1 **Lipid biomarkers and pertinent indices from aquatic environment record**
2 **palaeoclimate and palaeoenvironment changes**

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15 **Abstract**

16 Lipid biomarkers and their pertinent indices have been used as the most effective
17 proxies for palaeoclimate and palaeoenvironment conditions. This paper conducts a
18 systematic review on a variety of lipid biomarkers in aquatic sediments and water
19 column that are used as proxies tracing palaeoclimate and palaeoenvironment
20 information. The sources of those lipid biomarkers are autochthonous and/or
21 allochthonous. General mechanisms of lipid biomarkers used as paleoclimate and
22 palaeoenvironment archives include characteristics of carbon chain distribution,
23 temperature adaptation and combined temperature and humidity adaptation. Different
24 lipid indices underpinned by the mechanisms are surrogates for the past precipitation,
25 temperature and humidity as well as plant succession. We propose that the combined
26 use of lipid indices and other biomarkers can expand the outlook of individual index,
27 and provide a better understanding of paleoclimate and palaeoenvironment
28 reconstruction.

29 **Keywords:** Aquatic environment; lipid; palaeoclimate; palaeoenvironment

30 **Highlights**

- 31 ► Lipids from aquatic environment are ubiquitous biomarkers in organic
- 32 geochemistry.
- 33 ► Lipids are increasingly used as proxies for palaeoclimate and palaeoenvironment.
- 34 ► Lipid indices from aquatic sediments and water column have been developed.
- 35 ► Lipids are suggested to be combined with other biomarkers as proxies.

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1. Introduction

The study of lipid dynamics is germane to understanding the consequences of numerous threats confronted by the global ecosystem, e.g. climate change, contaminants, cultural eutrophication and invasive species (Arts et al., 2009). Among the branches of this study, one of the priorities is given to apply geochemical biomarkers in terms of lipids from the aquatic environment (including sediments and water column) to extrapolate changes in palaeoclimate and palaeoenvironment. Lipid biomarkers are biochemicals from a limited range of organic compounds, and thereby offer a highly selective means of isolating substances of specific origins (Sauer et al., 2001a). The hydrophobic nature of lipid biomarkers results in a convenient way of separating them from other compounds in an aquatic sample matrix (Arts & Wainmann, 1999), while the application of other sedimentary matter as palaeoclimate and palaeoenvironment proxies such as carbonate, kerogen and cellulose, are often hindered by isolating purely autochthonous substances (Hedges et al., 1997; Sauer et al., 2001b). Hence, lipid biomarkers have been used as the most effective palaeoclimate and palaeoenvironment proxies in the aquatic organism communities.

Lipid biomarkers and related indices from coastal peat receiving nutrients and moisture from precipitation provide special archives of continental climate change (Barber et al., 1994; Blackford, 2000; van der Linden & van Geel, 2006; Xie et al., 2004). Oceanic sediments regulate high-resolution, continuous and widespread palaeoceanographic archives from a noticeable portion of geologic history (Seki et al., 2012). In particular, due to the ubiquity of oceanic Archaea, of which membrane lipids are sensitive to temperature variation, these lipids have served as palaeoclimate proxies (Kim et al., 2008; Kim et al., 2010; Leider et al., 2010). Lipid biomarkers and their indices from

65 lacustrine sediments could record environmental variability and indicate high
66 sensitivity to regional climate change (Romero-Viana et al., 2012). Also Lacustrine
67 sediment records with annual laminations are one of the primary targets for acquiring
68 high-resolution climate records (Brauer et al., 2008), and thus understanding the
69 underlying forces (Jones et al., 2009). They are especially useful records of
70 palaeoclimate information since they may reflect continuous time series and contain
71 multiple geochemical and microfossil proxies, which may be employed to verify
72 extrapolated palaeoclimate signals (Birks & Birks, 1980; Faegri et al., 1989; Meyers &
73 Lallier-Verge's, 1999; Smol, 1995). In addition, there is increasing concern upon lipid
74 biomarkers in water column as climatic archives. Some lipid biomarkers such as
75 crenarchaeal isoprenoid glycerol dibiphytanyl glycerol tetraethers (iGDGTs),
76 synthesized by marine crenarchaeota in the water column, can be used to record the
77 variation of sea surface temperatures (SSTs) (Kim et al., 2010). Furthermore, different
78 indices based on lipid biomarkers from aquatic sediments and water column are
79 practical proxies tracing palaeoclimate and palaeoenvironmental variability (Prah &
80 Wakeham, 1987; Street-Perrott et al., 1997; Xie et al., 2004). These indices involve a
81 variety of members such as δD or D/H ratios, U_{37}^K , n-Alkane chain length index,
82 glycerol dibiphytanyl glycerol tetraethers (GDGTs) based indexes, carbon preference
83 index (CPI) and various fatty acid indices. They have been applied to reconstruct past
84 precipitation, temperature and humidity, and some are used as SSTs.

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86 To date, there is a lack of systematical syntheses with regard to the lipid biomarkers
87 and related indices from aquatic environment indicating palaeoclimate and
88 palaeoenvironment, although palaeoclimate and palaeoenvironment studies in terms of
89 organisms in aquatic sediments and water column have been undertaken since last

century (Brassell et al., 1986; Cranwell, 1973; Schiegl, 1972). Kim et al. (2008) conducted a review of TetraEther index of tetraethers consisting of 86 carbon atoms (TEX86) derived from GDGTs in the marine environment, implicating past SSTs. Barron and Anderson (2011) compiled lacustrine and marine proxies for the Pacific climate from the northeastern Pacific, including carbonate, pollen evidence, ice core but only one lipid biomarker (i.e. alkenone) was used. Castaneda (2011) reviewed organic proxies for lacustrine environments. Bianchi (2011) referred to the lipid biomarkers from aquatic ecosystems but tend to extrapolate their application in deducing sources of organic matter, except for a brief description of TEX86 and GDGTs as paleoclimatic biomarkers. However, these reviews either focus on the specific proxy for climate conditions or on a wide range of proxies for specific aquatic environment (e.g. lacustrine or marine environment (Volkman, 2006)) and regions. Therefore, a focused review of lipid biomarkers and related indices as proxies for palaeoclimate and palaeoenvironmental variability is urgent.

This study is presented to establish the framework of lipid biomarkers and their pertinent indices applied as palaeoclimate and palaeoenvironment proxies. We aimed to: (1) classify a variety of lipid biomarkers into different groups and propose their mechanisms as palaeoclimate and palaeoenvironment proxies; (2) analyse indices regarding various lipid biomarkers and compare them according to their suitability for different palaeoclimate parameters and aquatic environments; (3) evaluate the application of combined indices in estimating palaeoclimate and palaeoenvironmental conditions.

2. Lipid biomarkers used in palaeoclimate and palaeoenvironment estimation

2.1 Lipid biomarkers in aquatic environment and their sources

Organic compounds identified in aquatic sediments can be directly linked with their source organisms (Brassell et al., 1983). Lipid biomarkers from aquatic sediments, which are used as palaeoclimate and palaeoenvironment proxies, mainly consist of alkanes, alkenes, alkanols, sterols, ketones, fatty acids, GDGTs and so forth. These biomarkers are derived from a wide variety of origins, including but not limit to (1) upland terrestrial plants (Street et al., 2013; Vogts et al., 2009), (2) emergent macrophytes (Cranwell, 1973, 1974; Cranwell et al., 1987; Eglinton & Hamilton, 1967; Street et al., 2013; Wiesenberg & Schwark, 2006), (3) floating and submerged macrophytes (Seki et al., 2009; Street et al., 2013), (4) algae (Cranwell et al., 1987; Guo et al., 2015), (5) fauna (Fulco, 1983; Volkman et al., 1980a), (6) bacteria (including archaea) (Horikawa et al., 2010; Vogts et al., 2009), and moss (Nott et al., 2000).

Autochthonous macrophytes and microbes are natural origins of aquatic lipid biomarkers, while terrigenous and/or allochthonous origins remain confusing without clarification. Leaf wax constituents of terrestrial plants are a significant source of biomass in the geological records of soils, as well as lacustrine and marine sediments. Specifically, long-chain n-alkanes and n-alkan-1-ols of plant waxes are so rich that they represent over 60% of the epicuticular lipids (Tulloch, 1976). Leaf wax lipids may be transported over substantial distances by rivers and wind, relying on environmental conditions. Accordingly, biomarkers of land plants may end up occurring in soils and lacustrine or marine sediments, and present an integrated signal for wax composition of the plant species in the catchment area (Vogts et al., 2009).

140 Marine water column is also a unique source of lipid biomarkers. In marine waters,
141 iGDGTs are principally biosynthesized by Marine Group I Crenarchaeota, which are
142 one of the predominant prokaryotes in current oceans (Herndl et al., 2005; Karner et al.,
143 2001). Particularly, gas hydrate and/or methane-rich deep sea environments show
144 distinct GDGT distribution profiles, i.e. by the dominance of GDGTs with 1-3
145 cyclopentane rings, which are contributed by methane-oxidizing archaea related to the
146 methane hydrate (Blumenberg et al., 2004; Pancost et al., 2001).

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148 Molecular distributions of lipids from different origins are distinguished. The marine
149 coccolithophorid *Emiliana huxleyi* (Phymnesiophyceae) and members of the class
150 Prymnesiophyceae are now the recognized sources of the long-chain (C₃₇, C₃₈, C₃₉) di-,
151 tri- and tetra-unsaturated methyl and ethyl ketones (alkenones) (Brassell et al., 1986;
152 Prahl & Wakeham, 1987). Bacteria and algae generate short-chain alkanes and
153 n-alkanoic acids (Gelpi et al., 1970). The n-C₂₅ to n-C₃₅ alkanes originate from the leaf
154 waxes of upland vegetation (Cranwell et al., 1987; Eglinton & Hamilton, 1967; Street
155 et al., 2013). n-Alkanes in aquatic plants (floating and submerged) are featured with a
156 dominance of middle chain length, e.g. C₂₃ and C₂₅, whereas those of terrestrial
157 vegetation are predominated by long-chain homologues (> C₂₉) (Seki et al., 2012).
158 Emergent aquatic plants have a distribution pattern midway between those of
159 non-emergent and terrestrial vegetation (Ficken et al., 2000). Crenarchaeota and some
160 Euryarchaeota are capable of synthesizing iGDGTs (Blumenberg et al., 2004; Koga et
161 al., 1993; Macalady et al., 2004; Turich et al., 2007; Zhang et al., 2011), and it was
162 suggested that branched GDGTs (bGDGTs) are produced by some members of the
163 acidobacteria (Liu et al., 2010; Sinninghe Damsté et al., 2011; Weijers et al., 2009;

Weijers et al., 2006). The specific lipid biomarkers and their sources are indicated in Table 1.

2.2 Mechanisms of lipids as palaeoclimate and palaeoenvironment proxies

Different lipids serve as palaeoclimate and palaeoenvironment proxies according to various mechanisms: (1) characteristics of carbon chain distribution indicate lipid sources, of which changes are surrogates for fluctuations in continental climates (Meyers, 1997), and (2) temperature adaptation mechanisms of lipids, reflected by either lipid biomarkers in the source organisms or pertinent lipid indicators, e.g. the membrane lipids of Archea (Kim et al., 2008; Kim et al., 2010; Leider et al., 2010). Furthermore, (3) biochemical adaptation to combined temperature and humidity is another important mechanism, including the sensitivity of CPI and δD values to climatic conditions.

n-Alkanes preserve the history of lipid input to sediment owing to their resistance to degradation and early diagenetic change (Giger et al., 1980; Meyers, 1997; Radke et al., 2005), and the characteristics of carbon chains reflect their origins. For instance, sedimentary n-alkane distributions with a high preference of odd-over-even and long chain lengths ($>nC_{23}$) are indicative of a higher proportion of plant origin (Cranwell et al., 1987; Meyers, 1997). In comparison, algal n-alkanes are prone to maximize at shorter chain lengths (nC_{17} - nC_{19}) (Cranwell et al., 1987; Giger et al., 1980; Meyers, 1997).

Some lipid classes, e.g. alkyl diols, alkenones and highly branched isoprenoid alkenes appear to possess a limited occurrence in microalgae, and as such are useful

189 biomarkers for identifying sources of organic matter in sediments (Volkman et al.,
190 1998). The identical δD values for sterols originating from plankton suggest that
191 various primary producers all impart similar fractionation factors, such that any
192 phytoplanktonic sterol may potentially serve as a tracer for source water δD , and thus
193 climate information.

194
195 Long-chain unsaturated ketones (alkenones) have been discovered in several species of
196 haptophytes (Conte et al., 1994; Marlowe et al., 1984; Volkman et al., 1980b),
197 including the widely distributed coccolithophorids *Emiliana huxleyi* and
198 *Gephyrocapsa oceanica*, in which the ratio of tri- to di-unsaturated C_{37} alkenones
199 increases with declining growth temperatures (Brassell et al., 1986; Conte et al., 1994).

200
201 Fatty acids are an especially promising class of compounds for palaeoclimatic proxies
202 owing to the likelihood of simultaneously reconstructing changes of both temperature
203 and moisture trade-off (Hou et al., 2006). Saturated fatty acids has been reported to
204 accumulate more in high temperatures and decrease in cold temperatures (Guschina &
205 Harwood, 2006; Ravet et al., 2010), whereas polyunsaturated fatty acids accumulate
206 more in cold temperatures to increase cell membrane fluidity (Guschina & Harwood,
207 2006; Piepho et al., 2012).

208
209 GDGTs are very stable and resistant to degradation or oxidation in geological
210 formations (Kuypers et al., 2001). Hence GDGTs stored in sediments might act as
211 biomarkers recording abundant palaeo-biology and environmental information (Brocks
212 & Pearson, 2005; Eglinton & Eglinton, 2008). In particular, it was indicated by culture
213 experiments that the relative distribution of the cyclopentane rings in the iGDGTs of

some thermophilic archaea relies on growth temperature, which is in general regarded to be a mechanism for temperature adaptation of the membrane (De Rosa & Gambacorta, 1988; Gliozzi et al., 1983; Uda et al., 2001).

3. Mechanism oriented lipid indices tracing palaeoclimate and palaeoenvironment

3.1 Mechanism 1 oriented indices

Molecular distribution of n-alkanes, namely n-alkanes chain length index such as average chain length (ACL), C₂₇-C₃₁ n-alkane ratio (C₂₇/C₃₁), n-alkane C₃₁/(C₂₉+ C₃₁) ratio, and P_{aq} index might serve as conventional proxies of continental climate (Vogts et al., 2009), source inputs of plants (Ficken et al., 2000), and vegetation changes (Horikawa et al., 2010). Amongst this community, the most representative indices are P_{aq} and ACL.

(1) P_{aq}

Ficken et al. (2000) defines P_{aq} to reflect the proportion of non-emergent aquatic macrophyte input to lacustrine sediments in relation to that from the terrestrial and emergent plants. Later P_{aq} was also used to assess past changes in water level since vegetation in specific aquatic environment remarkably relies on water level (Nichols et al., 2006), and thereby palaeoprecipitation information. It expresses the relative percentage of mid-chain length to long-chain length homologues:

$$P_{aq} = \frac{C_{23}+C_{25}}{C_{23}+C_{25}+C_{29}+C_{31}} \quad (8)$$

The inference of palaeoprecipitation information via P_{aq} lies in the significant difference of n-alkane distribution for terrestrial and (non) emergent aquatic plants, and the linkage amongst vegetation variation, water level changes and effective

precipitation. To start with, the floating and submerged plants indicates n-alkane distribution tend to maximize at C₂₃ or C₂₅ (Ficken et al., 2000), while that of emergent and terrestrial plants maximizes at C₂₉ or C₃₁ (Cranwell, 1973; Ficken et al., 2000). Thus P_{aq} , reflecting different input of these plants to sediments (Fig. 4), does also measure the changes of water level. What's more, since effective precipitation controls the water level of bogs, past changes in precipitation can be estimated from water level changes (Seki et al., 2009; Zheng et al., 2007), and even have more implications. For example, Zheng et al. (2007) inferred low water level events from low P_{aq} values in sediment cores of a peat bog, likely associated with declined precipitation resulted from episodes of weakened Asian summer monsoons, and low water level fluctuations correspond to chilly and dry events.

(2) ACL

ACL is the concentration-weighted average chain length of the C₂₇ to C₃₃ n-alkanes that occur in a geological sample (Poynter et al., 1989), and is expressed as follows:

$$ACL = \frac{\sum(C_i * [C_i])}{\sum[C_i]} \quad (9)$$

where $\sum[C_i]$ denotes the concentration of the n-alkanes with carbon number C_i , over the range 27-33.

ACL is used to reconstruct temperature, and even the combination of humidity and temperature, attributing to distinguished biosynthetic pathways of n-alkanes in different climate conditions and the influence of precipitation mode (Fig. 5). First of all, differences in growing-season temperatures of the source regions have historically interpreted alterations in the chain length distributions of plant wax n-alkanes in

sediments (Poynter et al., 1989) and in dust samples (Gagosian & Peltzer, 1986; Simoneit, 1991). Specifically, terrestrial plants are postulated to biosynthesize somewhat shorter chain compounds in cooler temperate regions, while longer chain compounds are yielded for their wax coatings in warmer tropical regions (Gagosian & Peltzer, 1986). Furthermore, Zhou et al. (2005) suggested that the regional precipitation regime has an impact on the chain-length distribution of leaf-wax lipids. Accordingly, the n-alkane ACL might reflect a combination of both humidity and temperature.

3.2 Mechanism 2 oriented indices

(1) U_{37}^K

U_{37}^K refers to the alkenone unsaturation index, and was initiated for palaeoclimatic proxies by Brassell et al. (1986) to estimate SSTs 500, 000 cal yr BP in the east Atlantic ocean. Subsequently, its use as palaeoclimatic archive was extended to the north-east Atlantic ocean (Prah1 & Wakeham, 1987), the South China Sea (Zhao et al., 2006) and other regions (Meyers, 1997). It is originally expressed as follows

$$U_{37}^k = \frac{[C_{37:2}] - [C_{37:4}]}{[C_{37:2}] + [C_{37:3}] + [C_{37:4}]} \quad (1)$$

where $C_{37:2}$, $C_{37:3}$ and $C_{37:4}$ denotes the quantity of di-, tri- and tetra-unsaturated ketones, respectively. Later, Prah1 and Wakeham (1987) pointed out $C_{37:4}$ may be ignored from the definition of U_{37}^k because it is rarely found in sediments, and the above expression is simplified as

$$U_{37}^k = \frac{[C_{37:2}]}{[C_{37:2} + C_{37:3}]} \quad (2)$$

289

290 Since the initiation of U_{37}^k for SSTs proxy, studies using this proxy have focused on
 291 establishing the accuracy and calibration using cultures, particulate organic matter,
 292 sediment traps and sediment core-tops (Herbert, 2003). U_{37}^k used as the surrogate of
 293 SSTs is linked to the source of alkenones and the variability of alkenone unsaturation
 294 with growth temperatures. Firstly, alkenones come exclusively from several species of
 295 haptophyte algae, which require sunlight and in general prefer the upper photic zone.
 296 Secondly, Brassell, Eglinton et al. (1986) proposed that the variability of alkenone
 297 unsaturation found in different latitudes, as indicated by U_{37}^k , suggests mutual trends
 298 owing to the inherent global and regional variation in SSTs resulting from oceanic
 299 circulation features. Generally, U_{37}^k increases from the high southern or northern
 300 latitudes to the equator and is positively proportional to SSTs. Further, numerous
 301 studies have attempted to establish the calibration models for SST proxy via U_{37}^k
 302 since Prahl and Wakeham (1987) set up the linear relationship between SST and U_{37}^k .
 303 Conte et al. (2006) summarized the published studies and established global calibration
 304 models for SST from surface water and sediments (Fig. 2). The U_{37}^k proxy is rather
 305 robust since it does not require knowledge of the composition of original sea water and
 306 can be analyzed with relatively high precision (Herbert, 2003).

307

308 However, the application of U_{37}^k as a palaeoclimatic proxy seems to be limited to
 309 marine sediments and its accuracy may be disturbed by the impact of other factors on
 310 U_{37}^k in addition to temperature. Although alkenones have also been found in lacustrine
 311 sediments with U_{37}^k values of 0.16~0.58, attempts to employ U_{37}^k values in some
 312 lacustrine sediments have proved less successful (Li et al., 1996). Also it seems likely

from the anomalous compositional data reported from some aquatic environments that environmental factors in addition to temperature might also affect the proportions of these compounds (Meyers, 1997). Moreover, additional impacts on U_{37}^K values include the geological and evolutionary succession of species that contribute alkenones to sediments (Thierstein, 1977). Diagenetic effects can also influence the U_{37}^K values. Even in a given growth temperature, U_{37}^K values from Prahl and Wakeham (1987) were consistently higher than those of Brassell et al. (1986) and extrapolation of the discrepancy was lacking. Aside from the above restrictions, U_{37}^K values were revealed to be little altered at temperatures below $\sim 5^\circ\text{C}$ of the cold waters in the Southern Ocean (Sikes & Volkman, 1993), tri-unsaturated alkenones arrive at their detection limit which could complicate the reconstruction of SSTs above 28°C with U_{37}^K (Kim et al., 2008).

(2) GDGT-based index

Palaeoclimate archives have been widely reconstructed via GDGT-based indexes, including the iGDGT-based index, i.e. Tetraether index of tetraethers constituting 86 carbon atoms (TEX_{86}), and bGDGT-based indexes, i.e. the methylation index of bGDGTs (MBT).

1) TEX_{86}

Based on archaeal tetraether lipids, TEX_{86} was proposed to serve as a SST proxy. Schouten et al. (2002) initiated the application of TEX_{86} index as per the relative distribution of cyclopentane rings in core-top marine sediments, unravelling a linear relationship with SSTs. The archaeal tetraether lipids, biosynthesized by marine Crenarchaeota, consist of different GDGTs containing 0-3 cyclopentane moieties (I - IV) and crenarchaeol (V), as well as small quantities of a regio-isomer of crenarchaeol

(V'). Accordingly, TEX_{86} is proposed as a means to quantify the relative abundance of GDGTs and expressed as follows.

$$TEX_{86} = \frac{[III] + [IV] + [V']}{[II] + [III] + [IV] + [V']} \quad (4)$$

Later, Kim et al. (2010) defines two calibration models derived from TEX_{86} , namely TEX_{86}^L and TEX_{86}^H , and are expressed as follows.

$$TEX_{86}^L = lg \frac{[III] + [IV]}{[II] + [III] + [IV]} \quad (5)$$

$$TEX_{86}^H = lg TEX_{86} \quad (6)$$

It is suggested that TEX_{86}^L is more fit for SST estimates than TEX_{86} in (sub) polar ocean systems, as V' does not seem to be considerably important in the membrane adaptation of Marine Group I Crenarchaeota to temperature. In contrast, TEX_{86}^H is probably the most suitable index for reconstructing SSTs for (sub) tropical oceans and greenhouse periods where SSTs were much higher than today ($> 30^\circ\text{C}$) because V' seems to assume a much more important role in temperature adaptation, resulting in the smaller error of SST estimates derived from TEX_{86}^H in comparison with TEX_{86}^L (Kim et al., 2010).

The use of TEX_{86} as a SST proxy stems from the stability and ubiquitous distribution of GDGTs and the positive relationship between cyclopentane moieties and

temperature. Firstly, GDGTs are very stable and resistant to degradation or oxidation in geological formations (Kuypers et al., 2001). Hence, GDGTs stored in sediments might act as biomarkers recording abundant palaeo-biology, ecology and environmental information (Brocks & Pearson, 2005; Eglinton & Eglinton, 2008). Secondly, the relative amount of cyclopentane moieties rises with growth temperature from culture studies on the membrane composition of hyperthermophilic archaea (Gliozzi et al., 1983; Uda et al., 2001), and a rise in the relative number of GDGTs with 2 or more cyclopentane moieties for marine Crenarchaeota from an initial mesocosm study (Wuchter et al., 2004). Therefore, growth temperature can be determined from the relative number of GDGTs occurring in marine sediments, which can be quantified by TEX₈₆.

Different calibration models have been developed for TEX₈₆ and its derived indicators of SST proxy, with varied temperature ranges (Fig. 3). Generally, this array of indicators is best applicable in marine sediments, and application in lacustrine sediments primarily limited in large lakes with relatively high production in comparison with terrestrial input (Kim et al., 2008). Furthermore, different calibration models for marine sediments demonstrate difference. The different slope and intercept of the equations with regard to mesocosm experiments and core-top calibration models are probably due to lower relative abundance of V' in the mesocosm series than in the core-tops from the subtropical to tropical regions (Schouten et al., 2007; Wuchter et al., 2004). Despite the above linear models, the polynomial models, established by Kim et al. (2008), reflects the signal is represented by the global core-top TEX₈₆ data at water depth from 0 to 4000m. Collectively, the provided models all show the positive proportional relationship between TEX₈₆ or its derived indicators and temperature.

385

386 TEX_{86} outweighs U_{37}^{K} in SST reconstruction. Specifically, TEX_{86} has a potential to
387 be a useful proxy for temperature in Polar Oceans where U_{37}^{K} cannot be used, because
388 of the universal emergence of Crenarchaeota in oceans. However, the reconstruction of
389 SSTs with TEX_{86} is hampered by the impact of allochthonous sources and
390 Crenarchaeota, as well as the calibration approach. Weijers et al. (2006) pointed out
391 that a substantial bias in the TEX_{86} signal may emerge if the terrestrial organic matter
392 input to marine and lake systems is high. In addition, it is clear that the correlation
393 between TEX_{86} values and temperature varies in some parts of the ocean, likely
394 relying on the ecology and seasonality of Crenarchaeota (Kim et al., 2008). Moreover,
395 one of the most important problems is the calibration of TEX_{86} with s , which employs
396 less sensitive high performance liquid chromatography/mass spectrometry techniques.

397 2) MBT

398 Since Weijers et al. (2007a) reported that MBT is positively correlated with the mean
399 air temperature (MAT), MBT has widespread application in estimating
400 palaeotemperature. MBT accounts for the degree of methylation at position C-5 and
401 C-5' of the bGDGTs and is defined as follows.

402

$$403 \quad MBT = \frac{[I + Ib + Ic]}{[I + Ib + Ic] + [II + IIb + IIc] + [III + IIIb + IIIc]} \quad (7)$$

404

405 where I , II and III denotes bGDGTs containing none, one or two additional methyl
406 branches on the position C-5 and C-5', respectively, b and c denotes bGDGTs
407 containing one or two cyclopentyl moieties, respectively. A high MBT value represents
408 a low degree of methylation.

409

MBT reconstruction of MAT derives from the fact that the bGDGT-producing bacteria adapt their membrane lipid composition to temperature by altering the number of methyl groups on the carbon chains.

The application of MBT as palaeoclimate proxies is restrained by a number of factors. Firstly, its use in lacustrine sediments should be cautious, as there is a separate source of GDGTs except for a soil-derive source, likely from in situ production of bGDGTs with the lakes and/or rivers (Tierney & Russell, 2009). Secondly, with regard to marine sediments, it should only be utilized at sites with an adequate input of soil organic matter in relation to the amount of marine organic matter, i.e. at sites adjacent to the mouth of rivers with a catchment area where adequate soil forms (Blaga et al., 2010).

3.3 Mechanism 3 oriented indices

(1) δD or D/H ratio and $\delta^{13}C$

Compound-specific hydrogen isotope analysis (CSHIA) has been developed to acquire palaeoclimatic information from δD or D/H ratios of individual organisms in recent years (Andersen et al., 2001; Dawson et al., 2004; Huang et al., 2002; Huang et al., 2004; Sauer et al., 2001a; Sessions et al., 1999; Yang & Huang, 2003). Current knowledge suggests that the fractionation of hydrogen isotopes in biosynthesis is constant and tends to be controlled by the biochemical pathway used (Sessions et al., 1999). Consequently, δD values of lipid biomarkers have the potential to record alterations in the isotopic composition of the hydrogen source. Moreover, δD or D/H ratios as palaeoclimatic archives mainly stem from δD or D/H in lipid biomarkers recording the hydrogen isotope composition of the source water. For example, palmitic acid (C_{16} n-acid) extracted from recent lacustrine sediments across North America

records the δD of the source water (Huang et al., 2002). Other more specific biomarkers, e.g. several sterols, behenic acid and alkanes (particularly odd chain nC_{25} to nC_{31} alkanes), also record the δD value of the source water (Hou et al., 2006; Sachse et al., 2004; Sauer et al., 2001a). This correspondence results from: (1) hydrogen for most plants principally originates from meteoric water, (2) the observed indistinguishable fractionation factors between water and various lipid biomarkers extracted from both freshwater and marine sediments such as aquatic sterols (Sauer et al., 2001a). The hydrogen isotope composition of environmental water is dependent on climatic factors, e.g. temperature, evaporation and precipitation (Craig, 1961; Craig & Gordon, 1965; Gat, 1996; Gonfiantini, 1986), while the D/H ratio of environmental water is the major variable controlling the D/H ratio of some lipids in various environments such as algal sterols (Sauer et al., 2001a). Therefore, hydrogen isotope composition of some lipids has a potential to serve as a direct proxy of the past precipitation, temperature and relative humidity (Ficken et al., 2000; Hou et al., 2006; Liu & Huang, 2005; Seki et al., 2009; Shuman et al., 2006).

In addition, leaf wax δD values, which can rely on growing season moisture, may offer a useful comparison to the above lipid record of lake water δD values (Shuman et al., 2006). The evapotranspiration derived enrichment of terrestrial plants is variable, affected by temperature and humidity. Thus the δD values of terrestrial plant n-alkanes are sensitive to climate change (Seki et al., 2009). Similarly, the variation of leaf wax δD values is subject to climate factors, i.e. temperature and humidity, since leaf waxes are the only constituent of plant n-alkanes (Street et al., 2013). In contrast, aquatic plants do not undergo evapotranspiration and the δD values of their lipids are largely manipulated by hydrogen isotopic composition of their source water (Seki et al., 2009).

This may extrapolate the different records between leaf wax δD values and the above lipid δD values (Fig. 1).

The carbon isotopic composition ($\delta^{13}C$) of the long-chain n-alkanes can be employed to differentiate between vegetation using different photosynthetic pathways. Isotopic values of plants utilizing the C_3 , C_4 photosynthetic pathways differ between -34.7‰ and -21.7‰ for the C_{29} n-alkane, while those of the Crassulacean Acid Metabolism (CAM) pathway are intermediate between C_3 and C_4 plants (Castañeda, 2009; Deines, 1980). Hence, the $\delta^{13}C$ of plant leaf waxes preserved in sediments can be employed to infer the succession of past vegetation type, which can be associated with palaeoclimate, e.g. temperature and aridity (Cerling, 1993; Huang et al., 2001). In addition, the $\delta^{13}C$ of aquatic biomarkers such as short-chain n-alkanes are used to estimate past shifts in the predominant carbon source

(2) CPI

CPI is used to reconstruct palaeoclimate and palaeoenvironment, including temperature, humidity (Zheng et al., 2007) and dominant sources of related lipids (Horikawa et al., 2010; Meyers, 1997). It represents the relative proportions of odd-numbered versus even-numbered chain lengths in the n-alkane and n-alkanoic acid distributions of biological and geological samples (Zhou et al., 2005), and can be expressed as per below.

$$CPI = \frac{\sum_{odd} Cn}{\sum_{even} Cn} \quad (3)$$

where $\sum_{odd} Cn$ and $\sum_{even} Cn$ denotes the total carbon numbers of odd-carbon-chain and even-carbon-chain lipids in sediment samples, respectively.

485

486 The reconstruction of palaeoclimatic archives via CPI derives from the variation of
487 diagenesis and degradation rates with climatic conditions. Under dry and cold climates,
488 microbial diagenesis and degradation of organic material are reduced, corresponding to
489 a high CPI value, while the accelerated microbial diagenesis and degradation of
490 organic matter result in a low CPI value under a wet and warm climate (Xie et al., 2004;
491 Zhou et al., 2005). For instance, Zheng et al. (2007) proposed a lower CPI value may
492 result from the accelerated microbial degradation and changes of organic material
493 linked to a warm and humid climate in the case of no geothermal heating.

494

495 It is proved that CPI reflects dominant sources of pertinent lipids, and thereby growth
496 temperature and humidity. To begin with, Street et al. (2013) suggested a strong
497 odd-over-even predominance, which is recorded as a high CPI, amongst the more
498 abundant chain length (nC_{21} to nC_{35}) is an indicator of vascular plant dominated
499 sources over the sediment sequence, and vice versa. For example, n-alkanes from the
500 cuticular waxes of high plants have high CPI values (> 5). In comparison, n-alkanes
501 from bacteria and algae have low CPI values (ca. 1) (Zheng et al., 2007). On top of
502 different sources, odd-numbered long-chain n-alkanes are generated as
503 moisture-regulating epicuticular leaf waxes (Tulloch, 1976), and longer-chain length
504 n-alkanes tend to be synthesized under water stress responding to elevated
505 temperatures and aridity, in order to provide a more efficient wax coating (Dodd &
506 Rafii, 2000; Shepherd & Griffiths, 2006).

507

508 The application of CPI as climate proxies may be perturbed by alien factors. Pollution
509 is often considered to result in low CPI values of alkanes, e.g. vehicle exhaust

(Simoneit, 1984), fuel or wood burning (Standley & Simoneit, 1987), or even marine sources (Lichtfouse et al., 1994).

3.4 Exclusive fatty acid indexes

An array of indices exclusively related to fatty acids have been used as palaeoclimate proxies, including unsaturated/saturated n-fatty acid ratios (e.g. $C_{16:1}/C_{16:0}$ and $C_{18:1}/C_{18:0}$) (Zhou et al., 2005), the $C_{15}/(C_{15} + C_{16})$ alkanoic acid ratio and the ratio of the C_{23} n-alkan-2-one to the C_{24} n-alkanoic acid (C_{23}/C_{24}) (Zheng et al., 2007).

Differences among these exclusive fatty acid indexes are evident as per the underlying mechanisms, i.e. mechanism 2 and 3. The reconstruction of palaeoclimate archives with regard to unsaturated/saturated n-fatty acid ratios results from the distinguished reaction to diagenetic degradation, in response to the variation of palaeotemperature. The n- C_{16} and n- C_{18} fatty acids are main components of cell membranes of all organisms. In general, monounsaturated fatty acids are more prone to degradation than the corresponding saturated acids. The relative rates at which unsaturated and saturated acids decompose are sensitive to environmental conditions (Zhou et al., 2005). Hence, the proportion of these short-chain unsaturated fatty acids may be degraded more since microbial alteration is accelerated under warm climate, with low $C_{16:1}/C_{16:0}$ or $C_{18:1}/C_{18:0}$ values, corresponding to severe diagenetic degradation of the unsaturated fatty acids. In comparison, the utilization of $C_{15}/(C_{15} + C_{16})$ alkanoic acid ratio as palaeoclimate proxis derives from the distinctive bacterial source of n- C_{15} alkanoic acid in specific biogeochemical settings. Zheng et al. (2007) reasoned that the short odd carbon-numbered chain alkanoic acids such as n- C_{15} could be biomarkers indicative of microbial contributions. This assumption is supported by the fact that a

carbon isotopic composition of the n-C_{15:0} acid that is lighter than the n-C_{16:0}-n-C_{28:0} acids, implying its bacterial origin in peat from the Ruoergai Marsh and in sediments from the Nasha Sea. As a result, rises in relative contributions of the C₁₅ n-alkanoic acid might act as a proxy of the warm and humid conditions which favor microbial activity, similarly is the C₂₃/ C₂₄, with higher ratios related to stronger microbial activities, and attributing to higher temperatures.

The use of exclusive fatty acids derived indexes as palaeoclimate proxies should be cautious in case human disturbance is evident. For example, rice paddy farming is linked to increased methanogenic bacterial activity, and may compromise the attempt to interpret palaeotemperature from C_{18:1}/ C_{18:0} or C₁₅/(C₁₅+C₁₆), when sediment sampling area is adjacent to paddy fields.

4. The application of combined indices

Individual indices seem to be not reliable and comprehensive to reveal palaeoclimate and palaeoenvironment information. MBT can only be effectively used in marine sediments. U₃₇^K is affected by the geological and evolutionary sequence of species, as well as environmental factors and diagenetic effects. CPI may be dampened by alien factors, such as pollution. Fatty acid indices will be problematic if apparent human disturbance occurs in sampling sites. Also TEX₈₆ will be ineffective in case of high allochthonous sources in sampling sites, and its calibration method is less sensitive to temperature. The alkenone distributions may reflect changes owing to temperature and different sources of halophyte input but could not provide a clear picture at species level (Coolen et al., 2004).

The development of pertinent indices in terms of lipid biomarkers does tend to be combined with other proxies to improve the credibility and add implications of palaeoclimate and palaeoenvironment change. Coolen et al. (2004) extended the study of climate change on halophyte and diatom population at species level in deep lakes based on combined lipid and fossil DNA biomarkers. Hou et al. (2006) applied pollen analysis to test the palaeoprecipitation and palaeotemperature information derived by the δD values. Their results showed that decreases in the δ values of behenic acid (C_{22} n-acid) from a sediment core from Blood Pond, Massachusetts, USA and the pollen proportion of multiple taxa suggested a cooling trend. Similarly, Street et al. (2013) inferred palaeotemperature and humidity conditions on the grounds of combined pollen and ACL evidences in sediments from Swamp Lake, California, USA, with implication for the kurtosis (peakedness) and skewness (asymmetry) of the odd chain-length distributions regarding n-alkanes. Liu Z. (2009) combined TEX_{86} and U_{37}^K , along with $\delta^{18}O$ values of benthic foraminifera, to reconstruct SST records during the late Eocene-Oligocene climate transition from 45° to 70° in both hemispheres. Their result indicated discrepancies between $\delta^{18}O$ values and TEX_{86} or U_{37}^K in high-latitude estimates, and thus stressed the necessity of involving more biomarkers for interpretation (Fig. 6).

With the progress of palaeoclimate and palaeoenvironment study, it is anticipated that more combination of lipid and other biomarkers will enhance the understanding of palaeoclimate and palaeoenvironment changes more widely and deeply. Although in general there are no perfect biomarkers, the interactive verification of multiple biomarkers, if not in accordance with each other, could identify uncertainties where disagreement occurs. In addition, it is possible to broaden the horizon and provide

more details in palaeoclimate and palaeoenvironment reconstruction with the aid of other fossil records. Table 2 indicates various lipid indices and their combination with other indicators as palaeoclimate and palaeoenvironment proxies.

5. Conclusions

The application of lipid biomarkers and pertinent indices from aquatic environment as palaeoclimate and palaeoenvironment proxies is reviewed in this paper. Lipid biomarkers as palaeoclimate and palaeoenvironment proxies are linked to autochthonous and/or allochthonous sources, which can lead to distinct lipid molecular distributions. Three possible mechanisms, i.e. characteristics of carbon chain distribution, temperature adaption or combined temperature and humidity adaptation, are suggested to explain how different lipid biomarkers are used as palaeoclimate and palaeoenvironment proxies. A set of lipid indices oriented by the mechanisms are summarized and compared as proxies of various palaeoclimate and palaeoenvironment conditions. Molecular distribution of n-alkanes, δD or D/H ratios and various fatty acid indices can be applied to reconstruct the past precipitation, temperature and humidity as well as vegetation succession, while U_{37}^K and GDGT-based indexes serve as the surrogates of SST and/or MAT.

We suggest: (1) the combined use of different indices in order to overcome the limitations of individual indices and improve the overall interpretation. For palaeoclimate and palaeoenvironment reconstruction at long time-scales, lipid biomarkers from various aquatic environments are suggested as some tend to be restricted to centennial to millennia scales, e.g. peat (Xie and Evershed 2002, Xie, Nott et al. 2004, Nichols, Booth et al. 2006, Xu, Hong et al. 2006); (2) Future studies should

address the uncertainties of palaeoclimate and palaeoenvironment estimation by
verifying the results with multiple biomarkers from different aquatic environments; (3)
Indicators based on lipid biomarkers from lacustrine sediment should be involved to
reconstruct palaeoclimate and palaeoenvironment at long and continual time-scales;
and (4) It should be cautious to elucidate palaeoclimate and palaeoenvironment
information when disagreement occurs in verifying via multiple indices, and new
biomarkers suitable to address the discrepancies are suggested.

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995

Figure Captions

Fig. 1 Paq values of different lipid sources, including plants and sediments. Data come from Ficken et al. (2000). Non-emergent aquatic plants show the highest average Paq (0.69), whereas terrestrial plants show the lowest average Paq (0.09).

Fig. 2 Alkane chain indexes as temperature and humidity proxies. Data come from Zhou et al. (2010), reporting lipid biomarkers from the Hani peat, Northern China. Higher P_{aq} and ACL values account for drier and warmer climate, respectively, and vice versa.

Fig. 3 Calibration models for U_{37}^K derived SSTs proxy and latitudinal variation of U_{37}^K . Model functions in “a” are from Conte et al. (2006). U_{37}^K values of different latitudinal range, connected by the green and red line, in “b” are from Prahl and Wakeham (1987) and Müller et al. (1998), respectively. Generally, U_{37}^K values increase from the higher latitude to equator in both hemispheres.

Fig. 4 Calibration models for TEX_{86} and TEX_{86} -derived indicators for SSTs proxy. Model functions of the five graphs are from (Kim et al. (2008); Kim et al. (2010); Liu Z. (2009); Powers et al. (2004); Schouten et al. (2007); Schouten et al. (2002); Wuchter et al. (2005)), and Powers et al. (2010). Core-top model 11 in ‘a’ and mesocosm model 4 in ‘b’ are originally established based on TEX_{86}^H , and transformed to TEX_{86} in this figure.

Fig. 5 Schematic graph regarding different sources of δD from aquatic sediment samples as various climatic proxies. δD of terrestrial plants is determined by the effects

1021 of evaporation and transpiration, which are affected by temperature and humidity. In
1022 contrast, δD of aquatic plants is not influenced by evapotranspiration, and is linear
1023 correlated with δD of source water (Huang et al., 2004) , which is a signal for the
1024 influence of precipitation, temperature and humidity.

1025

1026 Fig. 6 The use of combined TEX_{86} and U_{37}^K , coupled with $\delta^{18}O$ values of benthic
1027 foraminifera as proxies for SST during the late Eocene-Oligocene transition. The
1028 figure is plotted from Zachos (1994) and Liu Z. (2009). There are discrepancies
1029 between lipid biomarkers and foraminiferal $\delta^{18}O$ derived temperatures, likely due to
1030 biases in lipid biomarkers introduced by seasonal production and diagenesis. For the
1031 indicators, 1090 U_{37}^K , 277 U_{37}^K , 336 U_{37}^K , 511 U_{37}^K and 913 U_{37}^K denote U_{37}^K at
1032 sites 1090, 277, 336, 511 and 913, respectively; 277 TEX_{86} and 511 TEX_{86} denote
1033 TEX_{86} at sites 277 and 511 respectively; δO denotes $\delta^{18}O$. The green line represent a
1034 composite foraminiferal $\delta^{18}O$ records.

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1051 a.

1052

1053 b.

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 1060 figure.

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 1080 composite foraminiferal δ¹⁸O records.

1081

1082 Table 1 Lipid biomarkers in terms of aquatic environment and their sources

Sources	Lipid biomarkers	Reference
Marine coccolithophorid <i>Emiliania huxleyi</i>	C ₃₇ -C ₃₉ n-alketones	Brassell et al. (1986); Prahl and Wakeham (1987))
Aquatic algae and photosynthetic bacteria	C ₁₇ n-alkane	Cranwell et al. (1987)
	Even-carbon-number C ₁₂ -C ₂₂ n-alkane	Grimalt and Albaiges (1987); Han and Calvin (1969)
	C ₁₆ and C ₁₈ n-alkanoic acids	Horikawa et al. (2010); Vogts et al. (2009)
	C ₁₆ -C ₂₂ n-alkanols	
Bacteria such as cyanobacteria, methanotrophic bacteria and members of the α -proteobacteria	Hapanoids	Peters (2005)
Higher plants and algae	Long-chain diols such as Triterpenoid and n-Alkyl diols	Bianchi (2011); Romero-Viana et al. (2012)
Upland terrestrial vegetation	C ₂₅ -C ₃₅ n-alkane	Cranwell et al. (1987); Eglinton and Hamilton (1967); Street et al. (2013)
Submerged and floating macrophytes	n-alkane (maximum C ₂₁ , C ₂₃ , or C ₂₅)	Cranwell (1984); Ficken et al. (2000); Seki et al. (2009); Street et al. (2013)
	C ₂₂ and C ₂₄ n-alkanols	Ficken (1998)
	C ₂₂ and C ₂₄ alkanoic acids	Romero-Viana et al. (2012)
Vascular land plants and emergent macrophytes	C ₂₇ , C ₂₉ and C ₃₁ n-alkanes	Cranwell (1973); Cranwell et al. (1987); Eglinton and Hamilton (1967); Ficken et al. (2000); Street et al. (2013)
	C ₂₄ -C ₃₀ n-alkanoic acids	Cranwell (1974); Wiesenbergs and Schwark (2006)

Sources	Lipid biomarkers	Reference
	C ₂₂ -C ₃₀ n-alkanols	Eglinton and Hamilton (1967)
Marine Group I Crenarchaeota and some <i>Euryarchaeota</i>	iGDGTs	Blumenberg et al. (2004); Koga et al. (1993); Macalady et al. (2004); Turich et al. (2007); Zhang et al. (2011)
Acidobacteria	bGDGTs	Liu et al. (2010); Sinninghe Damsté et al. (2011); Weijers et al. (2009); Weijers et al. (2006)

1083

1084 Table 2 Lipid indices as quaternary palaeoclimate and palaeoenvironment proxies with reference to pertinent studies

Lipid biomarkers	Indices	Sediment environment	Climate proxy	Time scale	Region	Reference
C ₃₇ ketones	U_{37}^k	Marine	SSTs	500, 000 cal yr BP	E Atlantic	Brassell et al. (1986)
C ₂₈ and C ₁₆ n-acids	δD and pollen content	Lacustrine	Precipitation	~ 8, 200 cal yr BP	NE USA	Shuman et al. (2006)
C ₁₈ and C ₁₆ n-acids	C _{16:1} /C _{16:0} and C _{18:1} /C _{18:0} ratios	Peat	Temperature	10, 450–6, 040 cal yr BP	S China	Zhou et al. (2005)
C ₂₁ -C ₃₅ n-alkanes and C ₁₆ -C ₃₄ n-acids	CPI	Peat	Temperature	220 cal yr BP	N England	Xie et al. (2004)
C ₁₇ -C ₃₅ n-alkanes	ACL and pollen contents	Lacustrine	Temperature and humidity	3, 000 cal yr BP	W USA	Street et al. (2013)
C ₂₃ , C ₂₅ , C ₂₉ and C ₃₁ n-alkanes	P _{aq}	Lacustrine	Precipitation	16, 000 cal yr BP	NE China	Seki et al. (2009)
bGDGTs	MBT	Marine	MAT	25, 000 cal yr BP	Tropical Africa	Weijers et al. (2007b)
iGDGTs	TEX ₈₆	Marine	SSTs	NA	Global	Kim et al. (2010)

1085