



Characterisation of *n*-alkanes and their hydrogen isotopic composition in sediments from Lake Qinghai, China

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ABSTRACT

The distributions of *n*-alkanes and their hydrogen isotopic composition (δD) in surface and core sediments from the saline Qinghai Lake were measured to assess whether or not biological source information was recorded in the δD values of *n*-alkanes. The results indicate that the *n*-alkane distributions between shallow water surface and core sediments were similar, and closer to those of terrestrial herbaceous plants from the Qinghai Lake surrounding areas, rather than the aquatic plants living in the lake. The *n*-alkanes in the surface and core sediments had similar mean δD values, ranging from -185‰ to -133‰ and -163‰ to -142‰ , respectively. The mean δD values of *n*-alkanes in the sediments showed that the even *n*-alkanes were heavier in D compared with the odd homologues.

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1. Introduction

It has been shown that the compound-specific stable hydrogen isotope composition (δD values) of *n*-alkanes from sediments can provide important information about sediment deposition (Xie et al., 2000; Sauer et al., 2001; Dawson et al., 2004; Grice and Brocks, 2011 for a review), such as sources of sedimentary organic matter (OM) in geological samples (Li et al., 2001; Dawson et al., 2005, 2007; Grice et al., 2009; Duan et al., 2010; McKirdy et al., 2010; Nabbefeld et al., 2010; Williford et al., 2011) and palaeoenvironments (Huang et al., 2002; Sachse et al., 2004; Duan and Wu, 2009). Numerous investigations of the *n*-alkane hydrogen isotopic composition of various plants and the hydrogen isotopic fractionation between plant *n*-alkanes and source water have been conducted (e.g. Bi et al., 2005; Sessions, 2006; Chikaraishi and Naraoka, 2007; Gessler et al., 2007; Grice et al., 2008; Duan and Wu, 2009; Zhou et al., 2010, 2011). At the same time, the hydrogen isotopic composition of *n*-alkanes in recent sedimentary OM has also been studied (Huang et al., 2004; Chikaraishi and Naraoka, 2005; Grice et al., 2009; Li et al., 2009; Seki et al., 2009, 2010). However, fewer studies have been performed on the hydrogen isotopic composition of individual *n*-alkanes related to depositional environments.

In general, lake sedimentary OM preserves a record of stable hydrogen isotope signals from lake water and precipitation (Sessions et al., 1999; Yang and Huang, 2003; Huang et al., 2004; Sachse et al., 2004). Therefore, the δD values of *n*-alkanes in lake sediments can provide information about palaeoclimate, but the record is strongly influenced by environmental variables such as lake hydrology and climatic parameters (Mügler et al., 2008; Duan et al.,

2010). Intense evaporation of water associated with saline lakes influences the δD values of *n*-alkanes in aquatic plants (Mügler et al., 2008). The *n*-alkanes in lake sediments can be derived from various organisms such as algae and bacteria living in the water column and also aquatic macrophytes and higher land plants (Eglinton and Hamilton, 1967; Han and Calvin, 1969; Rieley et al., 1991; Ficken et al., 2000). Thus, distinction between *n*-alkanes of various genetic origins in lake sediments is important for studies using stable hydrogen isotopes of *n*-alkanes. Lake sediments in shallow water generally contain a large proportion of terrigenous OM, so such areas are favourable for hydrogen isotopic studies of terrestrially-derived *n*-alkanes. Seasonal variations in *n*-alkane hydrogen isotope ratio values in deciduous leaves occur and most leaves are deposited in lakes during autumn (Sachse et al., 2006). The δD values of sedimentary *n*-alkanes in a lake most likely represent those *n*-alkanes synthesised from the entire growing season of the plants.

Lake Qinghai, as the largest saline lake in China, is under a dry climate with annual evaporation exceeding annual recharge. Plankton in the lake is rare as a result of the extremely low oxygen content of the water. Surface and core sediments from shallow water areas of the lake were sampled in autumn and analysed for the distributions of *n*-alkanes and their stable hydrogen isotopic compositions. At the same time, by comparing them with the plant *n*-alkane record investigated in a previous study (unpublished data), we assessed potential biological sources for the sedimentary *n*-alkanes. The data provide a scientific basis for the application of δD values of sedimentary *n*-alkanes in palaeoenvironmental studies.

2. Samples and analysis

Lake Qinghai is a saline lake on the northeastern edge of the Tibetan Plateau (Fig. 1). It is 106 km long from east to west and

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62 km wide from north to south, with a surface area of ca. 4260 km² and a water surface elevation of 3193 m above sea level. The average water depth is ca. 20 m. Average annual temperature ranges from −1.3 to 0.5 °C and average annual rainfall from 323 to 384 mm, whereas the annual evaporation ranges from 1378 to 1767 mm (Sun et al., 2007). There are 30 streams flowing into the lake. Over the last few decades evaporation of lake water has been greater than recharge, so that the lake level has decreased ca. 10 cm since 1955 (unpublished data). The present pH of the water is 9.2 and the average salinity 14.15‰.

Samples of surface sediments from shallow water areas of the lake were collected in August 2008 (Table 1). Some fragments of higher plant biomass, such as grass, were observed in the surface sediments. A sediment core was also obtained in shallow water from the northwest of the lake using a gravity corer (Fig. 1). The sediments grade from dark grey to black mud from top to bottom of the core.

The core was cut at 10 cm intervals and the five sediment samples were dried at room temperature and crushed to 80 mesh (size 0.180 mm) and kept frozen until analysis. Soluble OM was extracted from ca. 150 g sediment using a Soxhlet apparatus with a mixture of CH₂Cl₂–MeOH (2:1, v/v). The extracts were filtered and evaporated to dryness, and fractionated using column chromatography on alumina over silica gel (see Duan et al., 2004, 2005 for details). The saturated hydrocarbon, aromatic hydrocarbon, ketone and alcohol fractions were obtained using successive elution with *n*-hexane, CH₂Cl₂, 10% EtOAc in *n*-hexane and 20% EtOAc in *n*-hexane, respectively. The final fraction containing fatty acids was obtained by elution with MeOH.

The *n*-alkanes in the hydrocarbon fraction were identified using gas chromatography–mass spectrometry (GC–MS) with a 6890N gas chromatograph/5973N mass spectrometer equipped with a HP-5 column (30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC oven temperature was raised from 80 to 300 °C (held 30 min) at 4 °C min^{−1}. He was used as carrier gas. MS conditions were: electron ionization (EI) at 70 eV with an ion source temperature of 250 °C. The GC–MS system was operated in full scan mode from *m/z* 20 to 750.

Analysis of the stable hydrogen isotope composition of the individual compounds was performed with a Delta Plus XP gas chromatograph–pyrolysis–isotope ratio mass spectrometer. GC was

performed using a Thermo Finnigan GC Combustion III system equipped with an SE-54 fused silica column (60 m × 0.32 mm i.d. × 0.25 μm film thickness) and He as carrier gas at 1 ml/min. The oven temperature was raised from 80 to 300 °C (held 30 min) at 3 °C min^{−1}. The compounds were passed through an alumina tube heated at 1450 °C to convert them to hydrogen. The hydrogen was then introduced to the Delta Plus XP isotope ratio mass spectrometer. The reproducibility and accuracy of the analysis were evaluated routinely using laboratory standards of known δD values (*n*-C₁₄, *n*-C₁₆, *n*-C₁₈, *n*-C₂₃, *n*-C₂₈ and *n*-C₃₂). Typically, one injection of the standard was performed for every four sample analyses. The H₃⁺ correction factor measured daily was always in a range between 2.5 and 4.0 and the daily variability was within 0.1. Isotopic values are reported with respect to the international Vienna Standard Mean Ocean Water (VSMOW) standard. Samples were analyzed once or up to three times. The *n*-alkanes presented in Table 3 have standard deviation <5‰.

3. Results and discussion

3.1. Compositions of *n*-alkanes in lake surface sediment and core sediments

Sources of plant *n*-alkanes in sediments are generally inferred from their distributions, which are influenced by plant sources and growth environment (Ficken et al., 2000). The molecular parameters of *n*-alkanes extracted from the surface sediments and the core samples are presented in Table 1 and histograms are shown in Figs. 2 and 3. The surface and core sediments have similar distributions with 16–33 carbons, with *n*-C₂₃, *n*-C₂₅ and *n*-C₂₇ alkanes as the major compounds, corroborating previous observations for the vegetation in the Lake Qinghai and its surrounding areas (unpublished data). All samples have a strong odd predominance with the carbon preference index (CPI) between 3.4 and 5.7, with the exception of sample QM-2 being 8.0. This is similar to the CPI values (from 4.0 to 4.5, averaging at 4.3) of *n*-alkanes in *Poa* sp. from the surrounding area of the lake (Table 2). The ACL values in the sediments range from 27.0 to 28.0, which approximates to the average values (27.9–28.3) of *Kobresia* sp., *Poa* sp. and *Oxytropis ochrocephala* from the area surrounding the lake (Table 2).

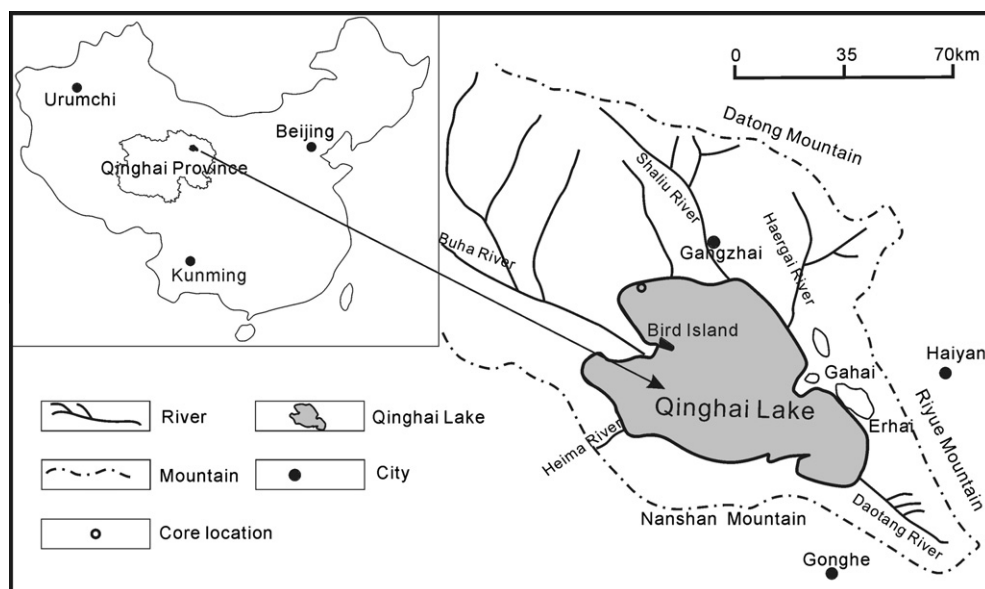


Fig. 1. Lake Qinghai location.

Table 1
Description and coordinates of sediment samples and alkane distribution in terms of range of chain length (C range), most abundant (C max), carbon preference index (CPI), and average chain length (ACL).

Sample	Sediment	Depth (cm)	Coordinates	C range	C max	ACL ^a	CPI ^b
<i>Surface sediment</i>							
QM-1	Black mud	Surface	37°11'15"N; 100°04'38"E	C ₁₆ –C ₃₃	C ₂₇	27.9	4.5
QM-2	Black mud	Surface	37°11'48"N; 99°49'34"E	C ₂₁ –C ₃₁	C ₂₉	27.9	8.0
QM-6	Grey mud	Surface	37°08'18"N; 100°20'44"E	C ₁₆ –C ₃₁	C ₂₇	27.4	4.7
QM-9	Grey mud	Surface	37°11'15"N; 100°04'38"E	C ₁₇ –C ₃₃	C ₂₅	27.7	4.1
QM-13	Grey mud	Surface	36°54'06"N; 99°38'01"E	C ₁₇ –C ₃₃	C ₂₇	27.8	5.7
QM-15	Black mud	Surface	36°32'52"N; 100°41'27"E	C ₂₁ –C ₃₁	C ₂₉	28.0	5.2
QM-17	Black mud	Surface	36°39'14"N; 100°16'16"E	C ₁₆ –C ₃₁	C ₂₇	27.5	4.0
QM-20	Black mud	Surface	36°37'59"N; 100°06'59"E	C ₁₆ –C ₃₁	C ₂₇	27.7	3.5
QH-2-3	Black mud	Surface	36°54'06"N; 99°38'01"E	C ₁₇ –C ₃₁	C ₂₇	27.1	4.9
<i>Core sediment</i>							
QZH-2-10	Dark grey mud	0–10	37°11'48"N; 99°49'34"E	C ₁₇ –C ₃₃	C ₂₇	28.0	3.7
QZH-2-20	Black mud	10–20	37°11'48"N; 99°49'34"E	C ₁₇ –C ₃₁	C ₂₅	27.5	3.9
QZH-2-30	Black mud	20–30	37°11'48"N; 99°49'34"E	C ₁₉ –C ₃₁	C ₂₅	27.0	3.4
QZH-2-40	Black mud	30–40	37°11'48"N; 99°49'34"E	C ₁₉ –C ₃₃	C ₂₉	27.9	3.8
QZH-2-50	Black mud	40–50	37°11'48"N; 99°49'34"E	C ₁₉ –C ₃₃	C ₂₉	28.0	4.8

^a $ACL = [25(nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})] / (nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})$.

^b $CPI = [(C_{25} + C_{27} + \dots + C_{33}) / (C_{24} + C_{26} + \dots + C_{32})] + [(C_{25} + C_{27} + \dots + C_{33}) / (C_{26} + C_{28} + \dots + C_{34})] / 2$.

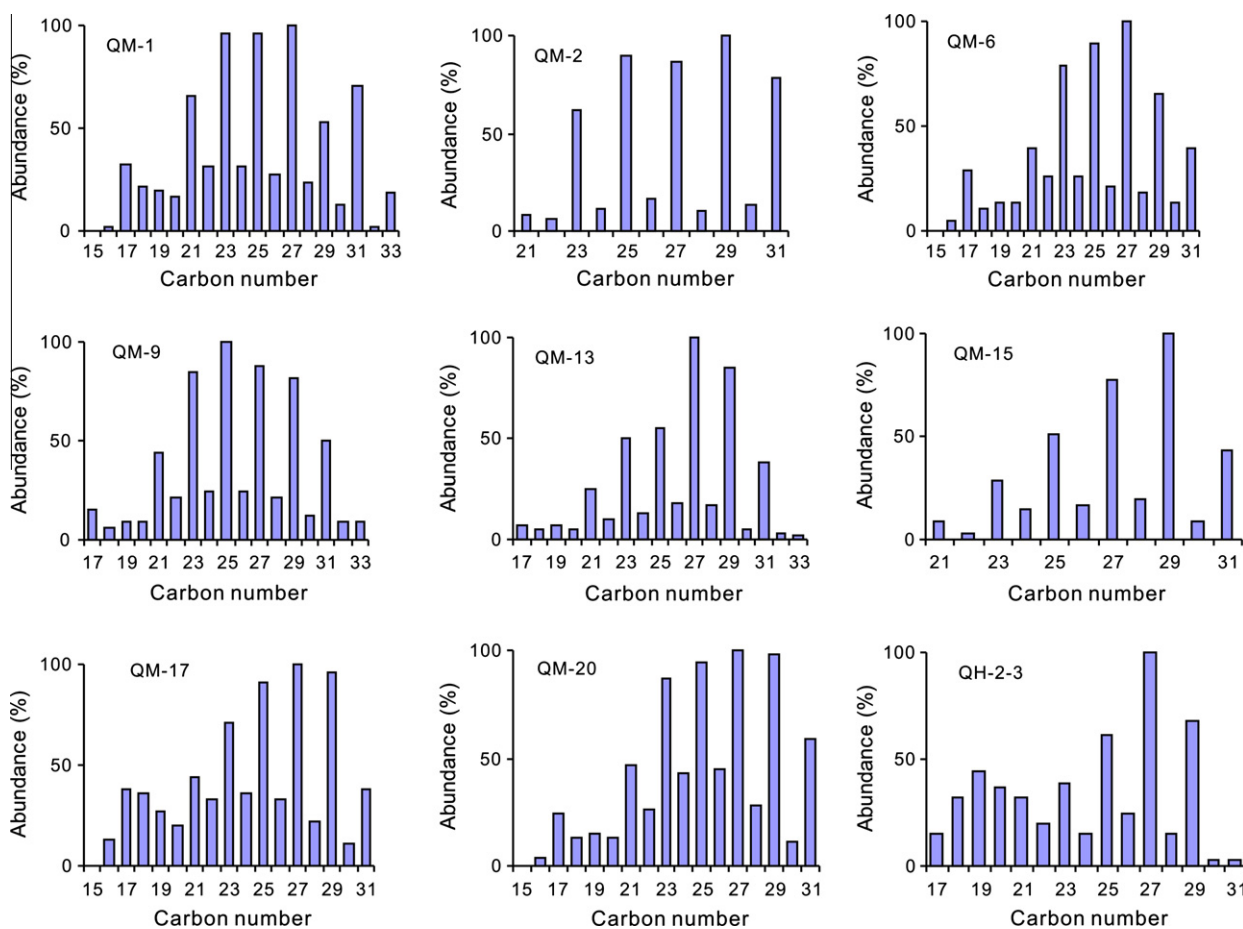


Fig. 2. Histograms for *n*-alkanes in surface sediments.

3.2. Stable hydrogen isotopic compositions of *n*-alkanes in lake surface sediment and core sediments

The δD values of individual *n*-alkanes in the surface and core sediments from the lake range from -211‰ to -113‰ and mean values vary between -185‰ and -133‰ (Table 3). The mean δD values in the surface sediments appear to be divided into two cat-

egories. The mean δD values of the samples QM-1, QM-2, QM-6, QM-17 and QM-20 are less than -157‰ whereas, the samples QM-9, QM-13, QM-15 and QH-2-3 are more than -151‰ . The mean δD values of the C₂₁–C₃₁ *n*-alkanes in the surface sediments exhibit the characteristic that even *n*-alkanes are isotopically heavier than the odd numbered homologues (Table 3). The δD values of *n*-alkanes in the core sediments, ranging from -187‰ to

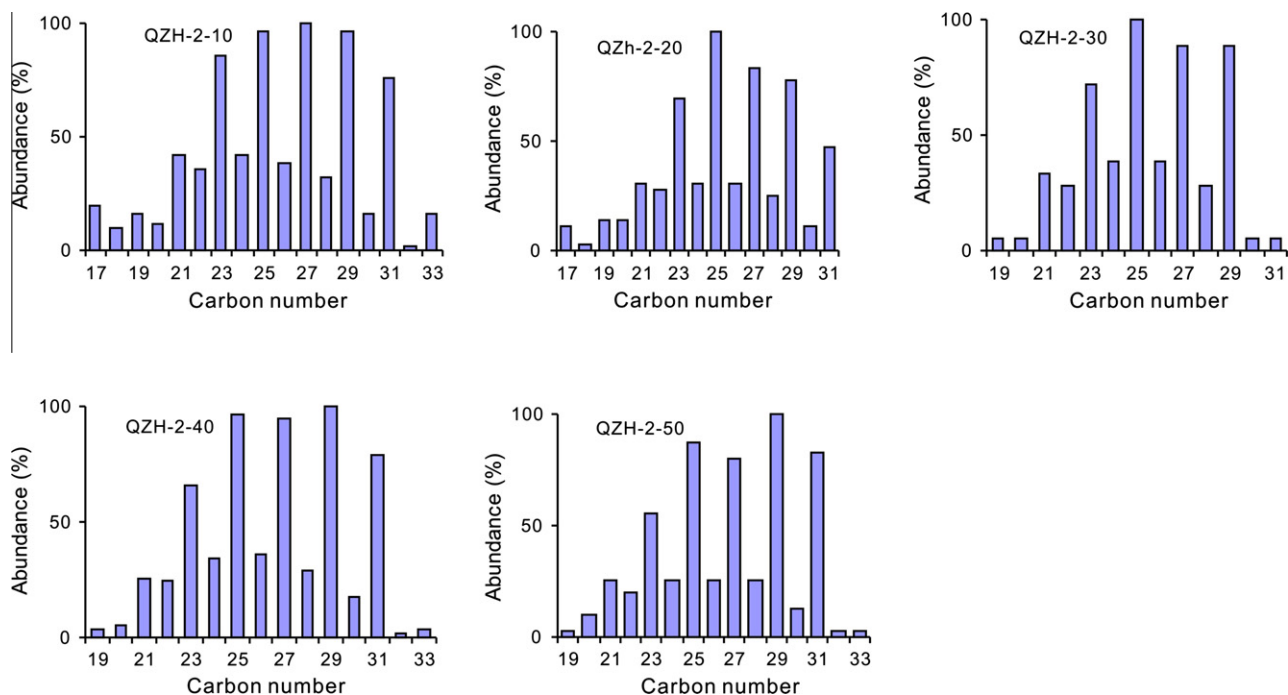


Fig. 3. Histograms for *n*-alkanes in core sediments.

Table 2

Mean ACL, CPI and δD values of *n*-alkanes in plants from Qinghai Lake and surrounding area (unpublished data).^a

Plant	Sample number	Mean ACL	Mean CPI	Mean δD value (‰)
<i>Potamogeton gramineus</i> and <i>Spirogyra intorta</i>	7	26.3	7.6	-130
<i>Triglochin maritimum</i>	3	28.4	18.4	-163
<i>Kobresia</i> sp.	3	28.1	13.3	-138
<i>Poa</i> sp.	3	27.9	4.3	-165
<i>Oxytropis ochrocephala</i>	1	28.3	25.7	-165
<i>Leymus</i> sp.	2	28.6	18.7	-150
<i>Populus cathayana</i> and <i>Salix</i> sp.	4	26.8	12.5	-122

^a ACL, average chain length of long chain *n*-alkanes; CPI: carbon preference index, δD : hydrogen isotopic composition.

Table 3

Hydrogen isotopic values of *n*-alkanes in sediments (‰).

Sample	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₄	C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁	Mean
<i>Surface sediment</i>														
QM-1			-194	-188	-179	-181	-173	-176	-165	-170	-158	-172	-174	-176
QM-2							-191	-190	-190	-172			-188	-185
QM-6	-152	-169	-159	-171	-172		-167	-155	-165	-139	-156	-120	-161	-157
QM-9	-121		-162	-161	-171	-152	-162	-146	-155	-131	-149		-155	-151
QM-13	-118	-120	-164	-132	-169		-161	-144	-158	-133	-165		-155	-147
QM-15			-119		-144	-154	-174		-149	-123	-149		-148	-145
QM-17	-183	-175	-201	-181	-202	-211	-188	-185	-172	-135	-155			-181
QM-20		-138	-167	-147	-167	-172	-163	-149	-159	-136	-162		-161	-157
QH-2-3			-113	-119	-140	-124	-143	-129	-150		-144			-133
Mean	-143	-150	-160	-157	-168	-166	-169	-155	-163	-138	-157	-146	-163	-159
<i>Core sediment</i>														
QZH-2-10		-144	-174	-163	-177	-187	-177	-151	-168	-150	-162	-133	-167	-163
QZH-2-20			-157	-141	-180	-158	-167	-136	-155	-125	-150		-145	-152
QZH-2-30			-138	-121	-165	-141	-159	-121	-152		-142			-142
QZH-2-40		-137	-170	-159	-171		-173	-148	-164	-143	-161	-131	-163	-156
QZH-2-50			-149	-130	-174	-149	-166		-158		-156		-158	-155
Mean		-140	-158	-143	-173	-159	-168	-139	-159	-139	-154	-132	-158	-154

-121‰ and averaging from -163‰ to -142‰, are similar to those in the surface sediments. For the sediment core, the mean δD values change with increasing depth, first increasing to the maximum δD value at depth of 30 cm and then decreasing below this (Table 3 and Fig. 4). The mean δD values of even *n*-alkanes in

the core sediments are also heavier than those of the odd homologues (Table 3). The δD and $\delta^{13}C$ values of *n*-alkanes from plants have been shown to be related to the biosynthetic pathway associated with the even numbered *n*-alkanes in the plants (Zhou et al., 2010).

3.3. Sources of *n*-alkanes in lake sediments

The vegetation surrounding the Lake Qinghai is specific for a semi-arid to arid climate and high altitude and consists principally of alpine meadows and steppe grasses. The vegetation species are dominated by *Oxytropis* sp., *Agropyron* sp., *Kobresia* sp., *Poa* sp., *Achnatherum* sp. and *Stipa* sp. and wood plants are rare. Therefore, the sources of *n*-alkanes in the sediments from the lake should be aquatic plants and organisms and terrestrial herbaceous plants. However, the average ACL values in the sediments are from 27.0 to 28.0, with a mean 27.6, which are obviously from aquatic emergent plants, but are different from the ACL values (from 26.0 to 26.8, unpublished data; 26.3 on average, Table 2) of *Potamogeton gramineu* and *Spirogyra intorta* in the lake. The ACL values for the terrestrial herbaceous plants such as *Kobresia* sp., *Poa* sp. *O. ochrocephala* and *Leymus* sp. surrounding the lake have a mean value of 27.6 (Table 2), the same as the mean ACL value measured for the sediments.

Previous results have shown that the stable hydrogen isotopic composition of *n*-alkanes in sediments reflects δD values of *n*-alkanes in their biological sources that are ultimately influenced by climate (Dawson et al., 2004; Sachse et al., 2004; Chikaraishi and Naraoka, 2006; Huang et al., 2006). For example, aquatic plant-derived *n*-alkanes have more negative δD values than *n*-alkanes from terrestrial plants at the same site under humid climate conditions. The opposite has been shown to occur in semi-arid to arid climate conditions (Mügler et al., 2008). For Lake Qinghai, evaporation under the semi-arid to arid climate led to a deuterium enrichment of 41‰ for lake water relative to the input water (unpublished data). Thus *n*-alkanes of aquatic *P. gramineu* and *S. intorta* (with mean δD values of -136 ‰ to -121 ‰, unpublished data) have heavier mean hydrogen isotopic compositions compared to the terrestrial herbaceous plants (with mean δD values of -173 ‰ to -136 ‰, unpublished data) at the same site. There is also a significant difference between their *n*-alkane δD profiles (Fig. 5). The C_{23} and C_{25} odd *n*-alkanes in the aquatic *P. gramineu* and *S. intorta* are isotopically heavier compared to adjacent even homologues, whereas the terrestrial herbaceous plants exhibit an opposite trend (Fig. 5).

The δD values of *n*-alkanes in the surface and core sediments from the lake are similar to those in the terrestrial plants growing in areas surrounding the lake (Table 3 and Fig. 5) and the mean δD values (-185 ‰ to -133 ‰) of *n*-alkanes in the surface and core sediments

are close to those (-173 ‰ to -136 ‰, unpublished data) in the terrestrial herbaceous plants (Tables 2 and 3). As shown in Fig. 6, δD values of C_{27} *n*-alkane in the sediments are also close to those from the terrestrial herbaceous plants. These clearly indicate that *n*-alkanes in the surface and core sediments are sourced mainly from the terrestrial herbaceous plants in the study region. This is consistent with the sampling having been carried out at a shallow water site where there is abundant terrigenous sedimentary OM.

It must be noted that the δD values of *n*-alkanes in plankton or microbial biomass from the lake are unknown, so the potential contribution of *n*-alkanes from these organisms to the sediments could not be assessed. Different carbon number *n*-alkanes in sediments may come from various biological sources. In general, C_{15} – C_{19} *n*-alkanes originate mainly from algae and bacteria (Han and Calvin, 1969; Cranwell et al., 1987; Grice et al., 1997; Meyers, 2003), mid-chain *n*-alkanes such as C_{23} and C_{25} can be produced by submerged aquatic plants (Baas et al., 2000; Ficken et al., 2000; McKirdy et al., 2010) and C_{27} – C_{29} *n*-alkanes are derived principally from the epicuticular wax of vascular higher plant leaves (Eglinton and Hamilton, 1967; Rieley et al., 1991; Meyers, 2003). The δD value of the C_{19} *n*-alkane in the surface sediments is heavier than those of the other odd alkanes (Table 3). Except for sample QM-17, mean δD value (from -152 ‰ to -118 ‰, -130 ‰ on average) of the C_{19} *n*-alkane in the surface sediments is similar to that (from -152 ‰ to -109 ‰, -128 ‰ on average, unpublished data) in *S. intorta* in the lake (Fig. 5), indicating that it is derived mainly from *S. intorta*. The mean δD values of other *n*-alkanes in the sediments indicate that they have originated principally from the terrestrial herbaceous plants in the lake surrounding area (Table 3 and Fig. 5).

For the distribution of *n*-alkane mean δD values in the different surface sediment samples, relatively depleted δD values for samples QM-1, QM-2, QM-6, QM-17 and QM-20 possibly suggest that their *n*-alkanes are derived mostly from the terrestrial *Poa* sp. and *O. ochrocephala*, whereas relatively enriched δD values for samples QM-9, QM-13, QM-15 and QH-2-3 potentially indicates that their *n*-alkanes are derived mostly from the terrestrial *Kobresia* sp. and *Leymus* sp. (Fig. 5). The phenomenon of initially increasing and then decreasing mean δD value in the core sediments with increasing depth (Fig. 4) may be attributed to (i) climate change; (ii) different biological sources. The trend in ACL values with increasing depth is precisely the opposite of the trend observed

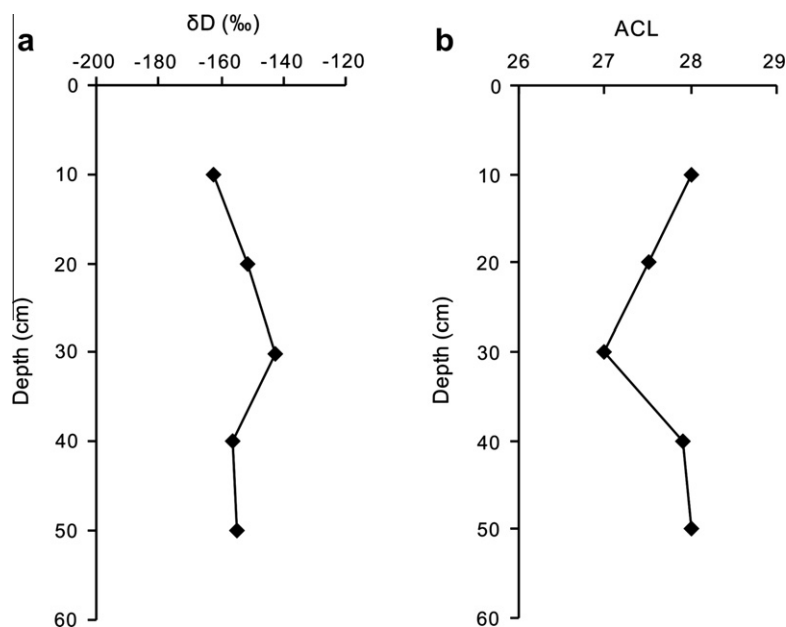


Fig. 4. Mean δD (a) and ACL (b) values of *n*-alkanes in core sediments vs. depth.

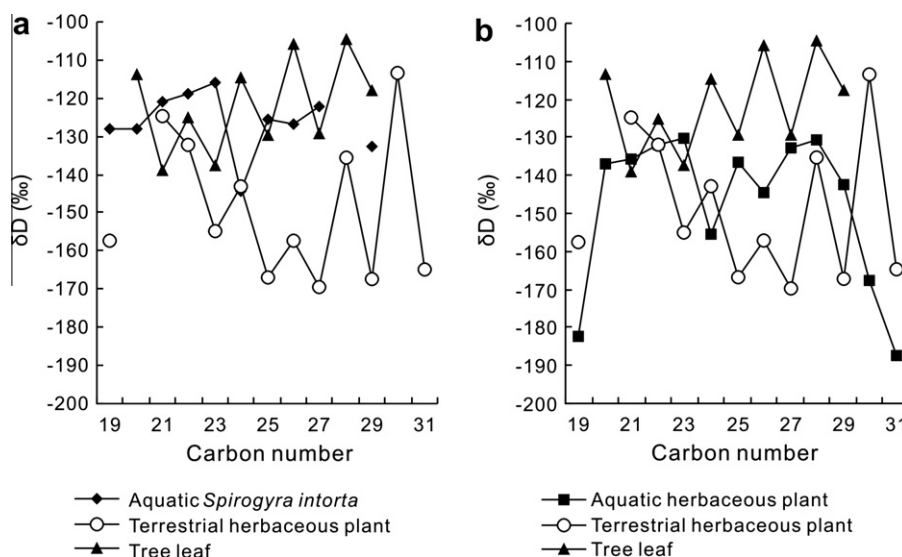


Fig. 5. Cross plot of mean δD value vs. carbon number of n -alkanes in plants from Qinghai Lake areas (unpublished data).

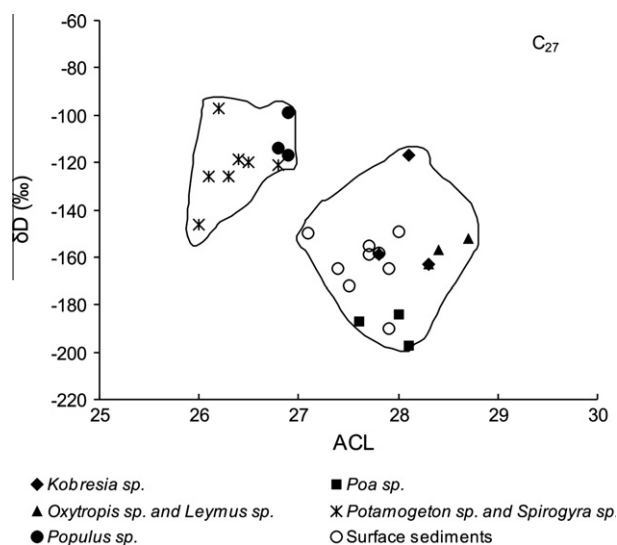


Fig. 6. δD values of C_{27} n -alkane and ACL values of n -alkanes in terrestrial and aquatic plants from Lake Qinghai and surrounding areas (unpublished data).

in the mean δD values. This is consistent with the relationship between ACL and δD values of n -alkanes in the flora from Lake Qinghai and its surrounding areas (unpublished data). Therefore, the difference in biological sources may be an important factor.

4. Conclusions

Stable hydrogen isotopic compositions of n -alkanes in sediments from the saline Qinghai Lake demonstrate that the n -alkane δD can be used to discriminate their biological sources.

n -Alkanes in the Lake Qinghai sediments exhibit an odd/even distribution with n - C_{23} , n - C_{25} and n - C_{27} as maxima in the majority of cases. Their CPI and ACL values range from 3.4 to 3.5 and from 27.0 to 28.0, respectively. These are close to those in the terrestrial herbaceous plants in the Qinghai Lake surrounding area. The n -alkane mean δD values are -185 to -133 ‰ for the surface sediments and -163 ‰ to -142 ‰ for the cored sediments and the even n -alkanes have heavier mean hydrogen isotopic compositions relative to the odd homologues.

The comparison of the sediments in the lake with the aquatic and terrestrial plants in the lake area shows that compositions of n -alkanes in the sediments and their hydrogen isotopes are similar to those in the terrestrial herbaceous plants, suggesting that n -alkanes in the sediments are derived mainly from the terrestrial herbaceous plants. However, a difference in the relative inputs from various herbaceous plant species was also evident. These data further show that hydrogen isotopic compositions of n -alkanes in lake sediment inherit the biological source δD signals that are related to environmental factors, so n -alkane δD values in lake sediments can be used as a geochemical indicator of palaeoclimate.

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