Lipid biomarkers and pertinent indices from aquatic environment record paleoclimate and paleoenvironment changes

Xiaoguang Ouyang [a, b, *], Fen Guo [c, d], Hongmei Bu [e]

[a] Australian Rivers Institute-Coast and Estuaries and School of Environment, Griffith University Gold Coast Campus, Southport, Qld 4222, Australia
[b] Sichuan Zhonghuanlixin Environmental Protection Consulting Co., Ltd., Bazhong, Sichuan Province 636000, PR China
[c] Australian Rivers Institute, Griffith University, Nathan, Qld 4111, Australia
[d] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, 8 Dayangfang, Beiyuan, Anwai, Beijing 100012, PR China
[e] Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Datun Road, A 11, Beijing 100101, PR China

ARTICLE INFO

ABSTRACT

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

© 2015 Elsevier Ltd. All rights reserved.

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 paleoclimate and paleoenvironment. 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 and Wainmann, 1999), while the application of other sedimentary matter as paleoclimate and paleoenvironment 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 paleoclimate and paleoenvironment 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 and van Geel, 2006; Xie et al., 2004). Oceanic sediments regulate high-resolution, continuous and widespread paleoceanographic 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 paleoclimate proxies (Kim et al., 2008, 2010; Leider et al., 2010). Lipid biomarkers and their indices from lacustrine sediments could record environmental variability and indicate high sensitivity to regional climate change (Romero-Viana et al., 2012). Also Lacustrine sediment records with annual laminations are one of the primary targets for acquiring high-resolution climate records (Brauer et al., 2008), and thus understanding the underlying forces (Jones et al., 2009). They

* Corresponding author. Australian Rivers Institute-Coast and Estuaries and School of Environment, Griffith University Gold Coast Campus, Southport, Qld 4222, Australia.
E-mail address: xiaoguang.ouyang@griffithuni.edu.au (X. Ouyang).

are especially useful records of paleoclimate information since they may reflect continuous time series and contain multiple geochemical and microfossil proxies, which may be employed to verify extrapolated paleoclimate signals (Birks and Birks, 1980; Faegri et al., 1989; Meyers and Lallier-Vergés, 1999; Smol, 1995). In addition, there is increasing concern upon lipid biomarkers in water column as climatic archives. Some lipid biomarkers such as crenarchaeal isoprenoid glycerol dibiphytanyl glycerol tetraethers (iGDGTs), synthesized by marine crenarchaeota in the water column, can be used to record the variation of sea surface temperatures (SSTs) (Kim et al., 2010). Furthermore, different indices based on lipid biomarkers from aquatic sediments and water column are practical proxies tracing paleoclimate and paleoenvironmental variability (Prahl and Wakeham, 1987; Street-Perrott et al., 1997; Xie et al., 2004). These indices involve a variety of members such as δD or D/H ratios, U^K_{37}, n-Alkane chain length index, glycerol dibiphytanyl glycerol tetraethers (GDGTs) based indexes, carbon preference index (CPI) and various fatty acid indices. They have been applied to reconstruct past precipitation, temperature and humidity, and some are used as SSTs.

To date, there is a lack of systematical syntheses with regard to the lipid biomarkers and related indices from aquatic environment indicating paleoclimate and paleoenvironment, although paleoclimate and paleoenvironment studies in terms of 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 (TEX$_{86}$) 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 and Schouten (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 TEX$_{86}$ 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 paleoclimate and paleoenvironmental variability is urgent.

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

2. Lipid biomarkers used in paleoclimate and paleoenvironment 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 paleoclimate and paleoenvironment 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 and Hamilton, 1967; Street et al., 2013; Wiesenberg and 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).

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

Molecular distributions of lipids from different origins are distinguished. The marine coccolithophorid Emiliania huxleyi (Phymnesiophyceae) and members of the class Prymnesiophyceae are now the recognized sources of the long-chain (C$_{37}$, C$_{38}$, C$_{39}$) di-, tri- and tetra-unsaturated methyl and ethyl ketones (alkenones) (Brassell et al., 1986; Prahl and Wakeham, 1987). Bacteria and algae generate short-chain alkanes and n-alkanoic acids (Gelpi et al., 1970). The n-C$_{25}$ to n-C$_{35}$ alkanes originate from the leaf waxes of upland vegetation (Cranwell et al., 1987; Eglinton and Hamilton, 1967; Street et al., 2013). n-Alkanes in aquatic plants (floating and submerged) are featured with a dominance of middle chain length, e.g. C$_{23}$ and C$_{25}$, whereas those of terrestrial vegetation are predominated by long-chain homologues (>C$_{29}$) (Seki et al., 2012). Emergent aquatic plants have a distribution pattern midway between those of non-emergent and terrestrial vegetation (Ficken et al., 2000). Crenarchaeota and some Euryarchaeota are capable of synthesizing iGDGTs (Blumenberg et al., 2004; Koga et al., 1993; Macalady et al., 2004; Turich et al., 2007; Zhang et al., 2011), and it was suggested that branched GDGTs (bGDGTs) are produced by some members of the acidobacteria (Liu et al., 2010; Sinninghe Damsté et al., 2011; Weijers et al., 2009, 2006). The specific lipid biomarkers and their sources are indicated in Table 1.

2.2. Mechanisms of lipids as paleoclimate and paleoenvironment proxies

Different lipids serve as paleoclimate and paleoenvironment 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, 2010; Leider et al., 2010). Furthermore, (3) biochemical