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Distribution and carbon isotope composition of lipid biomarkers in Lake Erhai and Lake Gahai sediments on the Tibetan Plateau

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ABSTRACT

Lipid biomarkers and carbon isotopes of *n*-alkanes, *n*-fatty acids, and *n*-alkan-2-ones were used to determine organic carbon sources to surface sediments in lakes Erhai and Gahai on the Tibetan Plateau. All sediment samples contained *n*-fatty acids with lower concentrations of *n*-alkanes and *n*-alkan-2-ones. Long chain *n*-alkanes in lake sediments were characteristic of a source mixture of epicuticular waxes of higher plants and submerged littoral zone plants while *n*-fatty acids sources were bacteria and floating and/or submergent macrophytes; the *n*-alkan-2-ones had a possible source in epicuticular waxes of higher plants and/or grass from catchment which entered the lake and were reworked by the microorganisms. Sediment samples examined from Lake Erhai had heavier $\delta^{13}C$ values of bulk organic carbon and specific carbon compounds than samples from Lake Gahai and meadow soil. This heavier isotopic composition can be best interpreted by the enhanced productivity occurring in Lake Erhai due to its lower salinity and possibly to limited CO_2 concentrations; for the latter, this may have enriched ^{13}C in the dissolved inorganic carbon pool of the lake water.

Introduction

Lake sediments contain a diverse range of lipid compounds; since lipids primarily are derived from organisms living within the lake and its catchment, differences in lipid composition directly reflect differences in lake and catchment biota (Pearson et al., 2007). In recent years, many new compounds have been identified in marine and lacustrine sediments; terrestrial higher plants and microalgal have been identified as sources for these lipids (Sikes et al., 2009; Volkman et al., 1998, 2008). Some compounds degrade slowly or are transformed to more stable chemical structures and thus they can be used as biomarkers for investigating sources of organic matter in sediments (Sauer et al., 2001; Schouten et al., 2003; Volkman et al., 1998). For example, investigations of the long chain *n*-alkanes or algal derived biomarkers can help identify primary producers and allow for the reconstruction of the local vegetation history and environmental conditions (e.g. Volkman et al., 2008; Zhang et al., 2004). The molecular distribution and carbon isotopic composition of lipid biomarkers provide particularly useful information about sources, preservation and historical changes in organic matter, as well as changes in trophic status of the lakes (Muri et al., 2004). Although making up only a small percentage of bulk organic matter (Meyers, 2003), lipids have been widely used in many geochemistry studies of lacustrine sediments (e.g. Muri et al., 2004).

The Tibetan Plateau is >3000 m above sea level and represents a unique tectonic feature. Catchment bedrock consists of sedimentary rocks, metamorphic rocks, and a small fraction of igneous rocks (Xu et al., 2006). Vegetation is predominantly C_3 plants, varying from swampy meadows to mountain shrubs (Lu et al., 2001; Xu et al., 2006). There also are numerous lakes in the area. This study was carried out near Lake Qinghai, the largest brackish lake on Tibetan Plateau, China. The goal of our study was to determine how lipid biomarkers and carbon isotopes may be used to delineate the source of organic matter and processes that may affect the isotopic composition of organic matter in contrasting lake environments.

Environmental setting

Qinghai lakes (Lake Qinghai and its surrounding satellite lakes) have interesting geochemical features due to their varying salinities that range from freshwater to saline (Liu et al., 2008). Lake Qinghai (Fig. 1) is located in the northeastern part of Qinghai–Xizang (Tibet) Plateau at 3193 m above sea level and with an area of 4400 km^2 (Liu et al., 2008). It is a 26.5 m deep perennial lake whose waters saline (14.07 g/l) and alkaline waters are rich in magnesium-sulfate. To the northeast and southeast are a few small satellite lakes which were

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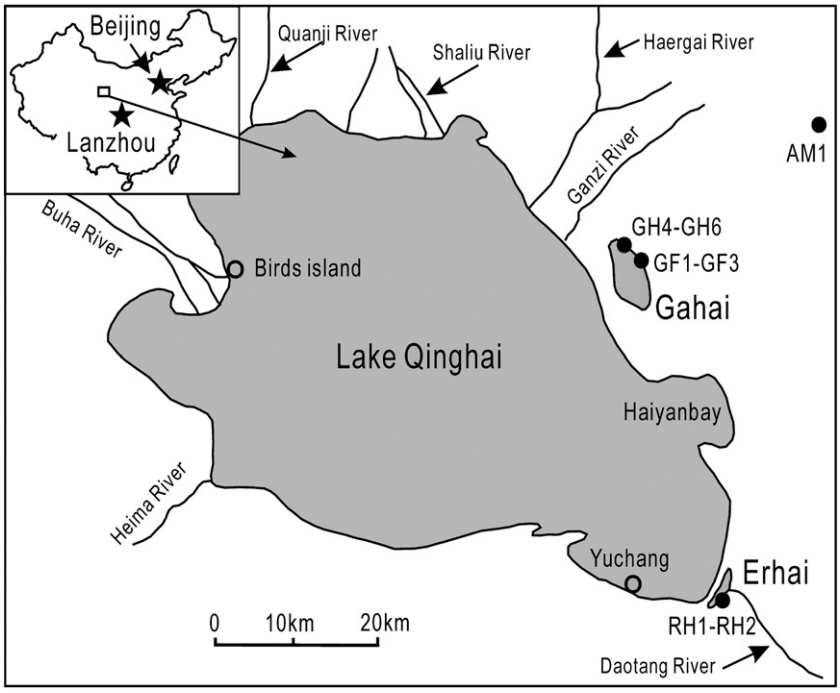

Fig. 1. Location map of Qinghai Lakes and sampling area.

formed as Qinghai Lake water level decreased over the past centuries (Li et al., 1996). Lake Erhai is located to the east and has a salinity of 1.22 g/l; Lake Gahai, a small lake to the northeast, has a salinity of 32.64 g/l. Lake Gahai is saline because of its very limited fresh water inputs. Lake Erhai has a low salinity because of its large fresh water inflows from the Daotang River (Liu et al., 2008).

Sediments in the Greater Lake Qinghai are characterized by homogenous carbonate (30%) and silicates (60–65%) with relatively high abundances of organic matter (0.70–5.90%) relative to those of other more saline lake sediments (Li et al., 2006; Tuo et al., 2005). The relatively high abundance of carbonate suggests that Lake Qinghai has been relatively arid over the last millennium with the oversaturation (and precipitation) of carbonate caused by the enhanced evaporation of lake water (Henderson and Holmes, 2009).

Material and methods

Field sampling

Surface sediment samples (Fig. 1) were collected from the east margin of Lake Erhai at RH1 (gray sandy mud with algal mats) and RH2 (gray sandy mud) in 10–30 cm of water. Samples also were collected in similarly shallow waters at the northeast margin of Lake Gahai at sites GF1 (brown sandy mud with algal mats), GF2 (gray sandy mud), GF3 (gray sandy mud with grass chips) where fresh water streams feed into the saline lake and at sites GH4 (brown algal mats), GH5 (gray carbonate mud) and GH6 (gray sandy mud) where authigenic white-gray carbonate minerals were deposited. Finally, a surface soil sample was collected at AM1 (top gray soil) in a catchment alpine meadow about 30 km from the Gahai and Erhai lakes (Fig. 1, Table 1) as a reference sample for terrestrial inputs.

Laboratory methods

Total organic carbon (TOC) was determined on freeze dried, pulverized sediments; carbonates were removed by treating the samples with 8% hydrochloric acid and organic carbon determined by LECO-CS344 analyses. In addition, $\delta^{13}C$ was determined on another decalcified aliquot by combusting it to release CO_2 which was then injected into a Finnigan MAT 252 mass spectrometer.

For lipid analyses, all samples were freeze dried and then extracted by a modified Bligh and Dyer (1959) procedure. Briefly, 1–5 g (depending on the TOC in the samples) of dried sediment samples were suspended in methanol-dichloromethane-phosphate buffer, treated for 2–3 min with an ultrasonic probe, and then kept overnight at room temperature. Samples then were centrifuged to separate the phases, and the dichloromethane phase was dried. The total lipid fraction was fractionated by column chromatography on silicic acid

Table 1
Basical geochemical characters and biomarker parameters for the recent sediment samples under studying (Appendix A).

Sample no	Sampling area	Sample characters	TOC (%)	$\delta^{13}C$ (TOC,‰)	CPI_{HC}	ATR_{HC}	Paq	CPI_{FA}	ATR_{FA}
RH1	Erhai	Gray algal mats	8.2	−21.9	3.8	0.0	0.6		1.0
RH2	Erhai	Gray sandy mud	0.4	−25.2	8.6	0.5	0.5		1.0
GF1	Gahai	Brown sandy mud with algal mats	8.5	−30.3	12.2	0.1	0.2		1.0
GF2	Gahai	Gray sandy mud	1.5	−31.6	6.4	0.3	0.3	13.3	1.0
GF3	Gahai	Gray sandy mud with grass chips	1.6	−31.3	14.3	0.1	0.2	13.5	0.9
GH4	Gahai	Brown algal mats	7.2	−28.0	2.3	0.0	0.2		1.0
GH5	Gahai	Gray carbonate mud	0.2		9.3	0.4	0.3		1.0
GH6	Gahai	black sandy mud	1.0	−30.0	7.9	0.2	0.3	100.0	1.0
AM1	Alpine meadow	Top gray soil	6.1	−28.6	11.0	0.1	0.5	12.4	0.9

and sequential elution with dichloromethane, acetone, and methanol which resulted in three fractions of different polarity: neutral lipids, glycolipids, and phospholipids. The phospholipid fractions were separately dissolved in 1 ml of dichloromethane-methanol and subjected to a mild-alkaline hydrolysis (1 M KOH-methanol) and the free fatty acids methylated to fatty acid methylesters.

The deuterated tetracosane ($C_{24}D_{50}$, Sigma-Aldrich) standard was used as an internal reference for comparative purposes. For each analysis the sample was diluted to an appropriate concentration and same weight of sample was separated and dissolved in the same volume of solvent and the same amount of internal standard was added. The same volume of each solution was injected into the GC–MS; therefore concentrations of individual compounds from sample to sample can be compared relative to the $C_{24}D_{50}$ peak area or height in the chromatograms (Tuo and Philp, 2003). GC–MS analyses of neutral and alkaline hydrolyzed phospholipid fractions were performed on a Hewlett Packard 6890N gas chromatograph interfaced to a Hewlett Packard 5973N mass spectrometer. The gas chromatograph was equipped with a DB-5 MS fused silica capillary column (30 m × 0.25 mm) and helium was used as carrier gas with a flow rate of 1 ml/min. The mass spectrometer was operated with an electron energy of 70 eV, and an ion source temperature of 230 °C. The oven temperature was isothermal for 1 min at 80 °C and then programmed from 80 to 280 °C at 3 °C/min and then held for 20 min at 280 °C. The GC–MS data were acquired and processed with a Hewlett–Packard Chemstation data system.

Carbon isotope analyses of individual compounds were performed on a Delta Plus XP gas chromatography–combustion–isotope ratio mass spectrometer. The gas chromatography was performed using a Thermo Finnigan GC COMBUSTION III system equipped with a DB-5 fused silica capillary column (30 m × 0.25 mm) and helium was used as carrier gas with a flow rate of 1 ml/min. The oven was programmed the same as the GC–MS analyses (see above). Isotopic values were calculated by integrating the m/z 44, 45 and 46 ion currents of the peaks produced by combustion of the chromatographically separated compounds and those of CO_2 standard spikes admitted at regular intervals. The reproducibility and accuracy of the analysis were evaluated routinely using laboratory standards of known $\delta^{13}C$ values (C_{16}–C_{32} n-alkanes). Typically, one injection of laboratory standard was performed for every eight sample analyses. Stable carbon isotope values are defined by the equation:

$$\delta^{13}C(‰) = \left[\left(R_{sample} - R_{standard}\right) / R_{standard}\right] \times 10^3;$$
$$R = {}^{13}C/{}^{12}C,$$

The isotope values are given with respect to the PDB standard. Based on the data, some of the analyses were run as duplicates or triplicates and the results were presented as an average value. The standard deviations for all analyses were less than 0.5‰.

The isotope composition of fatty acids was measured as methylated derivatives. The formation of fatty acid methyl ester from the free fatty acid involved the addition of one methanol carbon with known isotopic composition per fatty acid molecule. The isotopic composition in the methyl group of esterified fatty acids was calculated and the values for fatty acids corrected with the following formula (Abrajano et al., 1994):

$$\delta^{13}C_{FA} = \left[(n+1)\delta^{13}C_{FAME} - \delta^{13}C_{CH_3OH}\right] / n$$

where n is the carbon number of the particular fatty acids.

Identification of biomarkers

All the compounds were identified from interpretation of their mass spectra and by comparison of the mass spectra with previously published data or by comparison of mass spectra with spectra in libraries (NIST and Wiley libraries: Appendix A). Normal alkanes (n-alkanes: Appendix A) are the most abundant compounds in all the neutral fractions whereas fatty acids are the dominant compounds in the alkaline hydrolyzed phospholipid fractions. Trace amounts of n-alkan-ones (Appendix A) were also detected in 6 out of 9 samples analyzed. Fatty acids are designated as A:Bωnc(t), where A is the number of total carbon atoms, B is the number of double bonds, n is the number of carbon atoms of the closest double bond from the methyl end (ω), c(t) refer to cis (trans) of the molecular structure.

Results and discussion

Distribution patterns of lipids compounds in organisms in Lake Qinghai Area

Distribution patterns of lipids compounds in the typical organisms collected in Lake Qinghai and its surrounding satellite lakes and the catchment area have been studied by Zhang (1991) and LZBCZA (1994). A homologous series of n-alkanes was detected in the saturated fraction with the distribution patterns varying with the organism (Appendix B). In most terrestrial herbaceous plants (e.g., *Achnatherum splendens*, *Taraxacum sinicum*, *Brylkinia sinocompressus* Tang et Wang, *Potamogeton* sp., *Leymus secalinus*, *Poa pratensis* Linn), n-alkanes were characterized by a higher relative abundance of high-molecular-weight (HMW) homologues and dominated by C_{27} or C_{29}; straight chain n-alkanes from C_{23} to C_{29} showed distinct odd-to-even carbon number predominances. In two algae (*Chara* sp. and *Cladophora* sp.), n-alkanes were characterized by two peaks with a higher relative abundance of HMW homologues, dominated by C_{27} or C_{29} and lower amount of short chain n-alkanes, dominated by C_{18} (*Chara* sp.) or C_{17} (*Cladophora* sp.). In plankton and shrimp (*Noemacheilinae*); n-alkanes also were characterized by a higher relative abundance of high-molecular-weight (HMW) homologues and dominated by C_{27} or C_{29} with distinct odd-to-even carbon number predominances in the C_{23} and C_{29} carbon range. In *Polygonum sibiricum* Laxm and *Potamogeton pectinatus*, n-alkanes had a higher relative abundance of medium-molecular-weight homologues and were dominated by C_{23} with distinct odd-to-even carbon number predominances from C_{21} to C_{29}. n-Alkanes in *Spirogyra crassa* Kützing were characterized by two peaks maximizing at C_{17} and C_{23} respectively. *Gymnocypris przewalskii* was the only organism in which the n-alkanes are characterized by short chain compounds maximizing at C_{17}.

Fatty acids occurred in the range C_{12}–C_{18} for most organisms and were predominantly composed of even-carbon numbered compounds (Appendix C). In most species C_{16} n-fatty acid was the dominant compound although C_{14} n-fatty acid was the dominant compound in *G. przewalskii* and plankton.

Bulk sediments analysis

Sediment descriptions and geochemical parameters are given in Table 1. TOC varied from 0.2 to 8.2 wt.% (of total dry sediment weight), within the typical low range for sandy mud and carbonate mud samples, and relatively higher in algal mats and gray soil samples. TOC concentrations varied with sediment types and grain sizes rather than sample locations. The $\delta^{13}C$ signature of TOC ranged from −21.9‰ to −31.6‰. TOC and $\delta^{13}C$ were not significantly correlated with one another. The $\delta^{13}C$ values of TOC for the two Erhai samples (RH1, −21.9‰; RH2, −25.2‰) were about 5–10‰ heavier than those from Lake Gahai and the Alpine meadow (Table 1). Higher $\delta^{13}C$ values of TOC in sediments have been related to contributions from C_4 plants (Collister et al., 1994) or enhanced primary production that caused the residual dissolved inorganic carbon to be enriched in ^{13}C (Scherf and Rullkötter, 2009), or ^{13}C-enriched soil carbonate

resulting from low concentrations of CO_2 (Mackie et al., 2007). Our results favor the second explanation because the predominance of C_3 plants in the catchment (Lu et al., 2001; Xu et al., 2006) and because organic carbon in Alpine soils has low $\delta^{13}C$ (Kovda et al., 2006). Higher primary production has enriched the TOC of Lake Erhai sediments (7.65–14.91%) more than the sediments of Lake Qinghai and its satellite lakes (0.78–1.50%) (LZBCAS, 1994; Tuo et al., 2005). Henderson and Holmes (2009) also observed that higher productivity in the west basin of Lake Qinghai (and near the Buha River inflow) resulted in the $\delta^{13}C$ signature of TOC in two surface sediment samples to be 3–4‰ higher in ^{13}C than in all other Lake Qinghai sediments. Similarly, the inflow of freshwater into Lake Erhai (through Daotang River) brings nutrients and lowers lake water salinity both of which would enhance productivity. Floating grass and aquatic organisms are much abundant in the Lake Erhai than in other more saline lakes also suggesting that it has a greater productivity (LZBCAS, 1994).

Of the three lipid families (*n*-alkanes, fatty acids and *n*-alkan-ones), fatty acids were the most abundant, ranging from 70.8 to 99.5%; *n*-alkanes concentrations ranged between 0.4% and 25.4%, whereas the *n*-alkan-ones were detected in minor amounts in most samples, ranging between 0.1% and 5.16% (Fig. 2). Mono-unsaturated fatty acids and branched methyl-substituted fatty acids, whose sources can be attributed to be phytoplankton and bacteria (Muri et al., 2004), were detected in all of the sediments analyzed suggesting that autochthonous microalgal and/or bacteria were the major contributions of this type of organic matter to the sediments.

n-Alkanes

A homologous series of *n*-alkanes was detected in the neutral fractions in all of the sediment samples, with carbon numbers ranging from C_{18}–C_{33} and sometimes to C_{35} (Fig. 3a and Appendix D). All samples displayed a strong odd/even carbon number predominance. In most samples, long chain *n*-alkanes maximized at *n*-C_{29} or *n*-C_{31} and the CPI_{HC} (carbon preference index for hydrocarbons: Appendix A) in the C_{24}–C_{32} range varied between 2.3 and 14.3, which is typical for the cuticular waxes of higher plants (Kolattukudy, 1980; Muri et al., 2004); this indicates that *n*-alkanes in the organic matter in the lake sediments and soil originated mainly from higher plants (e.g., Eglinton and Hamilton, 1967; Wilkes et al. 1999).

Long-chain *n*-alkanes concentrations were relatively lower in RH1 (gray sandy mud with algal mats), GF1 (mat-containing samples) and GH4 (mat sample) than in sandy mud samples; *n*-alkanes in GF1 and GH4 maximized at *n*-C_{29} or *n*-C_{31} whereas in RH1 *n*-alkanes were distributed in two peaks maximizing at *n*-C_{23} and *n*-C_{29}, respectively (Fig. 3a). Ficken et al. (2000) developed a proxy ratio, P_{aq} which estimates non-emergent aquatic macrophyte input to lake sediments relative to that from the emergent aquatic and terrestrial plants. It is based on the fact that non-emergent species had enhanced abundances of mid-chain (C_{23} and C_{25}) n-alkanes whereas emergent plants, like terrestrial plants, were dominated by long-chain (>C_{29}) homologues. *P*aq values of 0.4 are the boundary between land and submerged plant *n*-alkane contributions, *P*aq<0.1 corresponds to terrestrial plants, 0.1–0.4 to emergent macrophytes and 0.4–1 to submerged/floating macrophytes. Very low *P*aq ratios (0.2–0.6) were observed in all lake sediment samples including algal mats and algal mat-containing samples suggesting that submerged plants in the littoral zone or emergent ones on the shore could be the source of long-chain *n*-alkanes (*n*-C_{29} and *n*-C_{31}). This observation is also consistent with the nearshore locations of the samples. Concentrations of short chain *n*-alkanes (*n*C_{19} or *n*C_{23}) were relatively high in the two Lake Erhai samples (RH1 and RH2) and two Lake Gahai samples (GH5 and GH6) where authigenic white-gray carbonate minerals had been deposited. This suggests that submerged/floating aquatic macrophytes and/or microorganisms may be significant contributors to the organic matter in these sediments.

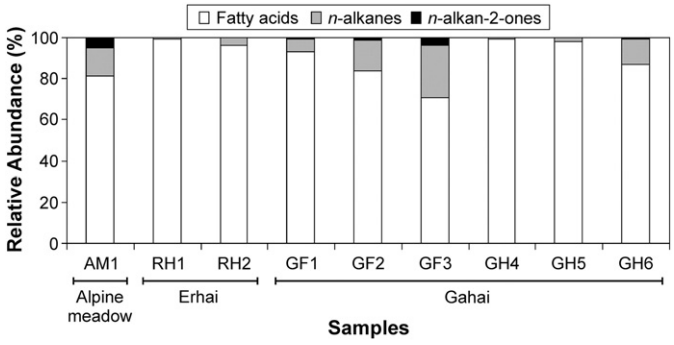

Fig. 2. Relative abundance of biomarker families in the extracts of the 9 sediments.

Principal component analysis (PCA) has been used in geochemical studies to identify the factors controlling organic matter composition in estuarine and coastal environments (Gordon and Goñi, 2003; Hernandez et al., 2001); PCA is similarly used in this study. PCA results (Fig. 3b, c) focus on the first two principal components, which together explained 77% of the variance in the *n*-alkane data set. The *n*-C_{27}, *n*-C_{29} and *n*-C_{31} *n*-alkanes plot within a tight cluster on the lower middle side of the PCA diagram (Fig. 3b), whereas the *n*-C_{20}, *n*-C_{21}, *n*-C_{23} and *n*-C_{25} *n*-alkanes plot fall within the upper middle portion of the diagram. From this observation, we assume that the vertical axis (Principal component 2 or PC2) discriminates between terrestrial herbaceous plants with *n*-C_{27}, *n*-C_{29} and *n*-C_{31} *n*-alkanes as the dominate peaks (such as *A. splendens*, *T. sinicum*, *B. sinocompressus* Tang et Wang, *Potamogeton* sp., *L. secalinus*, *P. pratensis* Linn, Appendix B) and those with *n*-C_{23} and *n*-C_{25} *n*-alkanes as the dominate peaks (such as *P. sibiricum* Laxm and *P. pectinatu*, Appendix B).

The *n*-C_{18} and *n*-C_{19} *n*-alkanes plot within the left middle side of the diagram, whereas the *n*-C_{22}, *n*-C_{24}, *n*-C_{26}, *n*-C_{28}, *n*-C_{30} and *n*-C_{32} *n*-alkanes plot within a tight cluster on the right middle side of the diagram. We assume that the horizontal axis (principal component 1 or PC1) discriminates aquatic/algal, bacterial organisms with *n*-C_{18} and *n*-C_{19} *n*-alkanes as the dominate peaks and terrigenous organic matter with *n*-alkanes distributed in reduced odd-to-even carbon number predominates due to bacterial reworking.

All the Lake Gahai samples (except GH4) plot in the low middle portion of the PCA diagram (Fig. 3c), suggesting the *n*-alkanes were mainly derived from terrestrial herbaceous plants in which *n*-C_{27}, *n*-C_{29} and *n*-C_{31} *n*-alkanes were the dominate peaks. The GH4 sample is located in the lower right quadrant of the diagram indicating that the organic matter in this sediment was also derived from terrestrial herbaceous plants but had probably been reworked by bacterial. RH1 and RH2 plot near the middle of PC1 with RH2 shifted towards the left and RH1 shifted towards the right (Fig. 3c); this indicates that the *n*-alkanes were mixture of inputs from terrestrial, emergent and suberged/floating aquatic macrophytes with relatively more aquatic organic matter being in RH2 and relatively more bacterial organic matter being in RH1. AM1 plots near the lower center of the diagram indicating that *n*-alkanes in the catchment alpine meadow sediments were mainly derived from terrestrial herbaceous plants.

Values of $\delta^{13}C$ measured for the *n*-alkanes from different regions of the samples varied from −21.2‰ to −36.9‰ (Fig. 3d, Appendix E). The isotopic composition of *n*-alkanes (especially short chain *n*-alkanes) in the two Lake Erhai samples were about 10‰ heavier than in other samples; similarly, the $\delta^{13}C$ of TOC in the two samples were much heavier than in other samples (Table 1). Thus *n*-alkanes (especially short chain *n*-alkanes) and TOC matter appeared to have the same sources for these two Lake Erhai samples. The isotopic compositions of short chain *n*-alkanes (nC_{23}–nC_{25}) in GH5 sample (gray carbonate mud) also were about 2–3‰ heavier than in most other Lake Gahai

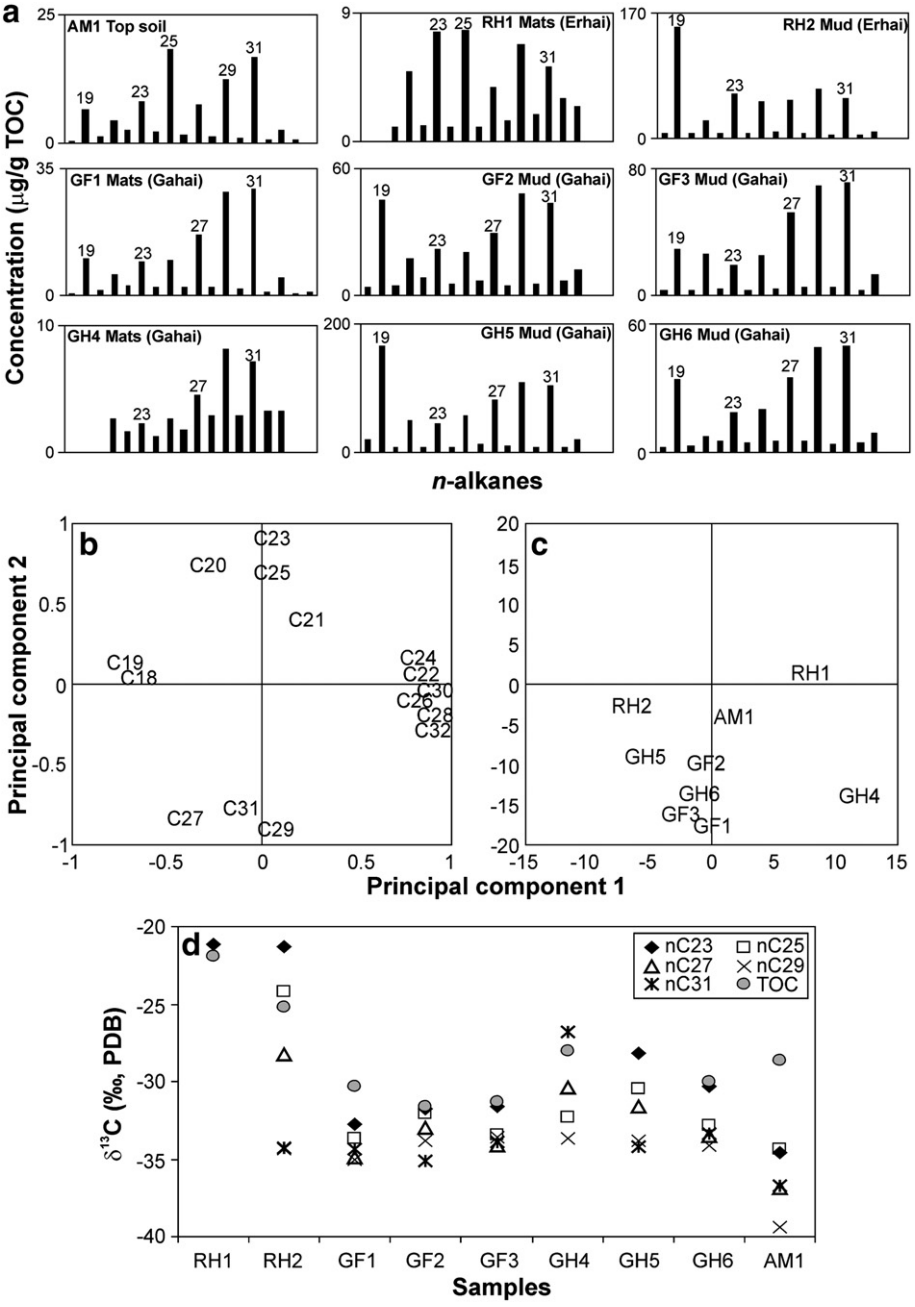

Fig. 3. Distributive and carbon isotopic compositional characteristics of *n*-alkanes (Appendix A) from lake sediments on the Tibetan Plateau. (a) distributions and concentrations (μg/g TOC (Total organic carbon)) of *n*-alkanes, peak numbers refer to chain length; (b) principal components diagram of *n*-alkanes; (c) sample principal components plot; (d) carbon isotopic composition of *n*-alkanes.

sediment samples (Fig. 3d, Appendix E). This suggests that the organic matter delivered to these sediments had higher ^{13}C vales that than in other lake sediments. Previous studies have demonstrated that enrichment of ^{13}C in natural samples may be derived from enriched substrates. For example, the ^{13}C enrichment of archaeols in New Zealand sinters was postulated to have been derived from ^{13}C enriched DIC (Pancost et al., 2006). Another possibility is that ^{13}C enriched lipids are derived from organisms with carbon assimilation pathways that do not strongly discriminate against the heavier isotope of carbon (Bradley et al., 2009). According to Håkansson (1985), a shift in $\delta^{13}C$ towards more positive values can be related to other three possible mechanisms: input of allochthonous materials derived from C_4 terrestrial vegetation; input of aquatic organic matter enriched in ^{13}C due to HCO_3^- metabolism or accelerated biomass production; and methanogenesis or accelerated mineralisation leaving behind ^{13}C enriched organic matter.

Considering that concentrations of short chain *n*-alkanes (*n*-C_{19} or *n*-C_{23}) were relatively higher in the two Lake Erhai samples (RH1 and RH2) and GH5 sample, the relatively ^{13}C enriched *n*-alkanes in these samples may have been derived from submergent/floating aquatic macrophytes or microorganisms. Such organisms probably have lived in relatively CO_2 limited environments, possibly due to the consumption by carbonate mineral precipitation at high pH (especially for the Gahai gray carbonate mud deposited sample GH5) or during high levels of productivity (Erhai freshwater samples) and reduced dissolved inorganic carbon (DIC) supply by in-flowing freshwater. Li and Ku (1997) and Leng and Marshall (2004) noted that the concentration of the DIC in in-flowing freshwater generally is much

lower than that of saline lake waters. The dilution of ^{13}C in DIC should be much larger in Lake Erhai than in Lake Gahai because its large fresh water inflow from the Daotang River. Although C_4 plants may also contribute to the heavier ^{13}C values of organic matter, they are minor components in the Lake Qinghai catchment or in the alpine soil (Lu et al., 2001; Xu et al., 2006).

Values of $\delta^{13}C$ measured for most of the *n*-alkanes from the sample AM1 collected in the alpine meadow were about 3–4‰ lighter than in other Lake Gahai sediments (GFs and GHs). Since *n*-alkanes in the AM1 sediments were distributed in two peaks maximizing at *n*-C_{25} and *n*-C_{31}, respectively (Fig. 3a), the epicuticular waxes from higher plant or grass that might have been reworked by bacteria probably were the main source of *n*-alkanes in the alpine meadow soil. Small amounts of branched fatty acids (12MeC13:0, 12MeC14:0, 14MeC15:0, 15MeC16:0 and 14MeC16:0) that have been reported to be of bacterial origin (Wilkes et al., 1999) were detected in this sample.

The neutral fractions also contained isoprenoid compounds that can probably be ascribed to archaeal lipids (Itoh et al., 2001). The isoprenoid unsaturated 2,6,10,14,18-pentamethyl-2,6,10,14,18-eicosapentene (PME) and 2,6,10,14,18,22-tetracosahexene-2,6,10,15,19,23-hexamethyl- (THM) were detected in neutral fractions in some lake sediments. Values of $\delta^{13}C$ for PME and THM varied from −25.6‰ to −31.0‰ (Appendix E) and probably were produced by different archaeal populations living under different environmental conditions.

n-Fatty acids

Fatty acids were abundant in all of samples analyzed and were characterized by a strong even/odd predominance (CPI_{FA} = 12.4–13.5, Appendix A) of long chain *n*-fatty acids with maxima at C_{16} and C_{18} (Fig. 4a and Appendix F). Other peaks with lower concentrations than C_{16} and C_{18}, maximized at *n*-C_{14}, *n*-C_{22}, *n*-C_{24} or *n*-C_{26} for most samples; the exception was RH1, which had no long chain compounds. Short chain fatty acids (<C_{20}) usually appeared in more than one isomer with both saturated and unsaturated structures. Hexadecanoic acid ($C_{16:0}$; 11.93–72.15%), 9-hexadecanoic acid ($C_{16:1\omega7c}$; 8.54–25.42%), 9-octadecanoic acid ($C_{18:1\omega9t}$; 1.32–21.4%) and 8-octadecenoic acid ($C_{18:1\omega10t}$; 6.10–10.79%) were the most abundant compounds. In contrast, carbon numbers greater than C_{20} were low in abundance (<3%).

Sources of fatty acids include bacteria, microalgae and higher plants; each of these has a distinctive fatty acid profile (Volkman et al. 1998). The *n*-fatty acids that are thought to be derived from higher plants have strong predominance of the even chain lengths and are characterized by higher molecular weight compounds (C_{20}–C_{32}) with C_{max} at C_{22}, C_{24}, C_{26} or C_{28} (Yang and Huang, 2003), whereas short chain compounds are characteristic of many algae and bacteria (Merritt et al., 1991). However, short chain fatty acids can also be detected in terrestrial herbaceous plants (e.g., *Saussurea salsa* (Pall.) *Spreng*, *Pedicularis. kansuensis* Maxim., *Pedicularis. longiflora* Rudolph) and some autochthonous aquatic organisms (e.g., *S. crassa* Kützing, *G. przewalskii* and plankton; Appendix C). Thus, the dominance of *n*-fatty acids by short chain compounds in all the sediment samples suggests that their origin mainly derived from submerged or floating aquatic macrophytes and bacterial organic matter input to the lake; catchment soil may also have contributed. The aquatic/terrigenous ratio for fatty acids (ATR_{FA}; after Wilkes et al., 1999, Appendix A) can be used as a relative measure of the autochthonous versus allochthonous input; high ATR_{FA} values (>0.4) indicate a high relative contribution of short-chain fatty acids which are believed to be produced mainly by aquatic organism (Wilkes et al., 1999). For our study, this ratio ranged between 0.9 and 1.0 which suggests a mainly autochthonous organic matter input to the sediments.

PCA was used to elucidate the origin of the fatty acids measured in this study (Fig. 4b, c). The short chain $12MeC_{13:0}$, $C_{16:1\omega7c}$, $C_{18:0}$ and $C_{18:1\omega9t}$ fatty acids plot within a tight cluster on the lower right side of the PCA diagram (Fig. 4b), whereas the long chain $C_{20:0}$, $C_{22:0}$, $C_{24:0}$, $C_{26:0}$ and $C_{28:0}$ *n*-fatty acids plot fall within the upper right portion of the diagram. We assume that PC2 discriminates between aquatic/algal organisms with C_{14}, C_{16} and C_{18} fatty acids as the dominate peaks and terrestrial herbaceous plants with *n*-C_{24}, *n*-C_{26} and *n*-C_{28} *n*-fatty acids as the dominate peaks. The *n*-C_{14} and *n*-C_{16} *n*-fatty acids and a few unsaturated fatty acids such as $C_{16:1\omega5t}$, $C_{18:1\omega10t}$, $C_{18:2\omega7}$ and $C_{20:1\omega9t}$ plot within the left side of the diagram, whereas most of branched and unsaturated fatty acids such as $12MeC_{14:0}$, $10MeC_{18:0}$, $15MeC_{16:0}$, $9MeC_{14:0}$, $14MeC_{15:0}$, $C_{18:1\omega11t}$, $iC_{17:1\omega5t}$ and $C_{16:1\omega9c}$ plot within a tight cluster on the right middle side of the diagram (Fig. 4b). We assume that PC1 discriminates aquatic/algal organisms with short chain *n*-fatty acids as the dominate peaks and bacterial organic matter with branched and unsaturated fatty acids as the significant compounds.

All Lake Erhai samples, Lake Gahai samples (except GH4 and GH5), and the AM1 sample plot within a tight cluster in the low right quadrant of the PCA diagram (Fig. 4c), suggesting the fatty acids in those sediments were mixture inputs derived from aquatic and bacterial organic matter. GH4 and GH5 were located in the left side of the diagram with GH4 shifted towards the up side and RH5 shifted towards the lower side (Fig. 4c), indicating that the fatty acids in both GH4 and GH5 sample sediments were inputs from aquatic/algal organisms with relatively more terrestrial herbaceous plants derived fatty acids being in GH4 and relatively more bacterial organic matter derived fatty acids being in GH5.

Values of $\delta^{13}C$ measured for the fatty acids from different regions of the samples varied from −23.5‰ to −41.0‰ (Fig. 4d, Appendix G). Similar to the *n*-alkanes, the fatty acids in different samples also showed much difference in the carbon isotopic compositions. The isotopic compositions for the fatty acids measured in RH1 and RH2 were about 7–10‰ heavier than in other samples (Fig. 4d, Appendix G). This difference agrees with the observations that the $\delta^{13}C$ of *n*-alkanes and TOC in these two Lake Erhai samples were also much heavier than in other samples (Table 1 and Appendix E). Again, we relate this to the higher productivity and possibly limited DIC supply in the Lake Erhai freshwater which has led to specialized submerged/floating aquatic macrophytes or microorganisms adapted to this relatively CO_2 limited environment.

Values of $\delta^{13}C$ for most of the fatty acids from samples GH4, GH5 and AM1 were relatively enriched in ^{13}C compared to other GF sediments, whereas the isotopic compositions of the fatty acids from sample GH6 were ^{13}C depleted by about 1–2‰ than any other GF sediments; the difference in the carbon isotopic compositions of fatty acids between GH6 and AM1 and other GH sediments was as much as 5‰ for most of the measured compounds (Fig. 4d). Moreover, the carbon isotopic compositions of *n*-alkanes measured in sample AM1 were more ^{13}C-depleted than other samples, whereas the isotopic composition of the fatty acids were more enriched in ^{13}C (Figs. 3d and 4d) than any other GFs and GHs samples. Thus, the carbon isotopic composition differences between the *n*-alkanes and fatty acids in sample AM1 are about 3–5‰ (Appendix E and Appendix G). These differences in $\delta^{13}C$ values may indicate different dietary sources for the *n*-alkanes and fatty acids, they may turn over at different rates, or they are synthesized via distinct pathways having different isotopic fractionations associated with them.

n-Alkan-2-ones

A homologous series of *n*-alkan-2-ones (Appendix A) was detected in very low abundance in six of the nine samples analyzed (not detected in samples RH1, GH4 and GH5), with carbon numbers ranging from C_{19} to C_{31}. The *n*-alkan-2-one distributions were characterized by a strong odd/even carbon number predominance and maximized at *n*-C_{23}, *n*-C_{25} or *n*-C_{29} (Fig. 5). Saturated *n*-alkan-2-ones are quite common in geological samples, occurring widely in soils, peat (Morrison and Bick, 1966), marine sediments (Simoneit,

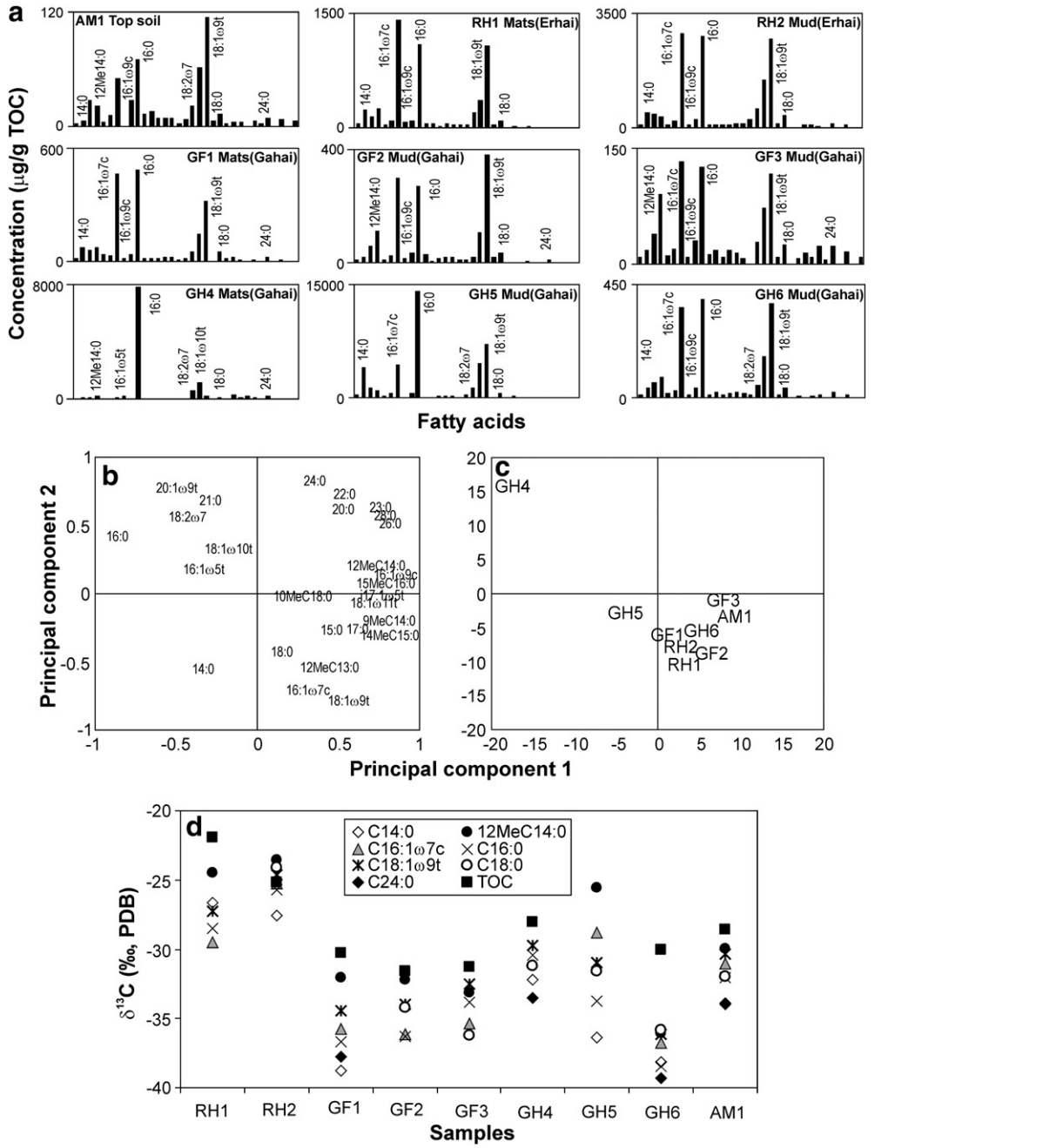

Fig. 4. Distributive and carbon isotopic compositional characteristics of fatty acids from lake sediments on the Tibetan Plateau. (a) Distributions and concentrations (μg/g TOC) of fatty acids, compound names were assigned in the peaks; (b) principal components diagram of fatty acids; (c) sample principal components plot; (d) carbon isotopic composition of fatty acids.

1978), lacustrine sediments (Rieley et al., 1991), and coal samples (Tuo and Li, 2005). Saturated *n*-alkan-2-ones have also been reported in higher plant phytoplankton biomass and seagrasses (Hernandez et al., 2001; Qu et al., 1999; Rieley et al., 1991). The alkanones occurring in higher plant waxes are C_{23}–C_{33} mid-chain ketones with a predominantly odd carbon number predominance and C_{max} at C_{29} or C_{31} in higher plant waxes (Baker, 1982) or at C_{25} in seagrasses (Hernandez et al., 2001). The distributions of the alkanones found in geological samples have been remarkably similar, typically showing a high predominance of odd/even carbon number homologous and C_{max} at *n*-C_{27} or *n*-C_{29}. The close resemblance of alkanones to the *n*-alkane distributions has led several authors to suggest that alkan-2-ones are formed by microbially mediated β-oxidation of the corresponding *n*-alkanes in the sediment (Cranwell et al., 1987; Lehtonen and Ketola, 1990) or β oxidation of fatty acids followed by decarboxylation (Volkman et al., 1981). Volkman et al. (1980) also proposed that the *n*-alkanes are derived from at least two sources with an algal/bacterial contribution of C_{15} to C_{31} *n*-alkanes with a low odd carbon number predominance superimposed on a distribution showing a much high odd-predominance, originating from plants. Microbial oxidation of the latter, prior to incorporation into the sediment, could generate a distribution of *n*-alkan-2-ones low in odd predominance and maximizing at shorter carbon numbers than those of the corresponding *n*-alkanes. Overall, there were no correlations between distribution patterns among *n*-alkanes, *n*-fatty acids and *n*-alkan-2-ones in the samples analyzed in this study; therefore, *n*-alkane and *n*-fatty acid series cannot be the sources of *n*-alkan-2-ones in the samples studied. Since no *n*-alkan-2-ones were detected in two

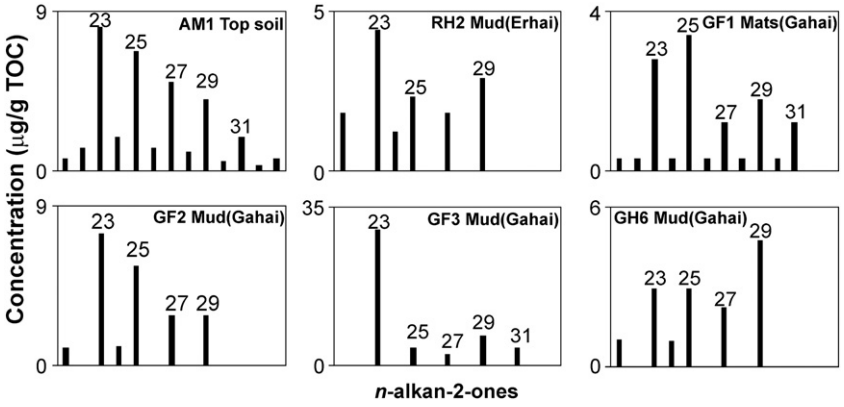

Fig. 5. Distributions and concentrations (μg/g TOC) of *n*-alkan-2-ones (Appendix A) from lake sediments on the Tibetan Plateau. Peak numbers refer to chain length.

of the three algal mats and algal mats-containing samples (RH1 and GH4) and only minimal amounts of *n*-alkan-2-ones were detected in the third one (GF1), it could be precluded that algae be the source material for *n*-alkan-2-ones. Considering that *n*-alkan-2-ones could be detected in most of the lake sediments and the catchment alpine meadow soil sample, epicuticular waxes of higher plants or grass from the catchment that have been reworked by bacteria may be the possible source for these compounds. Variable amounts of branched fatty acids (2- and 3-methyl fatty acids) which were reported to be of bacterial origin (Wilkes et al., 1999) were detected in all of the *n*-alkan-2-ones containing sediments. Unfortunately, the homologous series of *n*-alkan-2-ones were not abundant enough to allow their carbon isotopic analysis in the samples.

Conclusions

The contents and the distribution patterns of the lipid compounds and their carbon isotopic compositions can be used as proxies for assessing the sources of the organic matter in a lake sediments and soil in a catchment. In this study, abundant *n*-fatty acids and lesser amounts of *n*-alkanes and *n*-alkan-2-ones were detected with different distribution patterns for algal mats, sandy mud and alpine meadow soil samples collected from Lake Erhai and Lake Gahai and the catchment alpine meadow. Microalgal or bacterial sources were assumed to be the major contributors to the organic matter in the sediments analyzed. Although the three series of lipids could be detected in the same samples, they were assumed to have different precursors. From the distribution patterns and the carbon isotopic compositions of the lipid compounds, it is concluded that a mixture input of epicuticular waxes of higher plants and submergent plants in the littoral zone were the sources of long chain *n*-alkanes; *n*-fatty acids sources were mainly attributed to submergent or floating aquatic macrophytes and bacterial organic matter whereas epicuticular waxes of higher plants or grass from the catchment that have been reworked by the bacteria may be the possible source for the *n*-alkan-2-ones observed. Carbon isotopes of total organic carbon and lipid biomarkers distinguish Lake Erhai from Lake Gahai with of the enhanced productivity of the former, possibly caused by inflow of freshwater.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.jglr.2011.05.018.

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