolipids, docosanyl 3-*O*-methyl-α-rhamnopyranoside and docosanyl 3-*O*-methylxylopyranoside, were first reported in sediments from Ace Lake (Antarctica) and a cyanobacterial origin was suggested for these sedimentary glycolipids (Sinninghe Damsté et al., 2001b). Docosanyl 3-*O*-methylxylopyranoside was additionally reported from Lake Malawi (East Africa), where cyanobacteria are one of the dominant primary producers (Castañeda et al., 2009b). Both of these studies utilized GC and GC/MS techniques to analyze these glycolipids. More recently, HPLC/ESI-MS^2 techniques have been used to examine the glycolipid content of 34 axenic strains of cyanobacteria (Bauersachs et al., 2009a). It was found that species of the families Nostocaceae and Rivulariaceae, which are capable of biosynthesising heterocysts (specialized cells that contain the nitrogenise enzyme and that are the site of N_2 fixation), contain a suite of glycolipids that consist of a sugar moiety glycosidically bound to long-chain diols, triols, keto-ols and keto-diols (Bauersachs et al., 2009a). These compounds appear to be a unique structural component of the heterocyst cell envelope (Nichols and Wood, 1968; Gambacorta et al., 1998) and when found in sediments can be used as biomarkers of N_2-fixing heterocystous cyanobacteria (Bauersachs et al., 2010). Indeed, long-chain heterocyst glycolipids have been found in both the water column and sediments of Lake Challa (Kenya) and in sediments from the Baltic Sea where heterocystous cyanobacteria form an important component of the present-day phytoplankton community (Bauersachs et al., 2010). Furthermore, long-chain heterocyst glycolipids are excellent biomarkers since they are well preserved in several lake surface sediments and have been reported from Oligocene sediments from Lake Enspel as well as in Eocene sediments from Lake Messel and the Green River Shale (Bauersachs et al., 2010). Since nitrogen-fixing cyanobacteria are present in many lakes, the analysis of long-chain heterocyst glycolipids provides an opportunity to examine past cyanobacterial production and nitrogen cycling.

10.2. Tracing past anaerobic oxidation of ammonium

The anaerobic oxidation of ammonium (anammox) to dinitrogen gas with nitrate as an electron acceptor is a globally important microbial process in both marine and freshwater nitrogen cycling. The bacteria that perform the anammox process belong to a distinct phylogenetic group related to the *Planctomycetes* (Strous et al., 1999; Schmid et al., 2007). The anammox reaction occurs with a specialized intracellular compartment, the anammoxosome, which has a membrane consisting of a dense layer of ladderane lipids (Sinninghe Damsté et al., 2002b). These unusual lipids consist of three or five linearly linked cyclobutane rings (Fig. 15) that are either ester or ether bonded to a glycerol backbone (Sinninghe Damsté et al., 2002b) and can analyzed by GC and GC/MS (Sinninghe Damsté et al., 2005) but analysis by HPLC/APCI-MS^2 is shown to be superior in sensitivity (Hopmans et al., 2006).

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Ladderane lipids are unique to anammox bacteria and thus serve as excellent biomarkers for the detection of anammox in present and past environments (Sinninghe Damsté et al., 2002b; Jaeschke et al., 2007, 2009a,b; Rattray et al., 2008). Anammox bacteria have been detected in a wide variety of environments including marine and lacustrine environments, marshes, sea ice, and in permafrost and agricultural soils (Humbert et al., 2010 and references therein). In aquatic environments, they are active at redox transition zones such as oxygen-minimum zones (Kuypers et al., 2003; Jaeschke et al., 2009b).

Interestingly, it has been observed in culture studies that anammox bacteria alter their membrane lipid composition in response to temperature with increased amounts of shorter-chain ladderane fatty acids relative to the amount of longer-chain fatty acids occurring at lower temperatures (Rattray et al., 2010). An index, called NL_5, has been proposed to quantify this relative temperature change (Rattray et al., 2010). Rattray et al. (2010) note that most of the changes in ladderane lipid chain length occur between 12 °C and 20 °C with no significant changes observed at lower or higher temperatures. They suggest that the NL_5 index can be useful for distinguishing between fossil ladderane lipids that originate in the relatively warmer upper water column and those that are produced *in-situ* in relatively cold surface sediments, which is necessary for examining past anammox. Jaeschke et al. (2009b) utilized the NL_5 index to examine past anammox in a sediment core from the northern Arabian Sea spanning the last 140 kyr. They found that low concentrations of ladderane lipids, indicating low-anammox activity, coincided with periods when the oxygen-minimum zone was severely diminished while high concentrations of ladderane lipids coincided with periods characterized by an intense oxygen-minimum zone.

At present, little is known about the importance of anammox in past marine nitrogen cycles but essentially nothing is known about its importance in both present and past lacustrine nitrogen cycles. However, the anammox process has been reported from meromictic Lakes Tanganyika (East Africa) and Rassnitzer (Germany) (Schubert et al., 2006; Hamersley et al., 2009) and likely occurs in many lakes. To date, ladderane lipids have not yet been used to examine past anammox in lacustrine environments but thermally immature sediments from lakes with anoxic bottom waters are potentially excellent targets since the preservation potential of ladderane lipids is likely high in these environments. It should be noted that although not much is currently known about the diagenesis of ladderane lipids, a thermal degradation study revealed that structural alterations occur at relatively low temperatures of 120 °C and therefore, ladderane lipids are unlikely to occur in ancient sediments (Jaeschke et al., 2008). However, ladderane lipids will likely prove useful for examining past anammox at least on Quaternary time scales.

10.3. Compound-specific $\delta^{15}N$ of pigments as a tool to investigate past nitrogen cycling

The nitrogen isotopic composition ($\delta^{15}N$) of bulk sediments is a widely used paleolimnological proxy for examining sources of organic matter, reconstructing past productivity rates and for studying past nitrogen cycling (Meyers and Teranes, 2001; Meyers, 2003). However, interpretation of bulk $\delta^{15}N$ records can be complicated by a variety of factors including remineralization, input from terrestrial sources and shifts in phytoplankton or heterotroph assemblages. Thus, it is advantageous to examine the $\delta^{15}N$ of molecular fossils having a definitive biological origin. In aquatic environments pigments such as chlorophylls and bacteriochlorophylls are markers of photoautotrophic activity and these compounds also contain nitrogen, making them attractive targets for $\delta^{15}N$ analysis. The first $\delta^{15}N$ measurements of sedimentary geoporphyrins, the tetrapyrrole skeletons of chlorophyll molecules, were conducted by purifying compounds (e.g. by using preparative HPLC and size exclusion chromatography) and analyzing them with elemental analyzer isotope ratio mass spectrometry (EA-IRMS) (Sachs et al., 1999). Using these methods, Sachs and Repeta (1999) found evidence for the widespread occurrence of nitrogen fixation in the Eastern Mediterranean Sea during Late Pleistocene sapropel events. However, this approach is time consuming and requires large sample sizes, limiting its application to paleoenvironmental studies. While compound-specific isotope analysis requires minimal amounts of material, compounds such as tetrapyrroles are not very volatile and are difficult to analyze by GC-IRMS.

Recently, new techniques have been developed that allow for more rapid compound-specific $\delta^{15}N$ measurements of smaller samples. Chikaraishi et al. (2008) developed a method for analysing the $\delta^{15}N$ of tetrapyrroles by applying a chemical treatment to degrade them into monopyrrole unites (maleimides) and then subsequently measuring their isotopic composition by GC combustion IRMS (GC/C/IRMS). They found that the isotopic composition of the maleimides reflected the isotopic composition of the individual tetrapyrroles and also that no substantial differences existed in the isotopic composition of maleimides derived from a single tetrapyrrole. Polissar et al. (2009) developed a method termed nano-EA-IRMS, which can measure the isotopic composition of nanomolar quantities of C and N (for example, from individual compounds isolated by HPLC techniques). Higgins et al. (2009) developed a method for rapid analysis of sedimentary porphyrins that involves first separating and purifying them from sediment samples using HPLC, oxidizing them to nitrate in a two-step process, followed by isotopic analysis of the nitrate. Their approach measures the $\delta^{15}N$ of a mixture of porphyrins, rather than the $\delta^{15}N$ of individually purified compounds, which reduces sample preparation time and also the amount of sediment needed. These methods appear promising for examining compound-specific nitrogen signatures, and thus, past nitrogen cycling.

10.4. $\delta^{13}C$ of GDGTs as tracer of methanotrophic archaea

The stable carbon isotopic composition ($\delta^{13}C$) of biphytanes derived from GDGTs can be used to indicate the presence of methanotrophic archaea. These organisms utilize ^{13}C-depleted methane and thus ^{13}C-depleted isoprenoid GDGTs have been used as indicators for methanotrophic archaea in a variety of environments (Pancost et al., 2001; Schouten et al., 2001b, 2003; Wakeham et al., 2003; Blumenberg et al., 2004; van Dongen et al., 2007). For example, Pancost et al. (2000) examined biphytanes with 0–2 cyclopentane moieties in Holocene peat deposits and found relatively ^{13}C-depleted values for biphytanes with 1 and 2 cyclopentane moieties (−34 to −34‰) whereas those with 0 cyclopentane moieties were relatively ^{13}C-enriched (−27 to −30‰). They suggest that the biphytanes with 1 and 2 cyclopentane moieties were derived from acetotrophic methanogens while those with 0 cyclopentane moieties were derived from CO_2-reducing autotrophic methanogens.

Schouten et al. (2001a) examined the $\delta^{13}C$ of a range of organic compounds present in Ace Lake, Antarctica including sedimentary biomarkers of methanogenic archaea and methanotrophic bacteria. These included the diether lipid archaeol, which occurs ubiquitously in archaea, *sn2*-hydroxyarchaeol, which occurs in methanogenic archaea within the orders Methanococcoides and Methanosarcinales, and saturated and unsaturated 2,6,10,15,19-pentamethyleicosane (PME), which are also attributed to methanogenic archaea (Schouten et al., 2001a). Depleted ^{13}C values (−45‰ to −133‰) typically characterize lipids of methanotrophic

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

bacteria that oxidize methane aerobically. Schouten et al. (2001a) found relatively enriched isotopic compositions of archaeol (−17‰) and polyunsaturated PME (−23‰ to −28‰), and concluded that little anaerobic methane oxidation takes place in Ace Lake but rather the archaea are involved only in the methane generation process. They also note that the isotopic composition of 4α-methyl-5α-cholest-8(14)-en-3β-ol and its diagenetic derivatives displayed depleted ^{13}C values (−57‰), which is diagnostic for bacterial methanotrophy (aerobic consumption of methane). Coolen et al. (2004a) later provided additional support for bacterial methanotrophy in Ace Lake with a combined study of lipid biomarkers and 16S rDNA genes (see Section 7.4). These studies demonstrate that isotopic analysis of lipid biomarkers such as archaeol or GDGTs can provide detailed insights into past methane cycling but to date, these techniques have not been widely applied to lacustrine studies.

10.5. Advances in compound-specific radiocarbon analysis

A reliable sediment chronology is a fundamental requirement for paleoenvironmental investigations but creating an accurate age model can be difficult. Radiocarbon dating is a widely applied dating technique utilized in Quaternary studies; however, radiocarbon ages based on bulk organic matter can be unreliable since it consists of a complex mixture of organic carbon derived from multiple sources varying in radiocarbon age (e.g. Eglinton et al., 1997; Smittenberg et al., 2004). While AMS dating of macrofossils is a preferable approach for reconstructing sediment chronology, such macrofossils are not always present. An alternative approach is compound-specific radiocarbon analysis (CSRA), which utilizes accelerator mass spectrometry (AMS) techniques in combination with automated preparative capillary gas chromatography (Eglinton et al., 1996). CSRA is presently emerging as a powerful method for creating and improving marine and lacustrine chronologies.

Uchikawa et al. (2008) used CSRA to date long-chain *n*-alkanes in Holocene sediments from Ordy Pond (Hawaii) and compared these ages to those derived from bulk sediment and plant macrofossils. They found that ^{14}C ages of the *n*-alkanes and terrestrial plant macrofossils were in good agreement but note substantially older ^{14}C ages for the bulk sediment, which is mainly composed of algal material (Uchikawa et al., 2008 and references therein). They note that ^{14}C-depleted Pleistocene limestone likely contributes to the DIC pool in Ordy Pond and thus autochthonous material produced from the lake water should be avoided for ^{14}C dating.

More recently, Hou et al. (2010) developed a method for radiocarbon dating individual lignin phenols, which are produced by vascular plants and can be isolated using reversed phase HPLC. The authors argue that lignin phenols are a good choice for radiocarbon dating since they are abundant in lake sediments, they are generally transported to lake sediments by water and thus derive from within the lake catchment, and they are rapidly recycled in the soils making it is unlikely that ^{14}C-depleted lignin will reach lake sediments (Hou et al., 2010). Hou et al. (2010) constructed age models for several lakes based on ^{14}C dating of lignin phenols and found the ages of lignin phenols to be consistent with varve counts or ^{14}C ages of terrestrial plant fragments, supporting a short residence time of lignin phenols in the catchment. However, they note that in an arctic lake from southwest Greenland, which is surrounded by permafrost soils, the lignin phenol ^{14}C ages are significantly older than bulk sediment ages, which is likely due to remobilization or preserved lignin in soils (Hou et al., 2010). Thus, this method appears promising from developing more accurate chronologies although in some systems the long residence time of lignin phenols will hamper this approach. Although CSRA has not yet been widely applied to dating lacustrine sediments, it is likely that age differences exist between terrestrial and aquatic components of organic matter in many systems and thus this approach will be useful for creating reliable age models, which are especially important to high-resolution paleoclimate studies.

In addition to improving sediment chronologies, CSRA is a useful tool for examining the sources, fixation, and transport and fate of organic carbon in the geologic environment. CSRA can also be used to elucidate microbial metabolic pathways or to distinguish anthropogenic and natural inputs of organic carbon. In paleoceanography, CSRA has been widely applied to examine lateral transport. While age offsets between foraminifera and organic compounds such as alkenones have been noted in the same marine sediment samples and related to differences in lateral transport (e.g. Ohkouchi et al., 2002), age offsets also have been noted between different types of organic compounds. For example, several marine studies have examined the ^{14}C ages of crenarchaeol and alkenones and have concluded that isoprenoid GDGT distributions are less affected by lateral transport than those of alkenones (Mollenhauer et al., 2007, 2008; Shah et al., 2008). Although lateral transport likely does not induce substantial age differences between different aquatic components of organic matter in smaller lakes, it could conceivably be an issue in larger lakes. CSRA thus provide an important tool for assessing time lags between soil or vegetation derived organic matter and aquatic organic matter in lake sediments.

11. Outlook for the application of organic molecular proxies in Quaternary lacustrine studies

Molecular organic proxies are becoming increasingly popular for both marine and lacustrine investigations as they provide detailed (paleo)environmental information. A number of recent developments are especially exciting for Quaternary lacustrine studies, such as organic geochemical proxies for reconstructing continental temperature (lacustrine alkenones, TEX_{86}, MBT/CBT), hydrology (δD) and CSRA as a tool for improving sediment chronologies. Many of these molecular organic proxies are relatively new and there are currently limitations and outstanding questions associated with each proxy that remain to be answered. Nevertheless, there have been major developments and advances over recent years and currently much research is focused on further development and testing of these proxies. Clearly, the application of organic geochemical proxies to Quaternary lacustrine studies is an exciting and developing area of research, and as more studies are done to further refine these methods for use in lacustrine settings, they undoubtedly will be applied to an increasing number of studies.

In this review we discussed biomarkers that can be traced to a specific organism, group of organisms or process. However, there is still a need to identify both more organism and process-specific biomarkers in lacustrine environments. This can be achieved by large-scale surveys of lacustrine environments for common biomarkers, or trends in biomarker ratios, which may be related to environmental parameters (e.g. core top studies of TEX_{86}) assuming that the physical and chemical properties of the system being studied are also well-constrained. It is even possible that there may be biomarkers or organic geochemical proxies that can be specifically developed for use in lacustrine systems, which may or may not be applicable to marine systems. There is certainly a need to identify the source organisms of lacustrine biomarker lipids that have been widely identified in environmental samples but where the producer remains unknown (e.g. the branched GDGTs). This may be achieved by combining lipid studies with genetic and proteomic studies. Conversely, in some cases the organism

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

producing a particular lipid has been identified yet there is a need to learn more about its ecology in order to improve paleoenvironmental interpretations (e.g. relatively little is known about the ecology of Thaumarchaeota, which produce isoprenoid GDGTs). Furthermore, there is currently a lack of detailed screening of biomarker lipids in important freshwater microbes. Such studies would shed light on which lipids could be used as biomarkers of specific organisms or processes, and may also identify new biomarkers. Finally, confidence in paleoenvironmental reconstructions based on organic geochemical proxies can be gained through multi-proxy and interdisciplinary investigations (e.g. by combining organic geochemical studies with inorganic proxies or molecular biological techniques), which are essential for both accurate paleoenvironmental reconstructions and for providing information on additional factors and processes that may influence proxy records.

A challenge facing paleolimnologists is that the information gained from certain proxies will differ from location to location and some proxies may not be applicable to all locations. This contrasts with paleoceanographic applications of organic proxies where, to a certain extent, conditions are more homogenous and proxies are more widely applicable. For example, lacustrine alkenone distributions may be related to temperature at some locations and to salinity at others. In some lakes the BIT Index may reflect soil organic matter input whereas in others it may mainly reflect *in-situ* production. At some sites TEX_{86} may provide a robust tool for reconstructing past lake surface temperatures but at other sites the proxy may not work due to e.g. high soil organic matter input. Thus, in contrast to paleoceanographic proxies, paleolimnological proxies may not be generally widely applicable. Nevertheless, organic geochemical proxies can provide powerful tools for examining and reconstructing lacustrine environments but it is essential to be aware of limitations and to understand when and where they should, or should not, be used.

Acknowledgements

We are grateful to Guoqiang Chu, Marco Coolen, William D'Andrea, Piero Guilizzoni, Yongsong Huang, Zhonghui Liu, Helen Talbot, Martijn Woltering and Klaus Zink for providing data that was used in the figures and tables. Nicole Bale is thanked for providing helpful information regarding sedimentary pigments. We thank Phil Meyers and an anonymous reviewer for insightful comments that improved this manuscript. QSR editors José Carrión and Timothy Horscroft are thanked for their support throughout this project. The Netherlands Organization for Scientific Research (NWO) is thanked for financial support through a VICI grant to S. Schouten.

References

Aichner, B., Wilkes, H., Herzschuh, U., Mischke, S., Zhang, C.J., 2010a. Biomarker and compound-specific $\delta^{13}C$ evidence for changing environmental conditions and carbon limitation at Lake Koucha, eastern Tibetan Plateau. Journal of Paleolimnology 43, 873–899.

Aichner, B., Herzschuh, U., Wilkes, H., Vieth, A., Böhner, J., 2010b. δD values of *n*-alkanes in Tibetan lake sediments and aquatic macrophytes – a surface sediment study and application to a 16 ka record from Lake Koucha. Organic Geochemistry 41, 779–790.

Airs, R.L., Atkinson, J.E., Keely, B.J., 2001. Development and application of a high resolution liquid chromatographic method for the analysis of complex pigment distributions. Journal of Chromatography A 917, 167–177.

Allard, W.G., Belt, S.T., Masse, G., Naumann, R., Robert, J.M., Rowland, S., 2001. Tetra-unsaturated sesterterpenoids (Haslenes) from Haslea ostrearia and related species. Phytochemistry 56, 795–800.

Alley, R.B., 2004. GISP2 Ice Core Temperature and Accumulation Data. In: IGBP PAGES/World Data Center for Paleoclimatology Data Contribution Series #2004-013. NOAA/NGDC Paleoclimatology Program, Boulder CO, USA.

Amrani, A., Sessions, A.L., Adkins, J.F., 2009. Compound-specific $\delta^{34}S$ analysis of volatile organics by coupled GC/Multicollector-ICPMS. Analytical Chemistry 81, 9027–9034.

Ariztegui, D., Chondrogianni, C., Lami, A., Guilizzoni, P., Lafargue, E., 2001. Lacustrine organic matter and the Holocene paleoenvironmental record of Lake Albano (central Italy). Journal of Paleolimnology 26, 283–292.

Baas, M., Pancost, R., van Geel, B., Sinninghe Damsté, J.S., 2000. A comparative study of lipids in Sphagnum species. Organic Geochemistry 31, 535–541.

Battarbee, R.W., Juggins, S., Gasse, F., Anderson, N.J., Bennion, H., Cameron, N.G., 2000. European Diatom Database (EDDI): an information system for palaeoenvironmental reconstruction. In: European Climate Science Conference, Vienna City Hall, Vienna, 19–23 Oct 1998, pp. 1–10.

Bauersachs, T., Compaore, J., Hopmans, E.C., Stal, L.J., Schouten, S., Sinninghe Damsté, J.S., 2009a. Distribution of heterocyst glycolipids in cyanobacteria. Phytochemistry 70, 2034–2039.

Bauersachs, T., Hopmans, E.C., Compaore, J., Stal, L.J., Schouten, S., Sinninghe Damsté, J.S., 2009b. Rapid analysis of long-chain glycolipids in heterocystous cyanobacteria using high-performance liquid chromatography coupled to electrospray ionization tandem mass spectrometry. Rapid Communications in Mass Spectrometry 23, 1387–1394.

Bauersachs, T., Speelman, E.N., Hopmans, E.C., Reichart, G.-J., Schouten, S., Sinninghe Damsté, J.S., 2010. Fossilized glycolipids reveal past oceanic N_2 fixation by heterocystous cyanobacteria. Proceedings of the National Academy of Sciences of the United States of America 107, 19190–19194.

Beardall, J., Griffiths, H., Raven, J.A., 1982. Carbon isotope discrimination and the CO_2 accumulating mechanism in *Chlorella emersonii*. Journal of Experimental Botany 33, 729–737.

Bechtel, A., Schubert, C.J., 2009. A biogeochemical study of sediments from the eutrophic Lake Lugano and the oligotrophic Lake Brienz, Switzerland. Organic Geochemistry 40, 1100–1114.

Bechtel, A., Smittenberg, R.H., Bernasconi, S.M., Schubert, C.J., 2010. Distribution of branched and isoprenoid tetraether lipids in an oligotrophic and a eutrophic Swiss lake: insights into sources and GDGT-based proxies. Organic Geochemistry 41, 822–832.

Belicka, L.L., Harvey, H.R., 2009. The sequestration of terrestrial organic carbon in Arctic Ocean sediments: a comparison of methods and implications for regional carbon budgets. Geochimica et Cosmochimica Acta 73, 6231–6248.

Belt, S.T., Cooke, D.A., Robert, J.M., Rowland, S., 1996. Structural characterisation of widespread polyunsaturated isoprenoid biomarkers: a C_{25} triene, tetraene and pentaene from the diatom *Haslea ostrearia* Simonsen. Tetrahedron Letters 37, 4755–4758.

Belt, S.T., Allard, W.G., Massθ, G., Robert, J.M., Rowland, S.J., 2000. Highly branched isoprenoids (HBIs): identification of the most common and abundant sedimentary isomers. Geochimica et Cosmochimica Acta 64, 3839–3851.

Belt, S.T., Masse, G., Allard, W.G., Robert, J.M., Rowland, S.J., 2001a. C_{25} highly branched isoprenoid alkenes in planktonic diatoms of the *Pleurosigma* genus. Organic Geochemistry 32, 1271–1275.

Belt, S.T., Massé, G., Allard, W.G., Robert, J.M., Rowland, S.J., 2001b. Identification of a C_{25} highly branched isoprenoid triene in the freshwater diatom *Navicula sclesvicensis*. Organic Geochemistry 32, 1169–1172.

Bendle, J., Rosell-Melé, A., Ziveri, P., 2005. Variability of unusual distributions of alkenones in the surface waters of the Nordic seas. Paleoceanography 20, 1–15.

Bendle, J.A., Weijers, J.W.H., Maslin, M.A., Sinninghe Damsté, J.S., Schouten, S., Hopmans, E.C., Boot, C.S., Pancost, R.D., 2010. Major changes in glacial and Holocene terrestrial temperatures and sources of organic carbon recorded in the Amazon fan by tetraether lipids. Geochemistry Geophysics Geosystems 11, Q12007.

Berke, M.A., Johnson, T.C., Werne, J.P., Schouten, S., Sinninghe Damsté, J.S., 2009. Holocene TEX86 temperature reconstructions from Lake Turkana, East Africa. Eos, Transactions, American Geophysical Union 90 (52), Fall Meet. Suppl., Abstract PP21D-02.

Berke, M.A., Johnson, T.C., Werne, J.P., Schouten, S., Sinninghe Damsté, J.S., 2010. Temperature and hydrologic variability of Lake Victoria, East Africa since the Late Pleistocene. Abstract GC51C-0764 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13–17 Dec.

Bi, X., Sheng, G., Liu, X., Li, C., Fu, J., 2005. Molecular and carbon and hydrogen isotopic composition of n-alkanes in plant leaf waxes. Organic Geochemistry 36, 1405–1417.

Bissett, A., Gibson, J.A.E., Jarman, S.N., Swadling, K.M., Cromer, L., 2005. Isolation, amplification, and identification of ancient copepod DNA from lake sediments. Limnology and Oceanography-Methods 3, 533–542.

Blaga, C.I., 2010. Glycerol dialkyl glycerol tetraether membrane lipids in lacustrine environments and their application as proxies for paleoclimate reconstructions [Ph.D. thesis]. Universiteit Utrecht, Geologica Ultraiectina 322, 96 pp.

Blaga, C.I., Reichart, G.J., Heiri, O., Sinninghe Damsté, J.S., 2009. Tetraether membrane lipid distributions in water-column particulate matter and sediments: a study of 47 European lakes along a north–south transect. Journal of Paleolimnology 41, 523–540.

Blaga, C.I., Reichart, G.J., Schouten, S., Lotter, A.F., Werne, J.P., Kosten, S., Mazzeo, N., Lacerot, G., Sinninghe Damsté, J.S., 2010. Branched glycerol dialkyl glycerol tetraethers in lake sediments: can they be used as temperature and pH proxies? Organic Geochemistry 41, 1225–1234.

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

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Blumenberg, M., Kruger, M., Nauhaus, K., Talbot, H.M., Oppermann, B.I., Seifert, R., Pape, T., Michaelis, W., 2006. Biosynthesis of hopanoids by sulfate-reducing bacteria (genus *Desulfovibrio*). Environmental Microbiology 8, 1220–1227.

Blumenberg, M., Mollenhauer, G., Zabel, M., Reimer, A., Thiel, V., 2010. Decoupling of bio- and geohopanoids in sediments of the Benguela Upwelling System (BUS). Organic Geochemistry 41, 1119–1129.

Boere, A.C., Abbas, B., Rijpstra, W.I.C., Versteegh, G.J.M., Volkman, J.K., Sinninghe Damsté, J.S., Coolen, M.J.L., 2009. Late-Holocene succession of dinoflagellates in an Antarctic fjord using a multi-proxy approach: paleoenvironmental genomics, lipid biomarkers and palynomorphs. Geobiology 7, 1–17.

Boom, A., Marchant, R., Hooghiemstra, H., Sinninghe Damsté, J.S., 2002. CO_2 and temperature-controlled altitudinal shifts of C_4 and C_3 dominated grasslands allow reconstruction of palaeoatmospheric pCO_2. Palaeogeography, Palaeoclimatology, Palaeoecology 177, 151–168.

Boon, J.J., Rijpstra, W.I.C., de Lange, F., de Leeuw, J.W., Yoshioka, M., Shimizu, Y., 1979. Black sea sterol- a molecular fossil for dinoflagellate blooms. Nature 277, 125–127.

Bowen, G.J., Revenaugh, J., 2003. Interpolating the isotopic composition of modern meteoric precipitation. Water Resources Research 39.

Bradley, A.S., Pearson, A., Sáenz, J.P., Marx, C.J., 2010. Adenosylhopane: the first intermediate in hopanoid side chain biosynthesis. Organic Geochemistry 41, 1075–1081.

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., Sarnthein, M., 1986. Molecular stratigraphy – a new tool for climatic assessment. Nature 320, 129–133.

Bray, E.E., Evans, E.D., 1961. Distribution of normal-paraffins as a clue to recognition of source beds. Geochimica et Cosmochimica Acta 22, 2–15.

Brigham-Grette, J., Melles, M., Minyuk, P., Party, S., 2007. Overview and significance of a 250 ka paleoclimate record from El'gygytgyn Crater Lake, NE Russia. Journal of Paleolimnology 37, 1–16.

Brincat, D., Yamada, K., Ishiwatari, R., Uemura, H., Naraoka, H., 2000. Molecular-isotopic stratigraphy of long-chain n-alkanes in Lake Baikal Holocene and glacial age sediments. Organic Geochemistry 31, 287–294.

Brochier-Armanet, C., Boussau, B., Gribaldo, S., Forterre, P., 2008. Mesophilic crenarchaeota: proposal for a third archaeal phylum, the Thaumarchaeota. Nature Reviews Microbiology 6, 245–252.

Brown, E.T., Johnson, T.C., 2005. Coherence between tropical East African and South American records of the Little Ice Age. Geochemistry Geophysics Geosystems 6.

Carillo-Hernandez, T., Schaeffer, P., Adam, P., Albrecht, P., Derenne, S., Largeau, C., 2003. Remarkably well-preserved archaeal and bacterial membrane lipids in 140 million years old sediment from the Russian platform (Kasphpir oil shales, upper Jurassic. 21st International Meeting on Organic Geochemistry (IMOG 2003) Krakow Part 1, pp. 77–78.

Castañeda, I.S., Schefuss, E., Patzold, J., Sinninghe Damsté, J.S., Weldeab, S., Schouten, S., 2010. Millennial-scale sea surface temperature changes in the eastern Mediterranean (Nile River Delta region) over the last 27,000 years. Paleoceanography 25.

Castañeda, I.S., Werne, J.P., Johnson, T.C., 2007. Wet and arid phases in the southeast African tropics since the Last Glacial Maximum. Geology 35, 823–826.

Castañeda, I.S., Mulitza, S., Schefuss, E., dos Santos, R.A.L., Sinninghe Damsté, J.S., Schouten, S., 2009a. Wet phases in the Sahara/Sahel region and human migration patterns in North Africa. Proceedings of the National Academy of Sciences of the United States of America 106, 20159–20163.

Castañeda, I.S., Werne, J.P., Johnson, T.C., 2009b. Influence of climate change on algal community structure and primary productivity of Lake Malawi (East Africa) from the Last Glacial Maximum to present. Limnology and Oceanography 54, 2431–2447.

Castañeda, I.S., Werne, J.P., Johnson, T.C., Filley, T.R., 2009c. Late Quaternary vegetation history of southeast Africa: the molecular isotopic record from Lake Malawi. Palaeogeography, Palaeoclimatology, Palaeoecology 275, 100–112.

Castañeda, I.S., Werne, J.P., Johnson, T.C., Powers, L.A., 2011. Organic geochemical records from Lake Malawi (East Africa) of the last 700 years, part II: biomarker evidence for recent changes in primary productivity. Palaeogeography, Palaeoclimatology, Palaeoecology 303, 140–154.

Cerling, T.E., Wang, Y., Quade, J., 1993. Expansion of C_4 ecosystems as an indicator of global ecological change in the Late Miocene. Nature 361, 344–345.

Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD-delta $\delta^{13}C$ analyses of *n*-alkanes extracted from terrestrial and aquatic plants. Phytochemistry 63, 361–371.

Chikaraishi, Y., Kashiyama, Y., Ogawa, N.O., Kitazato, H., Satoh, M., Nomoto, S., Ohkouchi, N., 2008. A compound-specific isotope method for measuring the stable nitrogen isotopic composition of tetrapyrroles. Organic Geochemistry 39, 510–520.

Chu, G.Q., Sun, Q., Li, S.Q., Zheng, M.P., Jia, X.X., Lu, C.F., Liu, J.Q., Liu, T.S., 2005. Long-chain alkenone distributions and temperature dependence in lacustrine surface sediments from China. Geochimica et Cosmochimica Acta 69, 4985–5003.

Collatz, G.J., Berry, J.A., Clark, J.S., 1998. Effects of climate and atmospheric CO_2 partial pressure on the global distribution of C_4 grasses: present, past, and future. Oecologia 114, 441–454.

Collins, J.A., Schefuß, E., Heslop, D., Mulitza, S., Prange, M., Zabel, M., Tjallingii, R., Dokken, T.M., Huang, E., Mackensen, A., Schulz, M., Tian, J., Zarriess, M., Wefer, G., 2011. Interhemispheric symmetry of the tropical African rainbelt over the past 23,000 years. Nature Geosci 4, 42–45.

Conte, M.H., Volkman, J.K., Eglinton, G., 1994. Lipid biomarkers of the Haptophyta. In: The Haptophyte Algae. Claredon Press, Oxford, pp. 351–377.

Cooke, M.P., Talbot, H.M., Farrimond, P., 2008a. Bacterial populations recorded in bacteriohopanepolyol distributions in soils from Northern England. Organic Geochemistry 39, 1347–1358.

Cooke, M.P., Talbot, H.M., Wagner, T., 2008b. Tracking soil organic carbon transport to continental margin sediments using soil-specific hopanoid biomarkers: a case study from the Congo fan (ODP site 1075). Organic Geochemistry 39, 965–971.

Cooke, M.P., van Dongen, B.E., Talbot, H.M., Semiletov, I., Shakhova, N., Guo, L., Gustafsson, Ö, 2009. Bacteriohopanepolyol biomarker composition of organic matter exported to the Arctic Ocean by seven of the major Arctic rivers. Organic Geochemistry 40, 1151–1159.

Coolen, M.J.L., Gibson, J.A.E., 2009. Ancient DNA in lake sediment records. PAGES News 17, 104–106.

Coolen, M.J.L., Overmann, J., 1998. Analysis of subfossil molecular remains of purple sulfur bacteria in a lake sediment. Applied and Environmental Microbiology 64, 4513–4521.

Coolen, M.J.L., Hopmans, E.C., Rijpstra, W.I.C., Muyzer, G., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2004a. Evolution of the methane cycle in Ace Lake (Antarctica) during the Holocene: response of methanogens and methanotrophs to environmental change. Organic Geochemistry 35, 1151–1167.

Coolen, M.J.L., Muyzer, G., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2004b. Combined DNA and lipid analyses of sediments reveal changes in Holocene haptophyte and diatom populations in an Antarctic lake. Earth and Planetary Science Letters 223, 225–239.

Coolen, M.J.L., Talbot, H.M., Abbas, B.A., Ward, C., Schouten, S., Volkman, J.K., Sinninghe Damsté, J.S., 2008. Sources for sedimentary bacteriohopanepolyols as revealed by 16S rDNA stratigraphy. Environmental Microbiology 10, 1783–1803.

Craig, H., Gordon, L.I., 1965. Deuterium and oxygen 18 variations in the ocean and marine atmosphere. In: Proceedings of a Conference on Stable Isotopes in Oceanographic Studies and Paleotemperatures. V. Lischi & Figli, Pisa, Spoleto, Italy, pp. 9–130.

Cranwell, P.A., 1973. Chain-length distribution of *n*-alkanes from lake sediments in relation to post-glacial environmetal change. Freshwater Biology 3, 259–265.

Cranwell, P.A., 1985. Long-chain unsaturated ketones in recent lacustrine sediments. Geochimica et Cosmochimica Acta 49, 1545–1551.

Cranwell, P.A., Eglinton, G., Robinson, N., 1987. Lipids of aquatic organisms as potential contributors to lacustrine sediments II. Organic Geochemistry 11, 513–527.

Cullen, J.J., 1982. The deep chlorophyll maximum – comparing vertical profiles of chlorophyll-A. Canadian Journal of Fisheries and Aquatic Sciences 39, 791–803.

De Wever, A., 2006. Spatio-temporal Dynamics in the Microbial Food Web in Lake Tanganyika. University of Gent.

DeLong, E.F., 1992. Archaea in coastal marine environments. Proceedings of the National Academy of Sciences of the United States of America 89, 5685–5689.

Deines, P., 1980. The isotopic composition of reduced organic carbon. In: Fritz, P., Fontes, J.Ch (Eds.), Handbook of Environmental Isotope Geochemistry. Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, pp. 329–406.

Diefendorf, A.F., Mueller, K.E., Wing, S.L., Freeman, K.H., 2010. Global patterns in leaf ^{13}C discrimination and implications for studies of past and future climate. Proceedings of the National Academy of Sciences of the United States of America 107, 5738–5743.

Dykoski, C.A., Edwards, R.L., Cheng, H., Yuan, D.X., Cai, Y.J., Zhang, M.L., Lin, Y.S., Qing, J.M., An, Z.S., Revenaugh, J., 2005. A high-resolution, absolute-dated Holocene and deglacial Asian monsoon record from Dongge Cave, China. Earth and Planetary Science Letters 233, 71–86.

D'Andrea, W.J., Huang, Y., 2005. Long chain alkenones in Greenland lake sediments: low $\delta^{13}C$ values and exceptional abundance. Organic Geochemistry 36, 1234–1241.

D'Andrea, W.J., Huang, Y., Fritz, S.C., Anderson, J., 2011. Abrupt Holocene climate change as an important factor for human migration in West Greenland. Proceedings of the National Academy of Sciences of the United States of America.

D'Andrea, W.J., Lage, M., Martiny, J.B.H., Laatsch, A.D., Amaral-Zettler, L.A., Sogin, M.L., Huang, Y.S., 2006. Alkenone producers inferred from well-preserved 18S rDNA in Greenland lake sediments. Journal of Geophysical Research-Biogeosciences 111.

Eckardt, C.B., Keely, B.J., Maxwell, J.R., 1991. Identification of chlorophyll transformation products in a lake sediment by combined liquid chromatography-mass spectrometry. Journal of Chromatography A 557, 271–288.

Edwards, T.W.D., Fritz, P., 1988. Stable-isotope paleoclimate records for Southern Ontario, Canada – comparison of results from Marl and Wood. Canadian Journal of Earth Sciences 25, 1397–1406.

Edwards, T.W.D., Mcandrews, J.H., 1989. Paleohydrology of a Canadian Shield Lake inferred from ^{18}O in sediment cellulose. Canadian Journal of Earth Sciences 26, 1850–1859.

Eglinton, T.I., Eglinton, G., 2008. Molecular proxies for paleoclimatology. Earth and Planetary Science Letters 275, 1–16.

Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322–1335.

Eglinton, T.I., Aluwihare, L.I., Bauer, J.E., Druffel, E.R.M., McNichol, A.P., 1996. Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating. Analytical Chemistry 68, 904–912.

Eglinton, T.I., Benitez-Nelson, B.C., Pearson, A., McNichol, A.P., Bauer, J.E., Druffel, E.R.M., 1997. Variability in radiocarbon ages of individual organic compounds from marine sediments. Science 277, 796–799.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Elias, V.O., Simoneit, B.R.T., Cordeiro, R.C., Turcq, B., 2001. Evaluating levoglucosan as an indicator of biomass burning in Carajás, Amazônia: a comparison to the charcoal record. Geochimica et Cosmochimica Acta 65, 267–272.

Enders, S.K., Pagani, M., Pantoja, S., Baron, J.S., Wolfe, A.P., Pedentchouk, N., Nunez, L., 2008. Compound-specific stable isotopes of organic compounds from lake sediments track recent environmental changes in an alpine ecosystem, Rocky Mountain National Park, Colorado. Limnology and Oceanography 53, 1468–1478.

Englebrecht, A.C., Sachs, J.P., 2005. Determination of sediment provenance at drift sites using hydrogen isotopes and unsaturation ratios in alkenones. Geochimica et Cosmochimica Acta 69, 4253–4265.

Farrimond, P., Head, I.M., Innes, H.E., 2000. Environmental influence on the biohopanoid composition of recent sediments. Geochimica et Cosmochimica Acta 64, 2985–2992.

Fawcett, P.J., Werne, J.P., Anderson, R.S., Heikoop, J.M., Brown, E.T., Berke, M.A., Smith, S.J., Goff, F., Donohoo-Hurley, L., Cisneros-Dozal, L.M., Schouten, S., Damste, J.S.S., Huang, Y.S., Toney, J., Fessenden, J., WoldeGabriel, G., Atudorei, V., Geissman, J.W., Allen, C.D., 2011. Extended megadroughts in the southwestern United States during Pleistocene interglacials. Nature 470, 518–521.

Feakins, S.J., Sessions, A.L., 2010a. Controls on the D/H ratios of plant leaf waxes in an arid ecosystem. Geochimica et Cosmochimica Acta 74, 2128–2141.

Feakins, S.J., Sessions, A.L., 2010b. Crassulacean acid metabolism influences D/H ratio of leaf wax in succulent plants. Organic Geochemistry 41, 1269–1276.

Feakins, S.J., Eglinton, T.I., deMenocal, P.B., 2007. A comparison of biomarker records of northeast African vegetation from lacustrine and marine sediments (ca. 3.40 Ma). Organic Geochemistry 38, 1607–1624.

Ficken, K.J., Street-Perrott, F.A., Perrott, R.A., Swain, D.L., Olago, D.O., Eglinton, G., 1998. Glacial/interglacial variations in carbon cycling revealed by molecular and isotope stratigraphy of Lake Nkunga, Mt. Kenya, East Africa. Organic Geochemistry 29, 1701–1719.

Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. Organic Geochemistry 31, 745–749.

Filley, T.R., Freeman, K.H., Bianchi, T.S., Baskaran, M., Colarusso, L.A., Hatcher, P.G., 2001. An isotopic biogeochemical assessment of shifts in organic matter input to Holocene sediments from Mud Lake, Florida. Organic Geochemistry 32, 1153–1167.

Fogel, M.L., Cifuentes, L.A., 1993. Isotope fractionation during primary production. In: Organic Geochemistry: Principles and Applications. Plenum Press, New York, pp. 73–98.

Fox, D.L., 1944. Biochemical fossils. Science 100, 111–113.

Francis, C.A., Roberts, K.J., Beman, J.M., Santoro, A.E., Oakley, B.B., 2005. Ubiquity and diversity of ammonia-oxidizing archaea in water columns and sediments of the ocean. Proceedings of the National Academy of Sciences of the United States of America 102, 14683–14688.

Fritz, S.C., Baker, P.A., Seltzer, G.O., Ballantyne, A., Tapia, P., Cheng, H., Edwards, R.L., 2007. Quaternary glaciation and hydrologic variation in the South American tropics as reconstructed from the Lake Titicaca drilling project. Quaternary Research 68, 410–420.

Fuhrman, J.A., McCallum, K., Davis, A.A., 1992. Novel major archaebacterial group from marine plankton. Nature 356, 148–149.

Furlong, E.T., Carpenter, R., 1988. Pigment preservation and remineralization in oxic coastal marine-sediments. Geochimica et Cosmochimica Acta 52, 87–99.

Gambacorta, A., Pagnotta, E., Romano, I., Sodano, G., Trincone, A., 1998. Heterocyst glycolipids from nitrogen-fixing cyanobacteria other than Nostocaceae. Phytochemistry 48, 801–805.

Gao, L., Hou, J., Toney, J., MacDonald, D., Huang, Y., 2011. Mathematical modeling of the aquatic macrophyte inputs of mid-chain n-alkyl lipids to lake sediments: implications for interpreting compound specific hydrogen isotopic records. Geochimica et Cosmochimica Acta 75, 3781–3791.

Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. Annual Review of Earth and Planetary Sciences 24, 225–262.

Gibson, J.A.E., Bayly, I.A.E., 2007. New insights into the origins of crustaceans of Antarctic lakes. Antarctic Science 19, 157–164.

Giger, W., Schaffner, C., Wakeham, S.G., 1980. Aliphatic and olefinic hydrocarbons in recent sediments of Greifensee, Switzerland. Geochimica et Cosmochimica Acta 44, 119–129.

Grossi, V., Beker, B., Geenevasen, J.A.J., Schouten, S., Raphel, D., Fontaine, M.F., Sinninghe Damsté, J.S., 2004. C_{25} highly branched isoprenoid alkenes from the marine benthic diatom *Pleurosigma strigosum*. Phytochemistry 65, 3049–3055.

Guilizzoni, P., Lami, A., Marchetto, A., 1992. Plant pigment ratios from lake sediments as indicators of recent acidification in alpine lakes. Limnology and Oceanography 37, 1565–1569.

Guilizzoni, P., Marchetto, A., Lami, A., Gerli, S., Musazzi, S., 2011. Use of sedimentary pigments to infer past phosphorous concentration in lakes. Journal of Paleolimnology, 45, 433–445.

Hamersley, M.R., Woebken, D., Boehrer, B., Schultze, M., Lavik, G., Kuypers, M.M.M., 2009. Water column anammox and denitrification in a temperate permanently stratified lake (Lake Rassnitzer, Germany). Systematic and Applied Microbiology 32, 571–582.

Handley, L., Talbot, H.M., Cooke, M.P., Anderson, K.E., Wagner, T., 2010. Bacteriohopanepolyols as tracers for continental and marine organic matter supply and phases of enhanced nitrogen cycling on the late Quaternary Congo deep sea fan. Organic Geochemistry 41, 910–914.

Hanisch, S., Ariztegui, D., Pnttmann, W., 2003. The biomarker record of Lake Albano, central Italy – implications for Holocene aquatic system response to environmental change. Organic Geochemistry 34, 1223–1235.

Hanson, R.S., Hanson, T.E., 1996. Methanotrophic bacteria. Microbiological Reviews 60, 439–471.

Harvey, H.R., McManus, G.B., 1991. Marine ciliates as a widespread source of tetrahymanol and hopan-3β-ol in sediments. Geochimica et Cosmochimica Acta 55, 3387–3390.

Hayes, J.M., Freeman, K.H., Popp, B.N., Hoham, C.H., 1990. Compound-specific isotopic analyses: a novel tool for reconstruction of ancient biogeochemical processes. Organic Geochemistry 16, 1115–1128.

He, X.G., Lin, L.Z., Lian, L.Z., Lindenmaier, M., 1998. Liquid chromatography-electrospray mass spectrometric analysis of curcuminoids and sesquiterpenoids in turmeric (*Curcuma longa*). Journal of Chromatography A 818, 127–132.

Hecky, R.E., Kling, H.J., Johnson, T.C., Bootsma, H.A., Wilkinson, P., 1999. Algal and sedimentary evidence for recent changes in the water quality and limnology of Lake Malawi/Nyasa. In: Water Quality Report: Lake Malawi/Nyasa Biodiversity Conversation Project. Southern African Development Community/Global Environmental Facility (SADC/GEF), pp. 191–214.

Hedges, J.I., Mann, D.C., 1979. Characterization of plant-tissues by their lignin oxidation-products. Geochimica et Cosmochimica Acta 43, 1803–1807.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial matter in the ocean? Organic Geochemistry 27, 195–212.

Helbling, E.W., Zaratti, F., Sala, L.O., Palenque, E.R., Menchi, C.F., Villafane, V.E., 2002. Mycosporine-like amino acids protect the copepod *Boeckella titicacae* (harding) against high levels of solar UVR. Journal of Plankton Research 24, 225–234.

Henderson, A.K., Nelson, D.M., Hu, F.S., Huang, Y.S., Shuman, B.N., Williams, J.W., 2010. Holocene precipitation seasonality captured by a dual hydrogen and oxygen isotope approach at Steel Lake, Minnesota. Earth and Planetary Science Letters 300, 205–214.

Herbert, T.D. 2003. Alkenones as paleotemperature indicators. In: Holland, H.D., Turekian, K.K. (Eds.). The Ocean and Marine Geochemistry. Treatise on Geochemistry, vol. 6. Elsevier Pergamon, Oxford, pp. 365–390.

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

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

Higgins, M.B., Robinson, R.S., Casciotti, K.L., McIlvin, M.R., Pearson, A., 2009. A method for determining the nitrogen isotopic composition of porphyrins. Analytical Chemistry 81, 184–192.

Hinga, K.R., Arthur, M.A., Pilson, M.E.Q., Whitaker, D., 1994. Carbon-isotope fractionation by marine-phytoplankton in culture – the effects of CO_2 concentration, pH, temperature, and species. Global Biogeochemical Cycles 8, 91–102.

Hobbs, W.O., Lalonde, S.V., Vinebrooke, R.D., Konhauser, K.O., Weidman, R.P., Graham, M.D., Wolfe, A.P., 2010. Algal-silica cycling and pigment diagenesis in recent alpine lake sediments: mechanisms and paleoecological implications. Journal of Paleolimnology 44, 613–628.

Hodell, D.A., Anselmetti, F.S., Ariztegui, D., Brenner, M., Curtis, J.H., Gilli, A., Grzesik, D.A., Guilderson, T.J., Mnller, A.D., Bush, M.B., Correa-Metrio, A., Escobar, J., Kutterolf, S., 2008. An 85-ka record of climate change in lowland Central America. Quaternary Science Reviews 27, 1152–1165.

Hodgson, D.A., Vyverman, W., Verleyen, E., Leavitt, P.R., Sabbe, K., Squier, A.H., Keely, B.J., 2005. Late Pleistocene record of elevated UV radiation in an Antarctic lake. Earth and Planetary Science Letters 236, 765–772.

Hollander, D.J., McKenzie, J.A., 1991. CO_2 control on carbon-isotope fractionation during aqueous photosynthesis – a paleo-pCO_2 barometer. Geology 19, 929–932.

Hollander, D.J., Smith, M.A., 2001. Microbially mediated carbon cycling as a control on the $\delta^{13}C$ of sedimentary carbon in eutrophic Lake Mendota (USA): new models for interpreting isotopic excursions in the sedimentary record. Geochimica et Cosmochimica Acta 65, 4321–4337.

Holtvoeth, J., Vogel, H., Wagner, B., Wolff, G.A., 2010. Lipid biomarkers in Holocene and glacial sediments from ancient Lake Ohrid (Macedonia, Albania). Biogeosciences 7, 3473–3489.

Hopmans, E.C., Schouten, S., Pancost, R.D., van der Meer, M.T.J., Sinninghe Damsté, J.S., 2000. Analysis of intact tetraether lipids in archaeal cell material and sediments by high performance liquid chromatography/atmospheric pressure chemical ionization mass spectrometry. Rapid Communications in Mass Spectrometry 14, 585–589.

Hopmans, E.C., Weijers, J.W.H., Schefuss, E., Herfort, L., Sinninghe Damsté, J.S., Schouten, S., 2004. A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids. Earth and Planetary Science Letters 224, 107–116.

Hopmans, E.C., Kienhuis, M.V.M., Rattray, J.E., Jaeschke, A., Schouten, S., Sinninghe Damsté, J.S., 2006. Improved analysis of ladderane lipids in biomass and sediments using high-performance liquid chromatography/atmospheric pressure chemical ionization tandem mass spectrometry. Rapid Communications in Mass Spectrometry 20, 2099–2103.

Hou, J., D'Andrea, W.J., MacDonald, D., Huang, Y., 2007a. Evidence for water use efficiency as an important factor in determining the delta D values of tree leaf waxes. Organic Geochemistry 38, 1251–1255.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Hou, J., Huang, Y.S., Oswald, W.W., Foster, D.R., Shuman, B., 2007b. Centennial-scale compound-specific hydrogen isotope record of Pleistocene–Holocene climate transition from southern New England. Geophysical Research Letters 34.

Hou, J.Z., D'Andrea, W.J., MacDonald, D., Huang, Y.S., 2007c. Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). Organic Geochemistry 38, 977–984.

Hou, J.Z., D'Andrea, W.J., Huang, Y.S., 2008. Can sedimentary leaf waxes record D/H ratios of continental precipitation? Field, model, and experimental assessments. Geochimica et Cosmochimica Acta 72, 3503–3517.

Hou, J., Huang, Y., Brodsky, C., Alexandre, M.R., 2010. Radiocarbon dating of individual lignin phenols: a new approach for establishing chronology of Late Quaternary lake sediments. Analytical Chemistry 82, 7119–7126.

Huang, Y.S., Freeman, K.H., Eglinton, T.I., Street-Perrott, F.A., 1999a. $\delta^{13}C$ analyses of individual lignin phenols in Quaternary lake sediments: a novel proxy for deciphering past terrestrial vegetation changes. Geology 27, 471–474.

Huang, Y.S., Street-Perrott, F.A., Perrot, R.A., Metzger, P., Eglinton, G., 1999b. Glacial–interglacial environmental changes inferred from molecular and compound-specific delta C-13 analyses of sediments from Sacred Lake, Mt. Kenya. Geochimica et Cosmochimica Acta 63, 1383–1404.

Huang, Y., Street-Perrott, F.A., Metcalfe, S.E., Brenner, M., Moreland, M., Freeman, K.H., 2001. Climate change as the dominant control on glacial-interglacial variations in C_3 and C_4 plant abundance. Science 293, 1647–1651.

Huang, Y.S., Shuman, B., Wang, Y., Webb, T., 2002. Hydrogen isotope ratios of palmitic acid in lacustrine sediments record late Quaternary climate variations. Geology 30, 1103–1106.

Huang, Y.S., Shuman, B., Wang, Y., Webb, T., 2004. Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. Journal of Paleolimnology 31, 363–375.

Huang, Y., Shuman, B., Wang, Y., Webb III, T., Grimm, E.C., Jacobson, J., 2006. Climatic and environmental controls on the variation of C_3 and C_4 plant abundances in central Florida for the past 62,000 years. Palaeogeography, Palaeoclimatology, Palaeoecology 237, 428–435.

Huguet, C., Cartes, J.E., Sinninghe Damsté, J.S., Schouten, S., 2006a. Marine crenarchaeotal membrane lipids in decapods: implications for the TEX_{86} paleothermometer. Geochemistry Geophysics Geosystems 7, 1–12.

Huguet, C., Hopmans, E.C., Febo-Ayala, W., Thompson, D.H., Sinninghe Damsté, J.S., Schouten, S., 2006b. An improved method to determine the absolute abundance of glycerol dibiphytanyl glycerol tetraether lipids. Organic Geochemistry 37, 1036–1041.

Huguet, C., Schimmelmann, A., Thunell, R., Lourens, L.J., Sinninghe Damsté, J.S., Schouten, S., 2007. A study of the TEX_{86} paleothermometer in the water column and sediments of the Santa Barbara Basin, California. Paleoceanography 22, pp. PA3203-1–PA3203-9.

Huguet, C., de Lange, G.J., Gustafsson, Ö, Middelburg, J.J., Sinninghe Damsté, J.S., Schouten, S., 2008. Selective preservation of soil organic matter in oxidized marine sediments (Madeira Abyssal Plain). Geochimica et Cosmochimica Acta 72, 6061–6068.

Humbert, S., Tamawski, S., Fromin, N., Mallet, M.-P., Aragno, M., Zopfil, J., 2010. Molecular detection of anammox bacteria in terrestrial ecosystems: distribution and diversity. International Society for Microbial Ecology 4, 450–454.

Ingalls, A.E., Whitehead, K., Bridoux, M.C., 2010. Tinted windows: the presence of the UV absorbing compounds called mycosporine-like amino acids embedded in the frustules of marine diatoms. Geochimica et Cosmochimica Acta 74, 104–115.

Innes, H.E., Bishop, A.N., Fox, P.A., Head, I.M., Farrimond, P., 1998. Early diagenesis of bacteriohopanoids in recent sediments of Lake Pollen, Norway. Organic Geochemistry 29, 1285–1295.

Ionescu, D., Penno, S., Haimovich, M., Rihtman, B., Goodwin, A., Schwartz, D., Hazanov, L., Chernihovsky, M., Post, A.F., Oren, A., 2009. Archaea in the Gulf of Aqaba. FEMS Microbiology Ecology 69, 425–438.

Itoh, N., Tani, Y., Nagatani, T., Soma, M., 2003. Phototrophic activity and redox condition in Lake Hamana, Japan, indicated by sedimentary photosynthetic pigments and molybdenum over the last ~250 years. Journal of Paleolimnology 29, 403–422.

Jaeschke, A., Hopmans, E.C., Wakeham, S.G., Schouten, S., Sinninghe Damsté, J.S., 2007. The presence of ladderane lipids in the oxygen minimum zone of the Arabian Sea indicates nitrogen loss through anammox. Limnology and Oceanography 52, 780–786.

Jaeschke, A., Lewan, M.D., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2008. Thermal stability of ladderane lipids as determined by hydrous pyrolysis. Organic Geochemistry 39, 1735–1741.

Jaeschke, A., Rooks, C., Trimmer, M., Nicholls, J.C., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2009a. Comparison of ladderane phospholipid and core lipids as indicators for anaerobic ammonium oxidation (anammox) in marine sediments. Geochimica et Cosmochimica Acta 73, 2077–2088.

Jaeschke, A., Ziegler, M., Hopmans, E.C., Reichart, G.-J., Lourens, L.J., Schouten, S., Sinninghe Damsté, J.S., 2009b. Molecular fossil evidence for anaerobic ammonium oxidation in the Arabian Sea over the last glacial cycle. Paleoceanography 24, pp. PA2202-1-PA2202-11.

Jahnke, L.L., Summons, R.E., Hope, J.M., Des Marais, D.J., 1999. Carbon isotopic fractionation in lipids from methanotrophic bacteria II: the effects of physiology and environmental parameters on the biosynthesis and isotopic signatures of biomarkers. Geochimica et Cosmochimica Acta 63, 79–93.

Jaraula, C.M.B., Brassell, S.C., Morgan-Kiss, R.M., Doran, P.T., Kenig, F., 2010. Origin and tentative identification of tri to pentaunsaturated ketones in sediments from Lake Fryxell, East Antarctica. Organic Geochemistry 41, 386–397.

Jeffrey, S.W., Vesk, M., 1997. Introduction to marine phytoplankton and their pigment signatures. In: Phytoplankton Pigments in Oceanography: Guidelines to Modern Methods. UNESCO, Paris, pp. 37–84.

Johnson, T.C., Barry, S.L., Chan, Y., Wilkinson, P., 2001. Decadal record of climate variability spanning the past 700 yr in the Southern Tropics of East Africa. Geology 29, 83–86.

Jones, B.F., Eugster, H.P., Rettig, S.L., 1977. Hydrochemistry of the Lake Magadi basin, Kenya. Geochimica et Cosmochimica Acta 41, 53–72.

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

Kaneko, M., Kitajima, F., Naraoka, H., 2011. Stable hydrogen isotope measurement of archaeal ether-bound hydrocarbons. Organic Geochemistry 42, 166–172.

Karner, M.B., DeLong, E.F., Karl, D.M., 2001. Archaeal dominance in the mesopelagic zone of the Pacific Ocean. Nature 409, 507–510.

Keely, B.J., Brereton, R.G., Maxwell, J.R., 1988. Occurrence and significance of pyrochlorins in a lake sediment. Organic Geochemistry 13, 801–805.

Kemp, P., Lander, D.J., 1984. Hydrogenation in vitro of α-linolenic acid to stearic acid by mixed cultures of pure strains of rumen bacteria. Journal of General Microbiology 130, 527–533.

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

Killops, S., Killops, V., 2005. Introduction to Organic Geochemistry. Blackwell Publishing, Malden, MA.

Kim, J.H., Huguet, C., Zonneveld, K.A.F., Versteegh, G.J.M., Roeder, W., Sinninghe Damstθ, J.S., Schouten, S., 2009. An experimental field study to test the stability of lipids used for the TEX_{86} and palaeothermometers. Geochimica et Cosmochimica Acta 73, 2888–2898.

Kim, J.H., Zarzycka, B., Buscail, R., Peterse, F., Bonnin, J., Ludwig, W., Schouten, S., Sinninghe Damsté, J.S., 2010a. Contribution of river-borne soil organic carbon to the Gulf of Lions (NW Mediterranean). Limnology and Oceanography 55, 507–518.

Kim, J.H., van der Meer, J., Schouten, S., Helmke, P., Willmott, V., Sangiorgi, F., Koc, N., Hopmans, E.C., Sinninghe Damsté, J.S., 2010b. New indices and calibrations derived from the distribution of crenarchaeal isoprenoid tetraether lipids: implications for past sea surface temperature reconstructions. Geochimica et Cosmochimica Acta 74, 4639–4654.

Kim, J.H., Talbot, H.M., Zarzycka, B., Bauersachs, T., Wagner, T., 2011. Occurrence and abundance of soil-specific bacterial membrane lipid markers in the Têt watershed (Southern France): soil-specific BHPs and branched GDGTs. Geochemistry Geophysics Geosystems 12, Q02008.

Kleemann, G., Poralla, K., Englert, G., Kjøsen, H., Liaanen-Jensen, S., Neunlist, S., Rohmer, M., 1990. Tetrahymanol from the phototrophic bacterium *Rhodopseudomonas palustris*: first report of a gammacerane triterpene from a prokaryote. Journal of General Microbiology 136, 2551–2553.

Klok, J., Baas, M., Cox, H.C., de Leeuw, J.W., Schenck, P.A., 1984. Loliolides and dihydroactinidiolide in a recent marine sediment probably indicate a major transformation pathway of carotenoids. Tetrahedron Letters 25, 5577–5580.

Koga, Y., Nishihara, M., Morii, H., Akagawa-Matsushita, M., 1993. Ether polar lipids of methanogenic bacteria: structures, comparative aspects, and biosyntheses. Microbiological Reviews 57, 164–182.

Kokke, W.C.M.C., Fenical, W., Djerassi, C., 1981. Sterols with unusual nuclear unsaturation from three cultured marine dinoflagellates. Phytochemistry 20, 127–134.

Koopmans, M.P., Köster, J., van Kaam-Peters, H.M.E., Kenig, F., Schouten, S., Hartgers, W.A., de Leeuw, J.W., Sinninghe Damsté, J.S., 1996. Diagenetic and catagenetic products of isorenieratene: molecular indicators for photic zone anoxia. Geochimica et Cosmochimica Acta 60, 4467–4496.

Krishnamurthy, R.V., Syrup, K.A., Baskaran, M., Long, A., 1995. Late-Glacial climate record of Midwestern United-States from the hydrogen isotope ratio of lake organic-matter. Science 269, 1565–1567.

Kristen, I., Wilkes, H., Vieth, A., Zink, K.G., Plessen, B., Thorpe, J., Partridge, T.C., Oberhansli, H., 2010. Biomarker and stable carbon isotope analyses of sedimentary organic matter from Lake Tswaing: evidence for deglacial wetness and early Holocene drought from South Africa. Journal of Paleolimnology 44, 143–160.

Kuypers, M.M.M., Pancost, R.D., Sinninghe Damsté, J.S., 1999. A large and abrupt fall in atmospheric CO_2 concentration during cretaceous times. Nature 399, 342–345.

Kuypers, M.M.M., Sliekers, A.O., Lavik, G., Schmid, M., Jørgensen, B.B., Kuenen, J.G., Sinninghe Damsté, J.S., Strous, M., Jetten, M.S.M., 2003. Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. Nature 422, 608–611.

Laws, E.A., Popp, B.N., Bidigare, R.R., Kennicutt, M.C., Macko, S.A., 1995. Dependence of phytoplankton carbon isotopic composition on growth-rate and $[CO_2](Aq)$ – theoretical considerations and experimental results. Geochimica et Cosmochimica Acta 59, 1131–1138.

Leavitt, P.R., 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. Journal of Paleolimnology 9, 109–127.

Leavitt, P.R., Hodgson, D.A., 2001. Sedimentary pigments. In: Tracking Environmental Change using Lake Sediments. Terrestrial, Algal, and Siliceous Indicators, vol. 3. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 1–32.

Leavitt, P.R., Vinebrooke, R.D., Donald, D.B., Smol, J.P., Schindler, D.W., 1997. Past ultraviolet radiation environments in lakes derived from fossil pigments. Nature 388, 457–459.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Leavitt, P.R., Findlay, D.L., Hall, R.I., Smol, J.P., 1999. Algal responses to dissolved organic carbon loss and pH decline during whole-lake acidification: evidence from paleolimnology. Limnology and Oceanography 44, 757–773.

Leavitt, P.R., Cumming, B.F., Smol, J.P., Reasoner, M., Pienitz, R., Hodgson, D.A., 2003. Climatic control of ultraviolet radiation effects on lakes. Limnology and Oceanography 48, 2062–2069.

Leblond, J.D., Chapman, P.J., 2002. A survey of the sterol composition of the marine dinoflagellates *Karenia brevis*, *Karenia mikimotoi*, and *Karlodinium micrum* distribution of sterols within other members of the class Dinophyceae. Journal of Phycology 38, 670–682.

Lee, K.E., Kim, J.H., Wilke, I., Helmke, P., Schouten, S., 2008. A study of the alkenone, TEX_{86}, and planktonic foraminifera in the Benguela Upwelling System: implications for past sea surface temperature estimates. Geochemistry Geophysics Geosystems 9.

Leider, A., Hinrichs, K.U., Mollenhauer, G., Versteegh, G.J.M., 2010. Core-top calibration of the lipid-based and TEX_{86} temperature proxies on the southern Italian shelf (SW Adriatic Sea, Gulf of Taranto). Earth and Planetary Science Letters 300, 112–124.

de Leeuw, J.W., van de Meer, F.W., Rijpstra, W.I.C., Schenck, P.A., 1979. On the occurrence and structural identification of long chain unsaturated ketones and hydrocarbons in sediments. In: Advances in Organic Geochemistry. Pergamon Press, Oxford, pp. 211–217.

Li, J.G., Philp, R.P., Pu, F., Allen, J., 1996. Long-chain alkenones in Qinghai Lake sediments. Geochimica et Cosmochimica Acta 60, 235–241.

Lichtfouse, É., Derenne, S., Mariotti, A., Largeau, C., 1994. Possible algal origin of long chain odd *n*-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. Organic Geochemistry 22, 1023–1027.

Lipp, J.S., Morono, Y., Inagaki, F., Hinrichs, K.-U., 2008. Significant contribution of Archaea to extant biomass in marine subsurface sediments. Nature 454, 991–994.

Litt, T., Krastel, S., Sturm, M., Kipfer, R., Örcen, S., Heumann, G., Franz, S.O., Ülgen, U.B., Niessen, F., 2009. `PALEOVAN', International Continental Scientific Drilling Program (ICDP): site survey results and perspectives. Quaternary Science Reviews 28, 1555–1567.

Liu, W.G., Yang, H., 2008. Multiple controls for the variability of hydrogen isotopic compositions in higher plant n-alkanes from modern ecosystems. Global Change Biology 14, 2166–2177.

Liu, W.G., Yang, H., Li, L.W., 2006a. Hydrogen isotopic compositions of n-alkanes from terrestrial plants correlate with their ecological life forms. Oecologia 150, 330–338.

Liu, Z.H., Henderson, A.C.G., Huang, Y.S., 2006b. Alkenone-based reconstruction of late-Holocene surface temperature and salinity changes in Lake Qinghai, China. Geophysical Research Letters 33.

Liu, W.G., Liu, Z.H., Fu, M.Y., An, Z.H., 2008. Distribution of the C_{37} tetra-unsaturated alkenone in Lake Qinghai, China: a potential lake salinity indicator. Geochimica et Cosmochimica Acta 72, 988–997.

Liu, W., Liu, Z., Wang, H., He, Y., Wang, Z., Xu, L., 2011. Salinity control on long-chain alkenone distributions in lake surface waters and sediments of the northern Qinghai-Tibetan Plateau, China. Geochimica et Cosmochimica Acta 75, 1693–1703.

Livingstone, D.M., Lotter, A.F., 1998. The relationship between air and water temperatures in lakes of the Swiss Plateau: a case study with palaeolimnological implications. Journal of Paleolimnology 19, 181–198.

Lohr, A.J., Bogaard, T.A., Heikens, A., Hendriks, M.R., Sumarti, S., Van Bergen, M.J., Van Gestel, C.A.M., Van Straalen, N.M., Vroon, P.Z., Widianarko, B., 2005. Natural pollution caused by the extremely acidic crater Lake Kawah Ijen, East Java, Indonesia. Environmental Science and Pollution Research 12, 89–95.

Lopes dos Santos, R.A., Prange, M., Castañeda, I.S., Schefuß, E., Schulz, M., Niedermeyer, E.M., Sinninghe Damsté, J.S., Schouten, S., 2010. Glacial–interglacial variability in Atlantic meridional overturning circulation and thermocline adjustments in the tropical North Atlantic. Earth and Planetary Science Letters 300, 407–414.

` Lovan, N.A., Krishnamurthy, R.V. Inferring paleotemperature from the D/H ratio of lacustrine organic matter. Quaternary International, in press.

Mügler, I., Sachse, D., Werner, M., Xu, B.Q., Wu, G.J., Yao, T.D., Gleixner, G., 2008. Effect of lake evaporation on delta D values of lacustrine n-alkanes: a comparison of Nam Co (Tibetan Plateau) and Holzmaar (Germany). Organic Geochemistry 39, 711–729.

Müller, P.J., Kirst, G., Ruhland, G., von Storch, I., Rosell-Mele, A., 1998. Calibration of the alkenone paleotemperature index $U^{k'}_{37}$ based on core-tops from the eastern South Atlantic and the global ocean (60 degrees N–60 degrees S). Geochimica et Cosmochimica Acta 62, 1757–1772.

Mallorquí, N., Arellano, J.B., Borrego, C.M., Garcia-Gil, L.J., 2005. Signature pigments of green sulfur bacteria in lower Pleistocene deposits from the Banyoles lacustrine area (Spain). Journal of Paleolimnology 34, 271–280.

Mallory, F.B., Conner, R.L., Gordon, J.T., 1963. Isolation of a pentacyclic triterpenoid alcohol from a protozoan. Journal of the American Chemical Society 85, 1362–1363.

Marlowe, I.T., Green, J.C., Neal, A.C., Brassell, S.C., Eglinton, G., Course, P.A., 1984. Long-chain (n-C_{37}-C_{39}) alkenones in the Prymnesiophyceae. Distribution of alkenones and other lipids and their taxonomic significance. British Phycological Journal 19, 203–216.

Massé, G., Belt, S.T., Allard, W.G., Lewis, C.A., Wakeham, S.G., Rowland, S.J., 2004. Occurrence of novel monocyclic alkenes from diatoms in marine particulate matter and sediments. Organic Geochemistry 35, 813–822.

McInerney, F.A., Helliker, B.R., Freeman, K.H., 2011. Hydrogen isotope ratios of leaf wax n-alkanes in grasses are insensitive to transpiration. Geochimica et Cosmochimica Acta 75, 541–554.

Menzel, D., Hopmans, E.C., Schouten, S., Sinninghe Damsté, J.S., 2006. Membrane tetraether lipids of planktonic Crenarchaeota in Pliocene sapropels of the eastern Mediterranean Sea. Palaeogeography, Palaeoclimatology, Palaeoecology 239, 1–15.

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry 27, 213–250.

Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Organic Geochemistry 34, 261–289.

Meyers, P.A., Teranes, J.L., 2001. Sediment organic matter. In: Tracking Environmental Changes using Lake Sediment. Physical and Geochemical Methods, vol. 2. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 239–270.

Millie, D.F., Paerl, H.W., Hurley, J.P., 1993. Microalgal pigment assessments using high-performance liquid-chromatography – a synopsis of organismal and ecological applications. Canadian Journal of Fisheries and Aquatic Sciences 50, 2513–2527.

Mollenhauer, G., Inthorn, M., Vogt, T., Zabel, M., Sinninghe Damsté, J.S., Eglinton, T.I., 2007. Aging of marine organic matter during cross-shelf lateral transport in the Benguela upwelling system revealed by compound-specific radiocarbon dating. Geochemistry Geophysics Geosystems 8, 1–16.

Mollenhauer, G., Eglinton, T.I., Hopman, E.C., Sinninghe Damsté, J.S., 2008. A radiocarbon-based assessment of the preservation characteristics of crenarchaeol and alkenones from continental margin sediments. Organic Geochemistry 39, 1039–1045.

Murray, A.E., Blakis, A., Massana, R., Strawzewski, S., Passow, U., Alldredge, A., DeLong, E.F., 1999. A time series assessment of planktonic archaeal variability in the Santa Barbara Channel. Aquatic Microbial Ecology 20, 129–145.

Nichols, B.W., Wood, B.J.B., 1968. New glycolipid specific to nitrogen-fixing blue-green algae. Nature 217, 767.

Nishimura, M., Koyama, T., 1977. The occurrence of stanols in various living organisms and the behavior of sterols in contemporary sediments. Geochimica et Cosmochimica Acta 41, 379–385.

Ocampo, R., Repeta, D.J., 1999. Structural determination of purpurin-18 (as methyl ester) from sedimentary organic matter. Organic Geochemistry 30, 189–193.

Ocampo, R., Sachs, J.P., Repeta, D.J., 1999. Isolation and structure determination of the unstable 132, 173-Cyclopheophorbide a enol from recent sediments. Geochimica et Cosmochimica Acta 63, 3743–3749.

Ohkouchi, N., Eglinton, T.I., Keigwin, L.D., Hayes, J.M., 2002. Spatial and temporal offsets between proxy records in a sediment drift. Science 298, 1224–1227.

Osmond, C., Adams, W., Smith, S., 1989. Crassulacean acid metabolism. In: Plant Physiological Ecology. Chapman and Hall, New York, pp. 258–280.

Ostrom, P.H., Ostrom, N.E., Henry, J., Eadie, B.J., Meyers, P.A., Robbins, J.A., 1998. Changes in the trophic state of Lake Erie: discordance between molecular $\delta^{13}C$ and bulk $\delta^{13}C$ sedimentary records. Chemical Geology 152, 163–179.

Ott, D.W., Oldham-Ott, C.K., 2003. Eustigmatophyte, radiophyte, and tribophyte algae. In: Freshwater algae of North America. Academic Press, San Diego, pp. 423–469.

Ourisson, G., Albrecht, P., 1992. Hopanoids. 1. Geohopanoids: the most abundant natural products on earth? Accounts of Chemical Research 25, 398–402.

Pagani, M., Freeman, K.H., Arthur, M.A., 1999. Late Miocene atmospheric CO_2 concentrations and the expansion of C_4 grasses. Science 285, 876–879.

Pancost, R.D., van Geel, B., Baas, M., Sinninghe Damsté, J.S., 2000. $\delta^{13}C$ values and radiocarbon dates of microbial biomarkers as tracers for carbon recycling in peat deposits. Geology 28, 663–666.

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

Pearson, A., Pi, Y.D., Zhao, W.D., Li, W.J., Li, Y.L., Inskeep, W., Perevalova, A., Romanek, C., Li, S.G., Zhang, C.L., 2008. Factors controlling the distribution of archaeal tetraethers in terrestrial hot springs. Applied and Environmental Microbiology 74, 3523–3532.

Pearson, E.J., Farrimond, P., Juggins, S., 2007. Lipid geochemistry of lake sediments from semi-arid Spain: relationships with source inputs and environmental factors. Organic Geochemistry 38, 1169–1195.

Pearson, E.J., Juggins, S., Farrimond, P., 2008. Distribution and significance of long-chain alkenones as salinity and temperature indicators in Spanish saline lake sediments. Geochimica et Cosmochimica Acta 72, 4035–4046.

Peltzer, E.T., Gagosian, R.B., 1989. Organic geochemistry of aerosols over the Pacific Ocean. In: Chemical Oceanography 10. SEAREX: the Sea/Air Exchange Program. Academic Press, New York, pp. 281–338.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide: Biomarkers and Isotopes in Petroleum Exploration and Earth History. Cambridge University Press, New York.

Peterse, F., Kim, J.H., Schouten, S., Kristensen, D.K., Koτ, N., Sinninghe Damsté, J.S., 2009. Constraints on the application of the MBT/CBT palaeothermometer at high latitude environments (Svalbard, Norway). Organic Geochemistry 40, 692–699.

Piretti, M.V., Pagliuca, G., Boni, L., Pistocchi, R., Diamante, M., Gazzotti, T., 1997. Investigation of 4-methyl sterols from cultured dinoflagellate algal strains. Journal of Phycology 33, 61–67.

Pitcher, A., Hopmans, E.C., Mosier, A.C., Park, S.J., Rhee, S.K., Francis, C.A., Schouten, S., Sinninghe Damsté, J.S., 2011. Core and intact polar glycerol dibiphytanyl glycerol tetraether lipids of ammonia-oxidizing archaea enriched from marine and estuarine sediments. Applied and Environmental Microbiology 77, 3468–3477.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Placencia, J.A., Garcés-Vargas, J., Lange, C.B., Hebbeln, D., 2010. Alkenone-based temperature patterns along the eastern South Pacific Coastal Ocean: the effect of upwelling and advection on the sedimentary alkenone unsaturation-index ($U^{k'}_{37}$). Biogeosciences Discussions 7, 545–564.

Polissar, P.J., Freeman, K.H., 2010. Effects of aridity and vegetation on plant-wax delta D in modern lake sediments. Geochimica et Cosmochimica Acta 74, 5785–5797.

Polissar, P.J., Fulton, J.M., Junium, C.K., Turich, C.C., Freeman, K.H., 2009. Measurement of ^{13}C and ^{15}N isotopic composition on nanomolar quantities of C and N. Analytical Chemistry 81, 755–763.

Pollingher, U., Zemel, E., 1981. Insitu and experimental-evidence of the influence of turbulence on cell-division processes of *Peridinium cinctum* forma westii (Lemm) Lefevre. British Phycological Journal 16, 281–287.

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

Powers, L.A., Johnson, T.C., Werne, J.P., Castañada, I.S., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2005. Large temperature variability in the southern African tropics since the Last Glacial Maximum. Geophysical Research Letters 32.

Powers, L., Werne, J.P., Vander Woude, A.J., Sinninghe Damsté, J.S., Hopmans, E.C., Schouten, S., 2010. Applicability and calibration of the TEX_{86} paleothermometer in lakes. Organic Geochemistry 41, 404–413.

Powers, L.A., Johnson, T.C., Werne, J.P., Castañeda, I.S., Hopmans, E.C., Sinninghe Damsté, J.S., Schouten, S., 2011. Organic geochemical records of environmental variability in Lake Malawi during the last 700 years, Part I: the TEX_{86} temperature record. Palaeogeography, Palaeoclimatology, Palaeoecology 303, 133–139.

Prahl, F.G., Wakeham, S.G., 1987. Calibration of unsaturation patterns in long-chain ketone compositions for palaeotemperature assessment. Nature 330, 367–369.

Prahl, F.G., Mix, A.C., Sparrow, M.A., 2006. Alkenone paleothermometry: biological lessons from marine sediment records off western South America. Geochimica et Cosmochimica Acta 70, 101–117.

Pu, Z., Weiguo, L., 2011. Effect of plant life form on relationship between δD values of leaf wax *n*-alkanes and altitude along Mount Taibai, China. Organic Geochemistry 42, 100–107.

Quesada, A., Vincent, W.F., Lean, D.R.S., 1999. Community and pigment structure of Arctic cyanobacterial assemblages: the occurrence and distribution of UV-absorbing compounds. FEMS Microbiology Ecology 28, 315–323.

Rampen, S.W., Abbas, B.A., Schouten, S., Sinninghe Damsté, J.S., 2010. A comprehensive study of sterols in marine diatoms (Bacillariophyta): implications for their use as tracers for diatom productivity. Limnology and Oceanography 55, 91–105.

Rashby, S.E., Sessions, A.L., Summons, R.E., Newman, D.K., 2007. Biosynthesis of 2-methylbacteriohopanepolyols by an anoxygenic phototroph. Proceedings of the National Academy of Sciences of the United States of America 104, 15099–15104.

Rattray, J.E., van de Vossenberg, J., Hopmans, E.C., Kartal, B., van Niftrik, L., Rijpstra, W.I.C., Strous, M., Jetten, M.S.M., Schouten, S., Sinninghe Damsté, J.S., 2008. Ladderane lipid distribution in four genera of anammox bacteria. Archives of Microbiology 190, 51–66.

Rattray, J.E., van de Vossenberg, J., Jaeschke, A., Hopmans, E.C., Wakeham, S.G., Lavik, G., Kuypers, M.M.M., Strous, M., Jetten, M.S.M., Schouten, S., Sinninghe Damsté, J.S., 2010. Impact of temperature on ladderane lipid distribution in anammox bacteria. Applied and Environmental Microbiology 76, 1596–1603.

Repeta, D.J., 1989. Carotenoid diagenesis in recent marine sediments: II. Degradation of fucoxanthin to loliolide. Geochimica et Cosmochimica Acta 53, 699–707.

Richey, J.N., Hollander, D.J., Flower, B.P., Eglinton, T.I., 2011. Merging late Holocene molecular organic and foraminiferal-based geochemical records of sea surface temperature in the Gulf of Mexico. Paleoceanography 26.

Robinson, N., Eglinton, G., Brassell, S.C., Cranwell, P.A., 1984. Dinoflagellate origin for sedimentary 4α-methylsteroids and 5α(H)-stanols. Nature 308, 439–442.

Romero-Viana, L., Keely, B.J., Camacho, A., Vicente, E., Miracle, M.R., 2009. Photoautotrophic community changes in Lagunillo del Tejo (Spain) in response to lake level fluctuation: two centuries of sedimentary pigment records. Organic Geochemistry 40, 376–386.

Rommerskirchen, F., Eglinton, G., Dupont, l., Guntner, U., Wenzel, C., Rullkotter, J., 2003. A north to south transect of Holocene southeast Atlantic continental margin sediments: relationship between aerosol transport and compound-specific delta C-13 land plant biomarker and pollen records. Geochemistry Geophysics Geosystems 4.

Rosell-Melé, A., 1998. Interhemispheric appraisal of the value of alkenone indices as temperature and salinity proxies in high-latitude locations. Paleoceanography 13, 694–703.

Rosell-Melé, A., Jansen, E., Weinelt, M., 2002. Appraisal of a molecular approach to infer variations in surface ocean freshwater inputs into the North Atlantic during the last glacial. Global and Planetary Change 34, 143–152.

Rowland, S.J., Allard, W.G., Belta, S.T., Massae, G., Robert, J.M., Blackburn, S., Frampton, D., Revill, A.T., Volkman, J.K., 2001. Factors influencing the distributions of polyunsaturated terpenoids in the diatom, Rhizosolenia setigera. Phytochemistry 58, 717–728.

Russell, J.M., Mccoy, S.J., Verschuren, D., Bessems, I., Huang, Y., 2009. Human impacts, climate change, and aquatic ecosystem response during the past 2000 yr at Lake Wandakara, Uganda. Quaternary Research 72, 315–324.

Sachs, J.P., Repeta, D.J., 1999. Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. Science 286, 2485–2488.

Sachs, J.P., Repeta, D.J., Goericke, R., 1999. Nitrogen and carbon isotopic ratios of chlorophyll from marine phytoplankton. Geochimica et Cosmochimica Acta 63, 1431–1441.

Sachse, D., Sachs, J.P., 2008. Inverse relationship between D/H fractionation in cyanobacterial lipids and salinity in Christmas Island saline ponds. Geochimica et Cosmochimica Acta 72, 793–806.

Sachse, D., Radke, J., Gleixner, G., 2004. Hydrogen isotope ratios of recent lacustrine sedimentary *n*-alkanes record modern climate variability. Geochimica et Cosmochimica Acta 68, 4877–4889.

Sachse, D., Radke, J., Gleixner, G., 2006. δD values of individual *n*-alkanes from terrestrial plants along a climatic gradient – implications for the sedimentary biomarker record. Organic Geochemistry 37, 469–483.

Sanger, J.E., 1988. Fossil pigments in paleoecology and paleolimnology. Palaeogeography, Palaeoclimatology, Palaeoecology 62, 343–359.

Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A., Sessions, A.L., 2001. Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. Geochimica et Cosmochimica Acta 65, 213–222.

Schefuß, E., Schouten, S., Schneider, R.R., 2005. Climatic controls on central African hydrology during the past 20,000 years. Nature 437, 1003–1006.

Schefuss, E., Schouten, S., Jansen, J.H.F., Damste, J.S.S., 2003. African vegetation controlled by tropical sea surface temperatures in the mid-Pleistocene period. Nature 422, 418–421.

Schelske, C.L., Hodell, D.A., 1991. Recent changes in productivity and climate of Lake-Ontario detected by isotopic analysis of sediments. Limnology and Oceanography 36, 961–975.

Schelske, C.L., Hodell, D.A., 1995. Using carbon isotopes of bulk sedimentary organic-matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnology and Oceanography 40, 918–929.

Schimel, J., 2004. Playing scales in the methane cycle: from microbial ecology to the globe. Proceedings of the National Academy of Sciences of the United States of America 101, 12400–12401.

Schmid, M.C., Risgaard-Peterson, N., van de Vossenberg, J., Kuypers, M.M.M., Lavik, G., Petersen, J., Hulth, S., Thamdrup, B., Canfield, D., Dalsgaard, T., Rysgaard, S., Sejr, M.K., Strous, M., Op den Camp, H.J.M., Jetten, M.S.M., 2007. Anaerobic ammonium-oxidizing bacteria in marine environments: widespread occurrence but low diversity. Environmental Microbiology 9, 1476–1484.

Schouten, S., Rijpstra, W.I.C., Kok, M., Hopmans, E.C., Summons, R.E., Volkman, J.K., Sinninghe Damsté, J.S., 2001a. Molecular organic tracers of biogeochemical processes in a saline meromictic lake (Ace Lake). Geochimica et Cosmochimica Acta 65, 1629–1640.

Schouten, S., Wakeham, S.G., Sinninghe Damsté, J.S., 2001b. Evidence for anaerobic methane oxidation by archaea in euxinic waters of the Black Sea. Organic Geochemistry 32, 1277–1281.

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

Schouten, S., Wakeham, S.G., Hopmans, E.C., Sinninghe Damsté, J.S., 2003. Biogeochemical evidence that thermophilic archaea mediate the anaerobic oxidation of methane. Applied and Environmental Microbiology 69, 1680–1686.

Schouten, S., Hopmans, E.C., Sinninghe Damsté, J.S., 2004. The effect of maturity and depositional redox conditions on archaeal tetraether lipid palaeothermometry. Organic Geochemistry 35, 567–571.

Schouten, S., Ossebaar, J., Schreiber, K., Kienhuis, M.V.M., Langer, G., Benthien, A., Bijma, J., 2006. The effect of temperature, salinity and growth rate on the stable hydrogen isotopic composition of long chain alkenones produced by *Emiliania huxleyi* and *Gephyrocapsa oceanica*. Biogeosciences 3, 113–119.

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

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

Schubert, C.J., Durisch-Kaiser, E., Wehrli, B., Thamdrup, B., Lam, P., Kuypers, M.M.M., 2006. Anaerobic ammonium oxidation in a tropical freshwater system (Lake Tanganyika). Environmental Microbiology 8, 1857–1863.

Schwark, L., Zink, K., Lechterbeck, J., 2002. Reconstruction of postglacial to early Holocene vegetation history in terrestrial Central Europe via cuticular lipid biomarkers and pollen records from lake sediments. Geology 30, 463–466.

Sessions, A.L., 2006a. Isotope-ratio detection for gas chromatography. Journal of Separation Science 29, 1946–1961.

Sessions, A.L., 2006b. Seasonal changes in D/H fractionation accompanying lipid biosynthesis in Spartina alternflora. Geochimica et Cosmochimica Acta 70, 2153–2162.

Sessions, A.L., Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. Organic Geochemistry 30, 1193–1200.

Shah, S.R., Mollenhauer, G., Ohkouchi, N., Eglinton, T.I., Pearson, A., 2008. Origins of archaeal tetraether lipids in sediments: insights from radiocarbon analysis. Geochimica et Cosmochimica Acta 72, 4577–4594.

Sheng, G.Y., Cai, K.Q., Yang, X.X., Lu, J.L., Jia, G.D., Peng, P.A., Fu, J.M., 1999. Long-chain alkenones in Hotong Qagan Nur Lake sediments and its paleoclimatic implications. Chinese Science Bulletin 44, 259–263.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Shimada, H., Nemoto, N., Shida, Y., Oshima, T., Yamagishi, A., 2008. Effects of pH and temperature on the composition of polar lipids in Thermoplasma acidophilum HO-62. Journal of Bacteriology 190, 5404–5411.

Shimokawara, M., Nishimura, M., Matsuda, T., Akiyama, N., Kawai, T., 2010. Bound forms, compositional features, major sources and diagenesis of long chain, alkyl mid-chain diols in Lake Baikal sediments over the past 28,000 years. Organic Geochemistry 41, 753–766.

Shuman, B., Huang, Y.S., Newby, P., Wang, Y., 2006. Compound-specific isotopic analyses track changes in seasonal precipitation regimes in the Northeastern United States at ca 8200 cal yr BP. Quaternary Science Reviews 25, 2992–3002.

Sicre, M.A., Bard, E., Ezat, U., Rostek, F., 2002. Alkenone distributions in the North Atlantic and Nordic sea surface waters. Geochemistry Geophysics Geosystems 3.

Sinha, R.P., Klisch, M., Groniger, A., Hader, D.P., 1998. Ultraviolet-absorbing/screening substances in cyanobacteria, phytoplankton and macroalgae. Journal of Photochemistry and Photobiology B-Biology 47, 83–94.

Sinninghe Damsté, J.S., Schouten, S., 2006. Biological markers for anoxia in the photic zone of the water column. In: The Handbook of Environmental Chemistry. Springer-Verlag, Berlin, Heidelberg, pp. 128–163.

Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M., de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. Geochimica et Cosmochimica Acta 59, 1895–1900.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Schouten, S., Peletier, H., van der Maarel, M.J.E.C., Gieskes, W.W.C., 1999a. A C_{25} highly branched isoprenoid alkene and C_{25} and C_{27} n-polyenes in the marine diatom *Rhizosolenia setigera*. Organic Geochemistry 30, 95–100.

Sinninghe Damsté, J.S., Schouten, S., Rijpstra, W.I., Hopmans, E.C., Peletier, H., Gieskes, W.W.C., Geenevasen, J.A.J., 1999b. Structural identification of the C_{25} highly branched isoprenoid pentaene in the marine diatom *Rhizosolenia setigera*. Organic Geochemistry 30, 1581–1583.

Sinninghe Damsté, J.S., Hopmans, E.C., Pancost, R.D., Schouten, S., Geenevasen, J.A.J., 2000. Newly discovered non-isoprenoid glycerol dialkyl glycerol tetraether lipids in sediments. Chemical Communications, 1683–1684.

Sinninghe Damsté, J.S., Schouten, S., van Duin, A.C.T., 2001a. Isorenieratene derivatives in sediments: possible controls on their distribution. Geochimica et Cosmochimica Acta 65, 1557–1571.

Sinninghe Damsté, J.S., van Dongen, B.E., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., Geenevasen, J.A.J., 2001b. Novel intact glycolipids in sediments from an Antarctic lake (Ace Lake). Organic Geochemistry 32, 321–332.

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

Sinninghe Damsté, J.S., Strous, M., Rijpstra, W.I.C., Hopmans, E.C., Geenevasen, J.A.J., van Duin, A.C.T., van Niftrik, L.A., Jetten, M.S.M., 2002b. Linearly concatenated cyclobutane lipids form a dense bacterial membrane. Nature 419, 708–712.

Sinninghe Damsté, J.S., Muyzer, G., Abbas, B., Rampen, S.W., Masse, G., Allard, W.G., Belt, S.T., Robert, J.-M., Rowland, S.J., Moldowan, J.M., Barbanti, S.M., Fago, F.J., Denisevich, P., Dahl, J., Trindade, L.A.F., Schouten, S., 2004. The rise of the rhizosolenid diatoms. Science 304, 584–587.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Geenevasen, J.A.J., Strous, M., Jetten, M.S.M., 2005. Structural identification of ladderane and other membrane lipids of planctomycetes capable of anaerobic ammonium oxidation (anammox). FEBS Journal 272, 4270–4283.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Coolen, M.J.L., Schouten, S., Volkman, J.K., 2007. Rapid sulfurisation of highly branched isoprenoid (HBI) alkenes in sulfidic Holocene sediments from Ellis Fjord, Antarctica. Organic Geochemistry 38, 128–139.

Sinninghe Damsté, J.S., Ossebaar, J., Schouten, S., Verschuren, D., 2008. Altitudinal shifts in the branched tetraether lipid distribution in soil from Mt. Kilimanjaro (Tanzania): implications for the MBT/CGT continental palaeothermometer. Organic Geochemistry 39, 1072–1076.

Sinninghe Damsté, J.S., Ossebaar, J., Abbas, B., Schouten, S., Verschuren, D., 2009. Fluxes and distribution of tetraether lipids in an equatorial African lake: constraints on the application of the TEX_{86} palaeothermometer and BIT index in lacustrine settings. Geochimica et Cosmochimica Acta 73, 4232–4249.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Hopman, E.C., Weijers, J.W.H., Foesel, B.U., Overmann, J., Dedysh, S.N., 2011. 13,16-dimethyl octacosanedioic acid (*iso*-diabolic acid), a common membrane-spanning lipid of *Acidobacteria* subdivisions 1 and 3. Applied and Environmental Microbiology 77, 4147–4154.

Smith, F.A., Freeman, K.H., 2006. Influence of physiology and climate on δD of leaf wax *n*-alkanes from C_3 and C_4 grasses. Geochimica et Cosmochimica Acta 70, 1172–1187.

Smith, R.W., Bianchi, T.S., Savage, C., 2010. Comparison of lignin phenols and branched/isoprenoid tetraethers (BIT index) as indices of terrestrial organic matter in Doubtful Sound, Fiordland, New Zealand. Organic Geochemistry 41, 281–290.

Smittenberg, R.H., Hopmans, E.C., Schouten, S., Hayes, J.M., Eglinton, T.I., Sinninghe Damsté, J.S., 2004. Compound-specific radiocarbon dating of the varved Holocene sedimentary record of Saanich Inlet, Canada. Paleoceanography 19, pp. PA2012-1–PA2012-16.

Soma, Y., Tani, Y., Soma, M., Mitake, H., Kurihara, R., Hashomoto, S., Watanabe, T., Nakamura, T., 2007. Sedimentary steryl chlorin esters (SCEs) and other photosynthetic pigments as indicators of paleolimnological change over the last 28,000 years from the Buguldeika saddle of Lake Baikal. Journal of Paleolimnology 37, 163–175.

Spang, A., Hatzenpichler, R., Brochier-Armanet, C., Rattei, T., Tischler, P., Spieck, E., Streit, W., Stahl, D.A., Wagner, M., Schleper, C., 2010. Distinct gene set in two different lineages of ammonia-oxidizing archaea supports the phylum Thaumarchaeota. Trends in Microbiology 18, 331–340.

Squier, A.H., Hodgson, D.A., Keely, B.J., 2002. Sedimentary pigments as markers for environmental change in an Antarctic lake. Organic Geochemistry 33, 1655–1665.

Squier, A.H., Hodgson, D.A., Keely, B.J., 2004. A critical assessment of the analysis and distributions of scytonemin and related UV screening pigments in sediments. Organic Geochemistry 35, 1221–1228.

Steele, J.H., 1962. Environmental control of photosynthesis in the sea. Limnology and Oceanography 7, 137–150.

StreetPerrott, F.A., Huang, Y.S., Perrott, R.A., Eglinton, G., Barker, P., BenKhelifa, L., Harkness, D.D., Olago, D.O., 1997. Impact of lower atmospheric carbon dioxide on tropical mountain ecosystems. Science 278, 1422–1426.

Strous, M., Kuenen, J.G., Jetten, M.S.M., 1999. Key physiology of anaerobic ammonium oxidation. Applied and Environmental Microbiology 65, 3248–3250.

Sturt, H.F., Summons, R.E., Smith, K., Elvert, M., Hinrichs, K.-U., 2004. Intact polar membrane lipids in prokaryotes and sediments deciphered by high-performance liquid chromatography/electrospray ionization multistage mass spectrometry – new biomarkers for biogeochemistry and microbial ecology. Rapid Communications in Mass Spectrometry 18, 617–628.

Summons, R.E., Powell, T.G., 1987. Identification of aryl isoprenoids in source rocks and crude oils: biological markers for the green sulphur bacteria. Geochimica et Cosmochimica Acta 51, 557–566.

Summons, R.E., Jahnke, L.L., Hope, J.M., Logan, G.A., 1999. 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. Nature 400, 554–557.

Sun, D., Chu, G.Q., Li, S.Q., Lu, C.F., Zheng, M.P., 2004. Long-chain alkenones in sulfate lakes and its paleoclimatic implications. Chinese Science Bulletin 49, 2082–2086.

Sun, Q., Chu, G.Q., Liu, G.X., Li, S., Wang, X.H., 2007. Calibration of alkenone unsaturation index with growth temperature for a lacustrine species, *Chrysotila lamellosa* (Haptophyceae). Organic Geochemistry 38, 1226–1234.

Takahashi, K., Yoshioka, T., Wada, E., Sakamoto, M., 1990. Temporal variations in carbon isotope ratio of phytoplankton in a eutrophic lake. Journal of Plankton Research 12, 799–808.

Talbot, H.M., Farrimond, P., 2007. Bacterial populations recorded in diverse sedimentary biohopanoid distributions. Organic Geochemistry 38, 1212–1225.

Talbot, H.M., Squier, A.H., Keely, B.J., Farrimond, P., 2003a. Atmospheric pressure chemical ionisation reversed-phase liquid chromatography/ion trap mass spectrometry of intact bacteriohopanepolyols. Rapid Communications in Mass Spectrometry 17, 728–737.

Talbot, H.M., Summons, R., Jahnke, L., Farrimond, P., 2003b. Characteristic fragmentation of bacteriohopanepolyols during atmospheric pressure chemical ionisation liquid chromatography/ion trap mass spectrometry. Rapid Communications in Mass Spectrometry 17, 2788–2796.

Talbot, H.M., Watson, D.F., Pearson, E.J., Farrimond, P., 2003c. Diverse biohopanoid compositions of non-marine sediments. Organic Geochemistry 34, 1353–1371.

Talbot, H.M., Summons, R.E., Jahnke, L.L., Cockell, C.S., Rohmer, M., Farrimond, P., 2008. Cyanobacterial bacteriohopanepolyol signatures from cultures and natural environmental settings. Organic Geochemistry 39, 232–263.

Tartarotti, B., Baffico, G., Temporetti, P., Zagarese, H.E., 2004. Mycosporine-like amino acids in planktonic organisms living under different UV exposure conditions in Patagonian lakes. Journal of Plankton Research 26, 753–762.

ten Haven, H.L., Rohmer, M., Rullkötter, J., Bisseret, P., 1989. Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. Geochimica et Cosmochimica Acta 53, 3073–3079.

Theissen, K.M., Zinniker, D.A., Moldowan, J.M., Dunbar, R.B., Rowe, H.D., 2005. Pronounced occurrence of long-chain alkenones and dinosterol in a 25,000-year lipid molecular fossil record from Lake Titicaca, South America. Geochimica et Cosmochimica Acta 69, 623–636.

Theroux, S., D'Andrea, W.J., Toney, J., Amaral-Zettler, L., Huang, Y., 2010. Phylogenetic diversity and evolutionary relatedness of alkenone-producing haptophyte algae in lakes: implications for continental paleotemperature reconstructions. Earth and Planetary Science Letters 300, 311–320.

Thiel, V., Jenisch, A., Landmann, G., Reimer, A., Michaelis, W., 1997. Unusual distributions of long-chain alkenones and tetrahymanol from the highly alkaline Lake Van, Turkey. Geochimica et Cosmochimica Acta 61, 2053–2064.

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

Tierney, J.E., Russell, J.M., Huang, Y.S., Sinninghe Damsté, J.S., Hopmans, E.C., Cohen, A.S., 2008. Northern hemisphere controls on tropical southeast African climate during the past 60,000 years. Science 322, 252–255.

Tierney, J.E., Mayes, M.T., Meyer, N., Johnson, C., Swarzenski, P.W., Cohen, A.S., Russell, J.M., 2010a. Late-twentieth-century warming in Lake Tanganyika unprecedented since AD 500. Nature Geoscience 3, 422–425.

Tierney, J.E., Russell, J.M., Eggermont, H., Hopmans, E.C., Verschuren, D., Sinninghe Damsté, J.S., 2010b. Environmental controls on branched tetraether lipid distributions in tropical East African lake sediments. Geochimica et Cosmochimica Acta 74, 4902–4918.

Tierney, J.E., Russell, J.M., Huang, Y.S., 2010c. A molecular perspective on Late Quaternary climate and vegetation change in the Lake Tanganyika basin, East Africa. Quaternary Science Reviews 29, 787–800.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Tierney, J.E., Russell, J.M., Damsté, J.S.S., Huang, Y.S., Verschuren, D., 2011. Late Quaternary behavior of the East African monsoon and the importance of the Congo air boundary. Quaternary Science Reviews 30, 798–807.

Tiljander, M., Karhu, J.A., Kauppila, T., 2006. Holocene records of carbon and hydrogen isotope ratios of organic matter in annually laminated sediments of Lake Korttajarvi, central Finland. Journal of Paleolimnology 36, 233–243.

Toney, J.L., Huang, Y.S., Fritz, S.C., Baker, P.A., Grimm, E., Nyren, P., 2010. Climatic and environmental controls on the occurrence and distributions of long chain alkenones in lakes of the interior United States. Geochimica et Cosmochimica Acta 74, 1563–1578.

Toney, J.L., Leavitt, P.R., Huang, Y. Alkenones are common in prairie lakes of interior Canada. Organic Geochemistry, in press.

Trommer, G., Siccha, M., van der Meer, M.T.J., Schouten, S., Sinninghe Damsté, J.S., Schulz, H., Hemleben, C., Kucera, M., 2009. Distribution of Crenarchaeota tetraether membrane lipids in surface sediments from the Red Sea. Organic Geochemistry 40, 724–731.

Tyler, J.J., Nederbragt, A.J., Jones, V.J., Thurow, J.W., 2010. Assessing past temperature and soil pH estimates from bacterial tetraether membrane lipids: evidence from the recent lake sediments of Lochnagar, Scotland. Journal of Geophysical Research-Biogeosciences 115.

Uchikawa, J., Popp, B.N., Schoonmaker, J.E., Xu, L., 2008. Direct application of compound-specific radiocarbon analysis of leaf waxes to establish lacustrine sediment chronology. Journal of Paleolimnology 39, 43–60.

Vallentyne, J.R., 1954. Biochemical limnology. Science 119, 605–606.

Vallentyne, J.R., 1956. Epiphasic carotenoids in post-glacial lake sediments. Limnology and Oceanography 1, 252–262.

Vallentyne, J.R., 1957. Carotenoids in A 20,000-year-old sediment from Searles Lake, California. Archives of Biochemistry and Biophysics 70, 29–34.

van Dongen, B.E., Talbot, H.M., Schouten, S., Pearson, P.N., Pancost, R.D., 2006. Well preserved palaeogene and cretaceous biomarkers from the Kilwa area, Tanzania. Organic Geochemistry 37, 539–557.

van Dongen, B.E., Roberts, A.P., Schouten, S., Jiang, W.-T., Florindo, F., Pancost, R.D., 2007. Formation of iron sulfide nodules during anaerobic oxidation of methane. Geochimica et Cosmochimica Acta 71, 5155–5167.

Vandenbroucke, M., Largeau, C., 2007. Kerogen origin, evolution and structure. Organic Geochemistry 38, 719–833.

Verleyen, E., Hodgson, D.A., Sabbe, K., Vyverman, W., 2005. Late Holocene changes in ultraviolet radiation penetration recorded in an East Antarctic lake. Journal of Paleolimnology 34, 191–202.

Verschuren, D., Sinninghe Damsté, J.S., Moernaut, J., Kristen, I., Blaauw, M., Fagot, M., Haug, G.H., 2009. Half-precessional dynamics of monsoon rainfall near the East African Equator. Nature 462, 637–641.

Versteegh, G.J.M., Bosch, H.-J., de Leeuw, J.W., 1997. Potential palaeoenvironmental information of C_{24} to C_{36} mid-chain diols, keto-ols and mid-chain hydroxy fatty acids; a critical review. Organic Geochemistry 27, 1–13.

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. Organic Geochemistry 9, 83–99.

Volkman, J.K., 2003. Sterols in microorganisms. Applied Microbiology and Biotechnology 60, 495–506.

Volkman, J.K., Burton, H.R., Everitt, D.A., Allen, D.I., 1988. Pigment and lipid compositions of algal and bacterial communities in Ace Lake, Vestfold Hills, Antarctica. Hydrobiologia 165, 41–57.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., Jeffrey, S.W., 1992. C_{30}–C_{32} alkyl diols and unsaturated alcohols in microalgae of the class *Eustigmatophyceae*. Organic Geochemistry 18, 131–138.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., Jeffrey, S.W., 1993. Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. Organic Geochemistry 20, 7–15.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., 1994. C_{25} and C_{30} highly branched isoprenoid alkenes in laboratory cultures of two marine diatoms. Organic Geochemistry 21, 407–413.

Volkman, J.K., Barrett, S.M., Blackburn, S.I., Sikes, E.L., 1995. Alkenones in *Gephyrocapsa oceanica*: implications for studies of paleoclimate. Geochimica et Cosmochimica Acta 59, 513–520.

Volkman, J.K., Farmer, C.L., Barrett, S.M., Sikes, E.L., 1997. Unusual dihydroxysterols as chemotaxonomic markers for microalgae from the order Pavlovales (Haptophyceae). Journal of Phycology 33, 1016–1023.

Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., Gelin, F., 1998. Microalgal biomarkers: a review of recent research developments. Organic Geochemistry 29, 1163–1179.

Volkman, J.K., Rijpstra, W.I.C., de Leeuw, J.W., Mansour, M.P., Jackson, A.E., Blackburn, S.I., 1999. Sterols of four species of dinoflagellates from the genus *Prorocentrum*. Phytochemistry 52, 659–668.

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

Walsh, E.M., Ingalls, A.E., Keil, R.G., 2008. Sources and transport of terrestrial organic matter in Vancouver Island fjords and the Vancouver–Washington margin: a multiproxy approach using $\delta^{13}C_{org}$, lignin phenols, and the ether lipid BIT index. Limnology and Oceanography 53, 1054–1063.

Wang, R., Zheng, M., 1998. Occurrence and environmental significance of long-chain alkenones in Tibetan Zabuye Salt Lake, S.W. China. International Journal of Salt Lake Research 6, 281–302.

Wang, Y.J., Cheng, H., Edwards, R.L., An, Z.S., Wu, J.Y., Shen, C.C., Dorale, J.A., 2001. A high-resolution absolute-dated Late Pleistocene monsoon record from Hulu Cave, China. Science 294, 2345–2348.

Waters, M.N., Schelske, C.L., Kenney, W.F., Chapman, A.D., 2005. The use of sedimentary algal pigments to infer historic algal communities in Lake Apopka, Florida. Journal of Paleolimnology 33, 53–71.

Watson, D.F., Farrimond, P., 2000. Novel polyfunctionalised geohopanoids in a recent lacustrine sediment (Priest Pot, UK). Organic Geochemistry 31, 1247–1252.

Weijers, J.W.H., Schouten, S., Hopmans, E.C., Geenevasen, J.A.J., David, O.R.P., Coleman, J.M., Pancost, R.D., Sinninghe Damsté, J.S., 2006a. Membrane lipids of mesophilic anaerobic bacteria thriving in peats have typical archaeal traits. Environmental Microbiology 8, 648–657.

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

Weijers, J.W.H., Schefuß, E., Schouten, S., Sinninghe Damsté, J.S., 2007a. Coupled thermal and hydrological evolution of tropical Africa over the last deglaciation. Science 315, 1701–1704.

Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S., 2007b. Environmental controls on bacterial tetraether membrane lipid distribution in soils. Geochimica et Cosmochimica Acta 71, 703–713.

Welander, P.V., Coleman, M.L., Sessions, A.L., Summons, R.E., Newman, D.K., 2010. Identification of a methylase required for 2-methylhopanoid production and implications for the interpretation of sedimentary hopanes. Proceedings of the National Academy of Sciences of the United States of America 107, 8537–8542.

Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and fresh-water environments – CO_2 reduction vs acetate fermentation isotope evidence. Geochimica et Cosmochimica Acta 50, 693–709.

Willerslev, E., Cappellini, E., Boomsma, W., Nielsen, R., Hebsgaard, M.B., Brand, T.B., Hofreiter, M., Bunce, M., Poinar, H.N., Dahl-Jensen, D., Johnsen, S., Steffensen, J.P., Bennike, O., Schwenninger, J.L., Nathan, R., Armitage, S., de Hoog, C.J., Alfimov, V., Christl, M., Beer, J., Muscheler, R., Barker, J., Sharp, M., Penkman, K.E.H., Haile, J., Taberlet, P., Gilbert, M.T.P., Casoli, A., Campani, E., Collins, M.J., 2007. Ancient biomolecules from deep ice cores reveal a forested Southern Greenland. Science 317, 111–114.

Withers, N., 1983. Dinoflagellate sterols. In: Marine Natural Products: Chemical and Biological Perspectives. Academic Press, New York, pp. 87–130.

Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi, Y., Brock, B.E., Amour, N.A.S., Mark, W.A., Edwards, T.W.D., 2007. Progress in isotope paleohydrology using lake sediment cellulose. Journal of Paleolimnology 37, 221–231.

Woltemate, I., Whiticar, M.J., Schoell, M., 1984. Carbon and hydrogen isotopic composition of bacterial methane in a shallow fresh-water lake. Limnology and Oceanography 29, 985–992.

Woltering, M.L., Werne, J.P., Hicks, R.E., Kish, J.L., Schouten, S., Sinninghe Damsté, J.S., 2010. Spatial and temporal variability of Crenarchaeota in Lake Superior and implication for the application of the TEX_{86} temperature proxy. Abstract PP41A-1609 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13–17 Dec.

Woltering, M., Johnson, T.C., Werne, J.P., Schouten, S., Sinninghe Damsté, J.S., 2011. Late Pleistocene temperature history of Southeast Africa: a TEX_{86} temperature record from Lake Malawi. Palaeogeography, Palaeoclimatology, Palaeoecology 303, 93–102.

Wraige, E.J., Belt, S.T., Lewis, C.A., Cooke, D.A., Robert, J.M., Masse, G., Rowland, S.J., 1997. Variations in structures and distributions of C_{25} highly branched isoprenoid (HBI) alkenes in cultures of the diatom, Haslea ostrearia (Simonsen). Organic Geochemistry 27, 497–505.

Wraige, E.J., Belt, S.T., Masse, G., Robert, J.M., Rowland, S.J., 1998. Variations in distributions of C_{25} highly branched isoprenoid (HBI) alkenes in the diatom, Haslea ostrearia: influence of salinity. Organic Geochemistry 28, 855–859.

Wuchter, C., Schouten, S., Wakeham, S.G., Sinninghe Damsté, J.S., 2005. Temporal and spatial variation in tetraether membrane lipids of marine Crenarchaeota in particulate organic matter: implications for TEX_{86} paleothermometry. Paleoceanography 20, PA3013. doi:10.1029/2004PA001110.

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

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

Wunsam, S., Schmidt, R., 1995. A diatom-phosphorus transfer function for Alpine and pre-alpine lakes. Memorie dell'Istituto Italiano di Idrobiologia 53, 85–99.

Xu, Y., Jaffé, R., 2008. Biomarker-based paleo-record of environmental change for an eutrophic, tropical freshwater lake, Lake Valencia, Venezuela. Journal of Paleolimnology 40, 179–194.

Xu, Y., Simoneit, B.R.T., Jaffé, R., 2007. Occurrence of long-chain n-alkenols, diols, keto-ols and sec-alkanols in a sediment core from a hypereutrophic, freshwater lake. Organic Geochemistry 38, 870–883.

Zander, J.M., Caspi, E., Pandey, G.N., Mitra, C.R., 1969. The presence of tetrahymanol in *Oleandra wallichii*. Phytochemistry 8, 2265–2267.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009

Zhang, Z.H., Sachs, J.P., 2007. Hydrogen isotope fractionation in freshwater algae: I. Variations among lipids and species. Organic Geochemistry 38, 582–608.
Zhang, Z.H., Sachs, J.P., Marchetti, A., 2009. Hydrogen isotope fractionation in freshwater and marine algae: II. Temperature and nitrogen limited growth rate effects. Organic Geochemistry 40, 428–439.
Zheng, Y.H., Zhou, W.J., Xie, S.C., Yu, X.F., 2009. A comparative study of n-alkane biomarker and pollen records: an example from southern China. Chinese Science Bulletin 54, 1065–1072.
Zhu, C., Talbot, H.M., Wagner, T., Pan, J.M., Pancost, R.D., 2010. Intense aerobic methane oxidation in the Yangtze Estuary: a record from 35-aminobacteriohopanepolyols in surface sediments. Organic Geochemistry 41, 1056–1059.
Zink, K.-G., Leythaeuser, D., Melkonian, M., Schwark, L., 2001. Temperature dependency of long-chain alkenone distributions in recent to fossil limnic sediments and in lake waters. Geochimica et Cosmochimica Acta 65, 253–265.
Zink, K.-G., Wilkes, H., Disko, U., Elvert, M., Horsfield, B., 2003. Intact phospholipids – microbial "life markers" in marine deep subsurface sediments. Organic Geochemistry 34, 755–769.
Zink, K.G., Vandergoes, M.J., Mangelsdorf, K., Dieffenbacher-Krall, A.C., Schwark, L., 2010. Application of bacterial glycerol dialkyl glycerol tetraethers (GDGTs) to develop modern and past temperature estimates from New Zealand lakes. Organic Geochemistry 41, 1060–1066.

Please cite this article in press as: Castañeda, I.S., Schouten, S., A review of molecular organic proxies for examining modern and ancient lacustrine environments, Quaternary Science Reviews (2011), doi:10.1016/j.quascirev.2011.07.009