

Available online at www.sciencedirect.com ScienceDirect

Organic Geochemistry 39 (2008) 711–729

**Organic
Geochemistry**

www.elsevier.com/locate/orggeochem

Effect of lake evaporation on δD values of lacustrine *n*-alkanes: A comparison of Nam Co (Tibetan Plateau) and Holzmaar (Germany)

Ines Mügler^a, Dirk Sachse^{a,1}, Martin Werner^{a,2}, Baiqing Xu^b,
Guangjian Wu^b, Tandong Yao^b, Gerd Gleixner^{a,*}

^a Max Planck Institute for Biogeochemistry, Hans-Knöll Straße 10, 07745 Jena, Germany

^b Institute for Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, China

Received 24 May 2007; received in revised form 10 February 2008; accepted 14 February 2008

Available online 10 March 2008

Abstract

Compound-specific hydrogen isotope ratio values of lacustrine *n*-alkanes from two contrasting ecosystems, the semi-arid to arid Nam Co, Central Tibet and the humid Holzmaar, Germany, were compared in order to assess whether or not these environmental conditions are recorded in the isotopic signatures of biomarkers. Increased evaporation of lake water at Nam Co is recorded by the *n*-alkanes of aquatic origin. Hence, isotopic enrichment results in a difference between terrestrial and aquatic *n*-alkanes in the opposite direction ($\sim -68\text{‰}$) from that known for humid climate conditions ($\sim +30\text{‰}$) predominating at Holzmaar. Based on this isotopic difference between terrestrial and aquatic *n*-alkanes, evaporation to inflow ratio (*E/I*) values were estimated and suggest that the isotopic difference is indicative of the general hydroclimatic characteristics of a lake system. Moreover, the comparison with *E/I* values calculated with actual stable water isotope data showed that the δD values of aquatic and terrestrial lacustrine *n*-alkanes serve as a proxy for the relative isotopic differences between lake and inflow waters and can be used to assess the proportion of water undergoing evaporation relative to the inflow, and thus to reconstruct the lake water balance in the past.

© 2008 Published by Elsevier Ltd.

1. Introduction

The importance of the stable isotopes of water (δD and $\delta^{18}O$) for palaeoclimate studies was recognized early on (Gonfiantini, 1986; Rozanski et al., 1992, 1997, 1982). Environmental parameters such as temperature, source and amount of precipitation, and elevation or distance to the ocean generally influence the isotopic signature of precipitation (Craig, 1961; Craig and Gordon, 1965; Dansgaard, 1964; Rozanski et al., 1982). Consequently,

* Corresponding author. Tel.: +49 3641 576172; fax: +49 3641 5770.

E-mail address: ggleix@bgc-jena.mpg.de (G. Gleixner).

¹ Present address: Potsdam University, Institute for Geosciences, Leibniz Center for Earth Surface and Climate Studies, 14476 Potsdam-Golm, Germany.

² Present address: Leibniz Association, Eduard-Pflüger-Straße 55, D-53113 Bonn, Germany.

terrestrial or aquatic remains that preserve the isotope signal of palaeoprecipitation such as tree rings, organic matter (OM) in lacustrine sediments, ice cores, loess sequences or microfossils can potentially be used to infer past temperatures or hydrological oscillations. Taking into account the benefits and disadvantages of each archive material, this study uses lacustrine sediments to reconstruct regional climatic information. Lake sediments can, for instance, preserve both the primary isotopic composition of precipitation and secondary modifications of the lake water isotope signal through the lake hydrology, i.e. evaporation, inflow and outflow.

In order to study the imprint of lake hydrology and environmental parameters on lacustrine sedimentary material, three closed lake systems in humid and semi-arid to arid climates were investigated. The water balance of closed basin lakes is controlled mainly by the input through precipitation in the catchment and the amount of evaporation from the lake surface. The interplay of both processes affects the stable isotope composition of the lake water, as summarized by Craig and Gordon (1965), Dansgaard (1964), Gat (1996), Gibson et al. (1998, 2005), Gonfiantini (1986). The isotope signal of the lake water itself can be preserved in various constituents of the lake deposits, such as carbonates (Kelts and Talbot, 1990; Morinaga et al., 1993; Schwalb, 2003; von Grafenstein et al., 1999), fossil shells or sedimentary cellulose from algae (Danis et al., 2006; De Niro and Epstein, 1977; Pendall et al., 1999). There are, however, difficulties in obtaining a pristine autochthonous isotope signal (e.g., Huang et al., 2004). In this study, we use compound-specific hydrogen isotope ratios of sedimentary biomarkers to distinguish between autochthonous and allochthonous material. In general, the abundance and composition of biomarkers can serve to identify past ecosystems and environmental parameters during their formation (Meyers, 2003; Meyers and Lallier-Verges, 1999). Amongst biomarkers, *n*-alkanes are stable towards secondary structural and isotopic modification and so are well suited for palaeoclimatic reconstruction (Huang et al., 1996, 2002; Ohkouchi et al., 1997; Pagani et al., 2006; Sachse et al., 2004; Schefuss et al., 2005; Schmidt et al., 2004; Shuman et al., 2006; Yang and Huang, 2003). Major sources of *n*-alkanes in lacustrine sediments are aquatic organisms, i.e. photosynthetic bacteria or algae, for chain lengths of 15–19 carbons (Cranwell et al., 1987; Grimalt and Albaiges, 1987; Han and Calvin, 1969; Meyers,

2003), submerged or floating plants for *n*-C₂₁ to *n*-C₂₅ alkanes (Baas et al., 2000; Ficken et al., 2000) and terrestrial vascular plants for *n*-C₂₇ to *n*-C₃₁ alkanes (Eglinton and Hamilton, 1967; Meyers, 2003). Since photosynthetic organisms and plants that produce *n*-alkanes use the ambient water as a hydrogen source they preserve the isotopic information from lake water and precipitation (Huang et al., 2004; Sachse et al., 2004; Sessions et al., 1999). An isotope fractionation, ϵ , of $\sim -160\text{‰}$ for aquatic biomarkers was found in freshwater systems, i.e. *n*-C₁₇, *n*-C₂₁, and *n*-C₂₃ (Chikaraishi and Naraoka, 2003; Sachse et al., 2004; Sessions, 2006; Sessions et al., 1999). This fractionation through the incorporation of hydrogen during *n*-alkane biosynthesis of aquatic origin is assumed to be mostly independent of environmental factors and the majority is ascribed to the biosynthetic fractionation between *n*-alkanes and their hydrogen source. The apparent enrichment factor between precipitation water and terrestrial *n*-alkanes integrates the biosynthetic fractionation and an additional enrichment in deuterium of leaf water due to transpiration and evaporation of soil and leaf water (Sachse et al., 2006; Smith and Freeman, 2006). If both water reservoirs for aquatic and terrestrial organisms are fed by the same source, i.e. precipitation, the isotopic difference between terrestrial and aquatic *n*-alkanes depends solely on the rate of evapotranspiration. In humid climates where precipitation amount exceeds evapotranspiration and lakes show a positive water balance, aquatic *n*-alkanes are not affected by evapotranspirative enrichment, since lake water is in isotopic equilibrium with precipitation, at least on an annual time scale. Terrestrial *n*-alkanes on the other hand show enriched δD values compared to aquatic material, due to the evapotranspirational effect (Sachse et al., 2004). If evaporation exceeds precipitation, additional enrichment of the lake water is probable and will lead to the enrichment of aquatic *n*-alkanes compared to the precipitation source. This may result in an isotopic difference towards the opposite direction between aquatic and terrestrial *n*-alkanes in semi-arid to arid climate conditions. The direction of the isotopic difference between aquatic and terrestrial *n*-alkanes could thus be indicative of the general hydroclimatic conditions of a lake system. Here we test this hypothesis, by comparing sediments from lakes in two contrasting ecosystems in terms of their hydroclimatic characteristics. Surface sediments retrieved from three lakes, Nam Co and nearby Co Jiana

on the Central Tibetan Plateau and Holzmaar in Germany were analysed in order to answer the following questions:

- (i) Can the isotopic difference between terrestrial and aquatic *n*-alkanes be used to distinguish between humid and arid climate conditions in a sediment sequence and thus serve as a qualitative proxy for the hydro-climatological characteristics of a catchment?
- (ii) Is it possible to quantify a potential relationship between aquatic and terrestrial *n*-alkanes in different climate settings in order to apply it as a quantitative proxy for past evapotranspiration rates?

2. Study sites

Nam Co is the second largest (1961 km²) saline lake in Tibet. It is located in the central part of the Tibetan Plateau (30°30' to 35'N; 90°16' to 03'E; 4718 m above sea level; Fig. 1). The climate in the region is semi-arid to arid and is modified by altitude. Mean annual air temperature is low, around -1 to +3 °C. Modest mean annual precipitation of 280 mm occurs mainly in the summer during the monsoonal rains (You et al., 2006). As a result of strong solar radiation, annual evaporation

(1110 mm) exceeds annual precipitation. Nam Co is a closed lake, so its water balance is controlled only by precipitation or inflow and the rate of evaporation. The salinity is low, with values between 2.9 g/l⁻¹ and 1.3 g/l⁻¹ (Williams, 1991). Maximum water depth is suggested to be between 35 and 50 m (Williams, 1991; Zhu et al., 2004); however, seismic investigation during coring revealed a maximum depth of at least 100 m. The vegetation surrounding the lake is typical for semi-arid to arid climates and high altitudes and consists primarily of alpine meadows, steppe grasses and dicots including *Stipa* sp., *Artemisia* sp., *Kobresia* sp., *Oxytropis* sp., and *Morina* sp. all using the C₃ pathway. Species of *Carex*, an emergent macrophyte in lakes of low salinity, are also present. Typical phytoplankton species are *Bacillariophyta* (Williams, 1991).

Different lake terraces and highstand lacustrine deposits around Nam Co indicate periods of fluctuating water level (Lehmkuhl and Haselein, 2000; Zhu et al., 2002, 2004). Lake level changes are, among other things, attributed to alternating hydro-climatic conditions between pronounced humid and arid periods, and are therefore considered as a regional indication of monsoon strength fluctuation (Baier et al., 2004; Lehmkuhl and Haselein, 2000; Mingram et al., 2004; Morrill, 2004). Geomorphological features in the catchment, such as beach

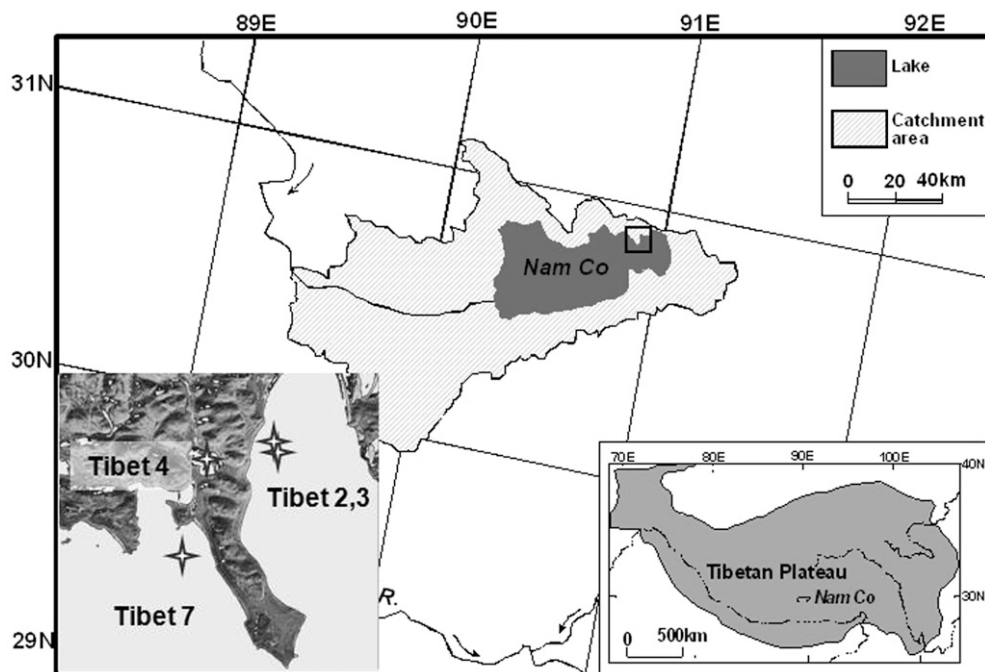


Fig. 1. Map of Nam Co and Co Jiana, Central Tibet. The stars in the extracted section mark the core locations.

ridges and lake terraces point to lake level high stands during the Late Glacial Maximum. Thereafter, the lake level and volume gradually decreased. Recent observations indicate a stable and periodically increasing level during the last two years. Lakeshore deposits in valley bottoms between several small lakes surrounding Nam Co confirm the former connection of these lakes to it. One is Co Jiana, located at the northeastern bank (see section in Fig. 1). Co Jiana, which also has no outflow, stretches 0.6 km from N to S and about 1 km from W to E, and is separated from Nam Co by a 200 m wide ridge.

Holzmaar is located in a humid climate setting in western Germany (50°7'N; 6°53'E; 425 m above sea level; Fig. 2). This small, nearly circular lake is a meso to eutrophic maar lake with a diameter of ca. 325 m. It has only one inflow stream, the Sammetbach. Typical of lakes of phreatomagmatic origin, it has steep slopes and a flat profundal region, with a maximum water depth of 20 m (Baier et al., 2004), a dimictic thermal pattern and a water residence time of about 7 months (Oehms, 1995). The climate in the region is defined as moist-temperate, with cool winters and wet summers (Closs, 1979). Mean annual temperature is around 7.5 °C (Deut-

scher Wetter Dienst (DWD); <http://www.dwd.de>). The annual precipitation shows maxima during the summer and winter months and minima in March/April and September/October, with an annual mean of about 796 mm. Precipitation exceeds the amount of evaporation (482 mm) within the annual mean, indicating humid climate conditions (Krause, 1980). The vegetation is dominated by beech (*Fagus sylvatica*) and spruce (*Picea abies*), as well as isolated oak (*Quercus petraea*), willow (*Salix* sp.) and birch (*Betula pendula*). Also, agronomically-used grassland and pasture border the southwestern lake bank.

3. Sampling

During a field campaign in August 2004 three short cores were retrieved from Nam Co and one from Co Jiana using a gravity corer (HTH-Teknik, Luleå, Sweden; Fig. 1). The Co Jiana core (Tibet 4) was collected from the deepest part of the lake, determined from echo sounding, in water depths of up to 7 m. The Nam Co cores (Tibet 2, 3, 7) were obtained near the shore in shallow water. The cores are between 15 cm and 25 cm long. The sedimentary data discussed below were determined from the core

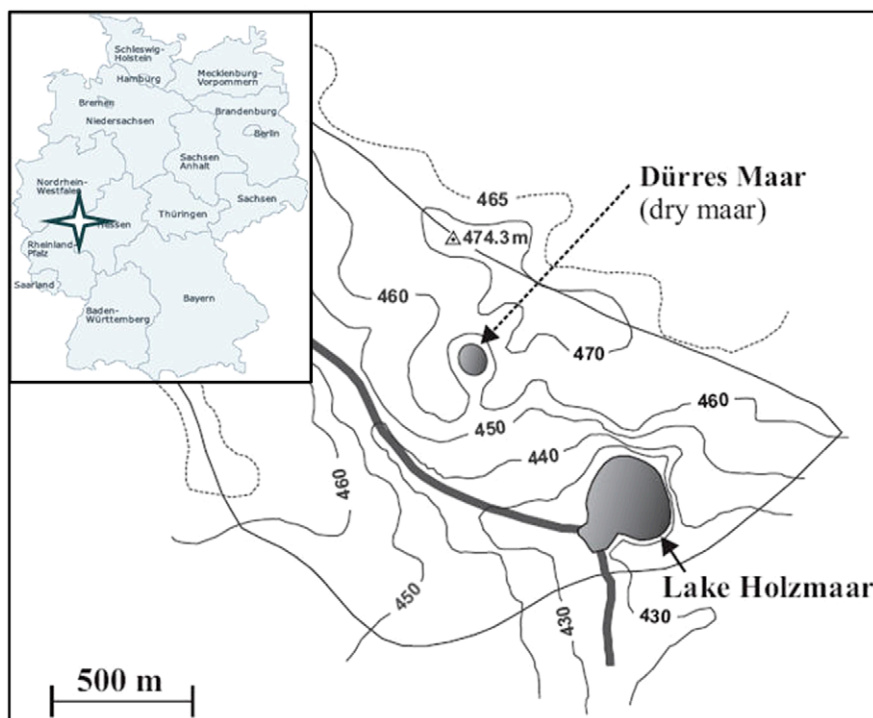


Fig. 2. Map of Holzmaar, Germany (modified after Moschen et al., 2006).

surface sediments (0–1.5 cm). Based on the sedimentation rate of ~ 1 mm/year, the surface sediments integrate the environmental signal of 15 years. Water samples from both lakes were collected in 2004 and 2005 with a water sampler (Hydro-Bios Apparatebau GmbH, Kiel, Germany). Additionally, about 40 inflow streams around both, including water from wetlands draining into Nam Co and Co Jiana, were sampled in both years, as well as pooled vegetation samples from the dominant species around the lake, including *Kobresia schoenoides*, *Morina cryptothladia*, *Oxytropis* sp., *Stipa* sp. and submerged aquatic macrophytes from both and one unidentified alga from Nam Co.

Coring at Holzmaar was performed in the frame of the European lake transect study in August and September 2002 (Sachse et al., 2004). The surface sediment (0–1 cm) is assumed to represent the deposition of material from the previous year (Sachse et al., 2004). In addition to the short sediment cores, sampling included water from the lake and the inflow stream as well as the dominant surrounding vegetation (*B. pendula* and *F. sylvatica*; data published by Sachse et al., 2004, 2006).

Precipitation has been measured and continuously sampled at Nam Co climate station since 2005 (You et al., 2006). Precipitation data for the Holzmaar catchment have been recorded at the Manderscheid station (50.1°N; 6.8°E; DWD) since 1961 and the isotope data are provided by the IAEA GNIP database from the IAEA GNIP station in Trier, located about 50 km to the SW of the lake (<http://isohis.iaea.org>).

4. Methods

4.1. Analysis of water samples for δD and $\delta^{18}O$

Water isotope ratios were measured by online high temperature reduction in the modified carbon reactor of a high temperature elemental analyser (TC/EA) coupled to an isotope ratio mass spectrometer (Delta^{plus}XL, Finnigan MAT Bremen, Germany) (Gehre et al., 2004). The average standard deviation was 0.5‰ for δD and below 0.1‰ for $\delta^{18}O$.

4.2. Sample preparation, *n*-alkane extraction and quantification

The sediment samples and plant material were freeze dried and ground. Between 3 and 6 g of sed-

iment or ca. 1 g of plant biomass were used for lipid extraction with an accelerated solvent extractor (ASE-200, DIONEX Corp., Sunnydale, USA) operated with $CH_2Cl_2/MeOH$ (10:1) at 100 °C and 2000 psi for 15 min in 2 cycles. The total extract was separated using solid phase extraction on silica gel. Glass columns (ca. 20 cm height, $\varnothing 2.5$ cm; QVF Labortechnik GmbH; Ilmenau, Germany) were filled with ca. 25 cm³ activated silica gel (0.04–0.063 mesh; Merck KGaA, Darmstadt, Germany). Alkanes were eluted with hexane (60 ml). The components were identified and quantified using gas chromatography with flame ionization detection (GC–FID; TraceGC, ThermoElectron, Rodano, Italy) with a DB5ms column (30 m, 0.32 mm ID, 0.5 μm film thickness, Agilent, Palo Alto, USA). For quantification, peak areas for *n*-alkanes were compared with those from an external *n*-alkane standard mixture.

4.3. Analysis of δD values of *n*-alkanes

The alkane fraction in hexane was injected (1 μl) into a HP5890 gas chromatograph equipped with a DB5 ms column (30 m, 0.32 mm ID, 0.5 μm film thickness, Agilent). The injector was operated at 280 °C in splitless mode. The oven was maintained for 2 min at 60 °C, heated at 6 °C/min to 320 °C (held 10 min). The carrier gas flow was constant at 1.7 ml/min. To monitor possible co-elution of *n*-alkanes with other components, part of the column effluent went to an ion trap mass spectrometer (GCQ ThermoElectron, San Jose, USA). The remainder went to an isotope mass spectrometer, via quantitative conversion to H_2 in a high temperature oven operated at 1425 °C (Burgoyne and Hayes, 1998; Hilkert et al., 1999). Compound-specific δD values were obtained using isotope ratio mass spectrometry (IRMS; Finnigan MAT Bremen, Germany DeltaplusXL). Each sample was analysed in triplicate. The δD values were normalized to the Vienna standard mean ocean water (VSMOW) scale:

$$^2H/^1H = 155.95 \pm 0.08 \times 10^{-6} \quad (\text{De Wit et al., 1980})$$

using a standard mixture of *n*-C₁₀ to *n*-C₃₂ alkanes. The values in the standard mixture were calibrated against international reference substances (NBS-22; IAEA-OH22) using the offline high temperature pyrolysis technique (TC/EA; Gehre et al., 2004). The accuracy was evaluated by routine measurement of the standard mixture after every six injections (two samples). If necessary, a drift correction

was applied. To ensure stable ion source conditions during measurement the H_3^+ factor (Hilkert et al., 1999) was determined at least once a day. It was constant over the 10 day measurement period at 5.4 (SD 1.4).

5. Results and discussion

5.1. Meteorological and isotope precipitation data

Daily precipitation measured from August 2005 to November 2006 at Nam Co shows maximum amounts during the summer months between

August and October, caused by monsoonal rain or convective rain through moisture recycling (Fig. 3). The δD values are variable and range from D enriched precipitation ($\sim 25\text{‰}$) to remarkably lighter values around -200‰ , indicating either different moisture sources or precipitation regimes. The cumulative isotopic content in precipitation of $\delta D = -122\text{‰}$ is almost identical to the mean values determined for the inflow streams, groundwater and wetland water (Table 1) sampled in 2005. Thus, the mean isotope values of the inflow streams measured in 2004 are assumed to represent the hydrogen isotope signal of precipitation during 2004, where the

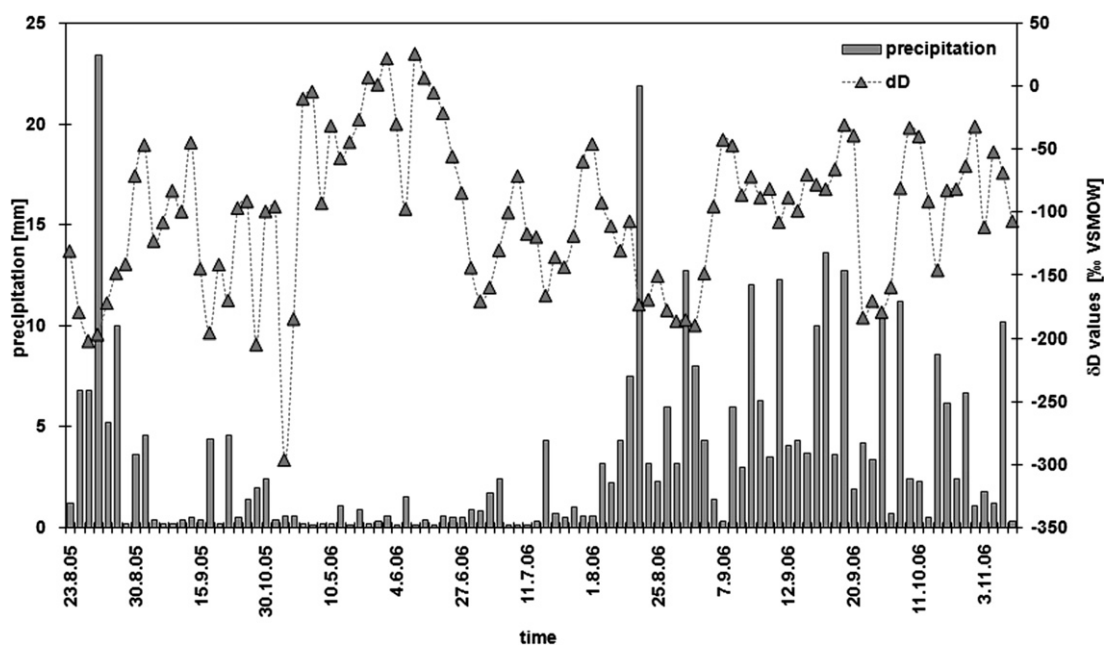


Fig. 3. Daily precipitation amount between August 2005 and November 2006 and corresponding δD values at Nam Co.

Table 1
Isotopic characteristics of Nam Co, Co Jiana and Holzmaar catchment waters

		2004				2005			
		Mean δ^2H (‰)	sd ^a	Mean $\delta^{18}O$ (‰)	sd	Mean δ^2H (‰)	sd ^a	Mean $\delta^{18}O$ (‰)	sd ^a
Nam Co	Inflow	-119	3	-16	1	-118	16	-15	2
	Lake water	-71	3	-6	1	-70	6	-6	1
Co Jiana	Inflow	-124	5	-14	4				
	Lake water	-87	1	-8	1	-93	1	-9	1
	Weighted mean precipitation						-122		
Holzmaar	Inflow	-54	1	-9	1				
	Lake water	-47	1	-6	1				
	Weighted mean precipitation			-57					

^a Standard deviation.

sediment cores and part of the vegetation was sampled and δD values for precipitation are not available for this period since the collection of rainfall only started in 2005.

At Holzmaar, the contribution via inflow and the weighted mean of annual precipitation, which results in a mean δD value of $\sim -55\text{‰}$, is almost in isotopic equilibrium with the lake water (Table 1).

5.2. Concentration of *n*-alkanes in lake surface sediments and plant biomass

The surface sediments from Nam Co and Co Jiana contain *n*-C₁₂ to *n*-C₃₁ alkanes with a bimodal distribution maximising at *n*-C₂₁/*n*-C₂₅ and *n*-C₂₉/*n*-C₃₁ (Fig. 4). The Holzmaar sediments show maximum concentrations for *n*-C₁₇ and, for the long chain odd numbered alkanes, *n*-C₂₅ to *n*-C₃₁ (Fig. 4). The total *n*-alkane concentration ranges between 4 and 16 $\mu\text{g/g}$ dry sediment for the Tibetan lakes (Table 2). The total *n*-alkane concentration of the Holzmaar sediments is significantly higher ($\sim 109 \mu\text{g/g}$ dry sediment), which was expected since it is eutrophic, whereas the primary production in the Tibetan lakes is low and they are classified as oligotrophic. The sedimentary *n*-alkanes of the three lakes show a clear odd/even predominance. The carbon preference index [CPI, (Bray and Evans, 1961)] has a lower value (3.4) for Holzmaar than Nam Co and Co Jiana sediments (~ 4 to 6), indicating fresh

OM. The significant contribution of aquatic plant material to the lacustrine OM is reflected in the average chain length (ACL) values that range between 23.9 and 25.3 at Nam Co and Co Jiana. The lower ACL (22.1) at Holzmaar is characteristic of a pronounced allochthonous aquatic algal or cyanobacterial source for the OM.

The composition of the *n*-alkanes and their concentration in the Tibetan lake plant biomass shows significant differences between the terrestrial and the aquatic vegetation (Figs. 5a and b; Table 2). The terrestrial grasses *K. schoenoides* and *Stipa* sp., and the terrestrial dicots *Oxytropis* sp. and *M. cryptothladia* contain mainly long chain odd *n*-alkanes with 25–31 carbons (Fig. 5a). Consequently, the long chain *n*-alkanes in the sediments are ascribed to an allochthonous contribution from these terrestrial plants. Mid-chain length *n*-alkanes with 21–25 carbons were found in the aquatic macrophytes sampled at Nam Co and Co Jiana (Fig. 5b). This corresponds with findings for submerged aquatic plants (Ficken et al., 2000) and *Sphagnum* species (Baas et al., 2000). The algae sample contained *n*-C₁₇ as the dominant *n*-alkane, in agreement with the compositions of cyanobacteria (Arp et al., 1999; Grimalt et al., 1992). Since the Nam Co and Co Jiana sediments show maximum concentrations for *n*-alkanes with 21 and 25 carbons these homologues are attributed to autochthonous sources within the lake from submerged plants and macrophytes. The sediments do not contain

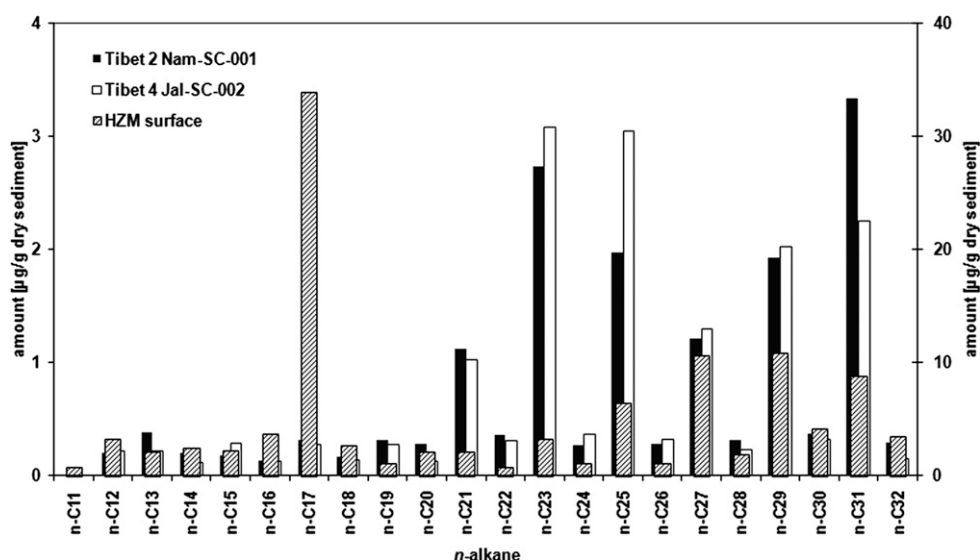


Fig. 4. Concentration and composition of *n*-alkanes in lake surface sediments from Holzmaar (HZM), Nam Co (Tibet 2) and Co Jiana (Tibet 4). Note that the Holzmaar sediments are plotted on the second y-axis where the scale is enlarged by a factor of 10.

Table 2

n-Alkane distribution of plant biomass and lake sediments: (C_{\max}), CPI and CPI_{23-32} , ACL and total concentration of *n*-alkanes HC_{tot} $\mu\text{g/g}$ dry weight)

No.	Plant/sample	Sampling date	C_{\max}	CPI ^a	CPI_{23-34} ^b	ACL ^c	HC_{tot}
998446	Macrophyte Co Jiana	2004	23	23.7	26.1	23.5	28
39	Macrophyte Nam Co	2005	23	3.2	16.0	22.5	159
40	Macrophyte Nam Co	2005	23	0.9	1.5	21.5	39
41	Algae Nam Co	2005	17	5.5	2.2	17.9	823
15	<i>Kobresia schoenoides</i>	2005	29	12.7	28.1	28.8	345
17	<i>Kobresia schoenoides</i>	2005	29	17.1	20.6	28.9	245
25	<i>Kobresia schoenoides</i>	2005	31	16.9	34.4	29.3	344
28	<i>Kobresia schoenoides</i>	2005	31	11.8	19.5	28.7	414
998444	<i>Morina</i> sp. 2005	2005	31	10.0	10.4	29.7	15
Tibet PB 1	<i>Morina</i> sp. 2004	2004	31	10.3	10.0	29.0	184
Tibet PB 5	<i>Oxytropis</i> sp. 2004	2004	29	6.4	11.4	27.4	218
Tibet PB 2	<i>Stipa</i> 2004	2004	31	16.6	14.1	29.5	105
998442	<i>Stipa</i> sp. 2005	2005	31	34.9	25.0	29.8	111
Tibet 2	Lake sediment Nam Co	2004	31	5.2	7.2	25.3	16
Tibet 3	Lake sediment Nam Co	2004	31	4.5	4.8	23.9	4
Tibet 4	Lake sediment Co Jiana	2004	23	6.3	8.4	25.0	16
Tibet 7	Lake sediment Nam Co	2004	23	8.3	7.6	25.6	14
HZM	Lake sediment Holzmaar	2001	17	3.3	3.4	22.1	109

^a Calculated as $0.5 \times (\sum_{\text{odd}} C_{11-31} / \sum_{\text{even}} C_{10-32}) + (\sum_{\text{odd}} C_{11-31} / \sum_{\text{even}} C_{12-34})$ (Bray and Evans, 1961).

^b Calculated as $0.5 \times (\sum_{\text{odd}} C_{23-31} / \sum_{\text{even}} C_{22-32}) + (\sum_{\text{odd}} C_{23-31} / \sum_{\text{even}} C_{24-32})$.

^c Calculated as $\sum C_n \times n / \sum C_n$.

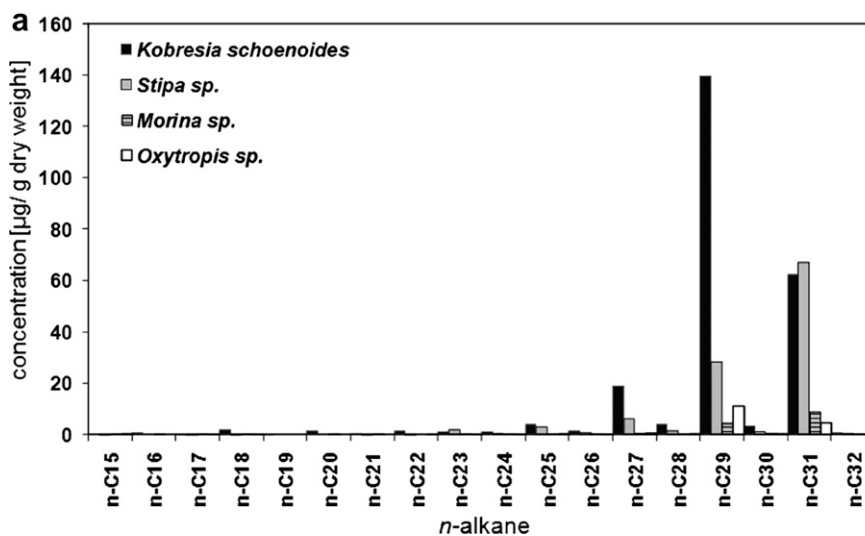


Fig. 5a. Concentration and composition of *n*-alkanes from terrestrial vegetation at Nam Co and Co Jiana.

significant amounts of *n*-C₁₇ suggesting that algal and cyanobacterial production is low or that preservation of this marker is poor.

The terrestrial vegetation around Holzmaar contains mainly long chain odd numbered *n*-C₂₅ to *n*-C₃₁ alkanes and their contribution to the lacustrine OM is reflected in high amounts of these homologues in the sediments (Sachse et al., 2004, 2006). Submerged aquatic plants or macrophytes, as well

as algae, were not sampled at Holzmaar but it is assumed that high amounts of *n*-C₁₇ in the sediments reflect autochthonous organic matter from algae or cyanobacteria. The mid-chain *n*-alkanes, *n*-C₂₁ and *n*-C₂₃, and thus the contribution of macrophytes to the lacustrine OM, show lower amounts.

Based on the composition of *n*-alkanes in the plant samples and sediments we conclude that the

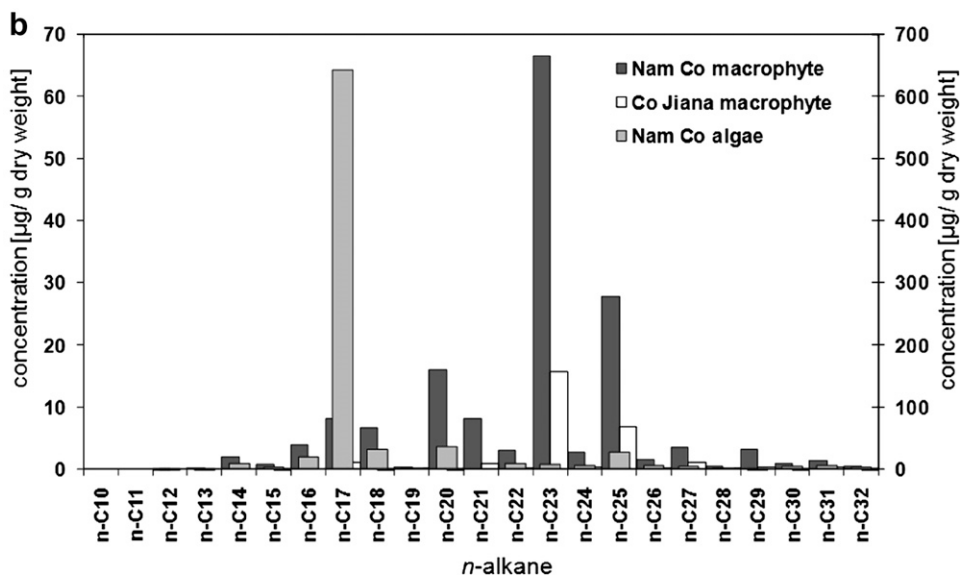


Fig. 5b. Concentration and composition of *n*-alkanes from aquatic vegetation at Nam Co and Co Jiana. Note that the alga is plotted on the second *y*-axis where the scale is enlarged by a factor of 10.

autochthonous OM is represented by *n*-C₁₇ and *n*-C₂₁ to *n*-C₂₅ alkanes, whereas the algal source of OM is of minor importance in the sediments from Nam Co and Co Jiana. Thus, only the mid-chain length, odd numbered *n*-alkanes are used as aquatic biomarkers for the following interpretation of the isotope values. The contribution of allochthonous OM from terrestrial plants is reflected in the long chain *n*-alkanes, *n*-C₂₇ to *n*-C₃₁, in the Tibetan lakes as well as in the Holzmaar sediments.

5.3. δD values of *n*-alkanes in lake surface sediments and plant biomass

The measured δD values of the vegetation from the Tibetan lakes vary between remarkably negative

values of -281‰ (*n*-C₂₉ *K. schoenoides*) and -143‰ (*n*-C₂₅ Nam Co macrophyte; Fig. 6a). Based on the plant biomass δD values, three groups can be differentiated at Nam Co and Co Jiana (Fig. 6a). The typical dry steppe vegetation, including *Stipa* sp., *M. cryptothladia* and *Oxytropis* sp., contains long chain odd *n*-C₂₇ to *n*-C₃₁ alkanes that are enriched in deuterium compared to the long chain *n*-alkanes of *K. schoenoides*, typical of moist to swampy or peaty habitats (Kürschner et al., 2005). The most positive δD values were determined for *n*-C₂₃ and *n*-C₂₅ from aquatic macrophytes sampled at Nam Co and Co Jiana.

The *n*-alkanes derived from the deciduous trees *B. pendula* and *F. sylvatica* from the Holzmaar catchment show comparable δD values for *n*-C₂₅

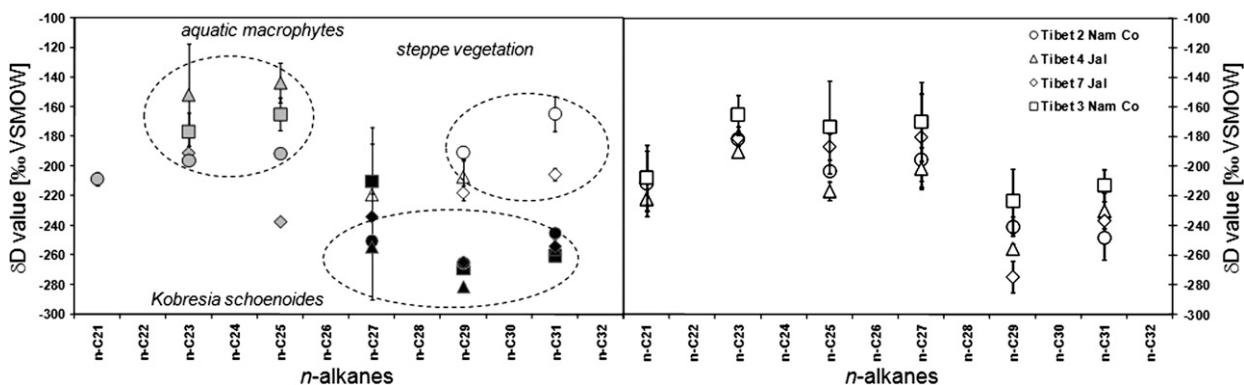


Fig. 6a. (a) δD values of *n*-alkanes from Nam Co and Co Jiana plant biomass. (b) δD values of *n*-alkanes from Nam Co and Co Jiana lake surface sediments.

to n -C₃₁. The variation in δ D values within a single plant is negligible (Fig. 7; Sachse et al., 2004, 2006).

Based on the n -alkane composition and the isotope signatures of the plant biomass, n -C₂₃ is used as the aquatic marker in the sediments since the terrestrial vegetation from Holzmaar also contained n -C₂₅ and thus could not be clearly specified as aquatic (Fig. 7). The n -C₂₉ alkane is assumed to be of only terrestrial origin and reflects the precipitation water modified by evapotranspiration.

The δ D values of the sedimentary n -C₂₁ to n -C₃₁ alkanes vary between -272‰ and -127‰ for the Tibetan lakes (Fig. 6b). The range of values for the Holzmaar sediments is smaller, from -225‰ to -180‰ (Fig. 7). The fluctuation in δ D values at Nam Co and Co Jiana suggests large isotopic differences in the hydrogen sources for aquatic and terrestrial OM, as already indicated by large variations in δ D values of plant biomass. Since the δ D values and their ranges are similar for the Nam Co and Co Jiana sediments a similar catchment is assumed. In general, the δ D values of the long chain n -alkanes ascribed to terrestrial vegetation are more negative than for the mid-chain n -alkanes in the sediments of Nam Co and Co Jiana. In contrast, the long chain n -alkanes from the Holzmaar sediments show enriched δ D values and n -C₂₃ is more negative.

5.4. Hydrogen isotope fractionation

According to the specification of the hydrogen isotope signal for aquatic and terrestrial sources, the fractionation factor ($\epsilon_{a/w}$) between the aquatic

marker n -C₂₃ and the terrestrial marker n -C₂₉ from plant biomass and sediments and their source water was calculated as

$$\epsilon_{\text{alkane/water}} = 1000[(\delta D_{n\text{-alkane}} + 1000)/(\delta D_{\text{water}} + 1000) - 1] \quad (1)$$

It has to be stressed that $\epsilon_{a/w}$ accounts for the net fractionation between source water and lipids. This fractionation will be modified by the effect of evapotranspiration in terrestrial biomarkers and is then termed “apparent fractionation” (Sachse et al., 2006; Smith and Freeman, 2006). The mean $\epsilon_{C_{29}/w}$ values are $-168 \pm 9\text{‰}$ for the wetland grass samples (*K. schoenoides*), $-102 \pm 14\text{‰}$ for C₃ steppe grasses and dicots (*M. cryptothladia*, *Oxytropis* sp., *Stipa* sp.) and $-146 \pm 24\text{‰}$ for the Nam Co and Co Jiana lake surface sediments. The average $\epsilon_{C_{23}/w}$ values for the aquatic macrophytes and algae are $-111 \pm 19\text{‰}$ and $-112 \pm 8\text{‰}$ for the lake surface sediments (Table 3).

The average $\epsilon_{C_{29}/w}$ value for *K. schoenoides* is in the range of values observed for C₃ grasses (Smith and Freeman, 2006; Table 4). The smaller apparent fractionation for the C₃ steppe grasses and dicots is the result of evaporative enrichment of soil and leaf water. Compared to the evapotranspirative enrichment in terrestrial higher plants from the European Transect ($\sim 30\text{‰}$; Sachse et al., 2004, 2006) the enrichment is even higher and suggests a considerable influence of evapotranspiration on the Tibetan Plateau (Table 3). For *K. schoenoides* growing under

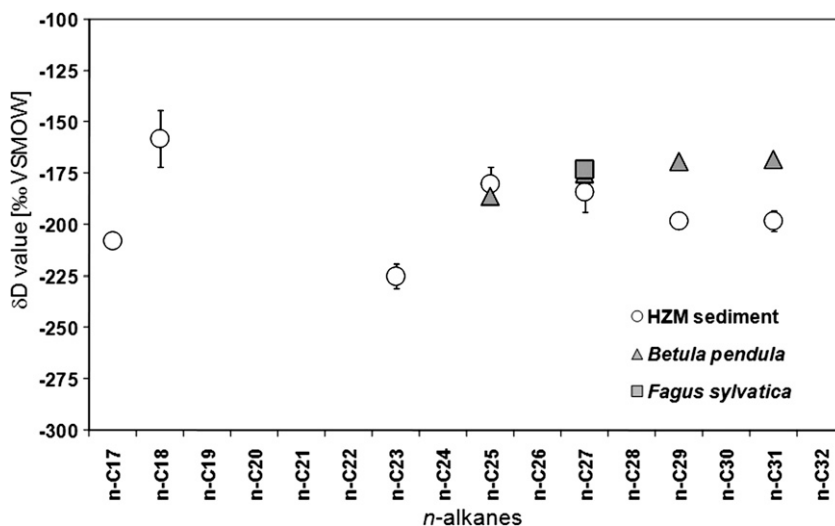


Fig. 7. δ D values of n -alkanes from Holzmaar vegetation and lake surface sediments.

Table 3

δD values and standard deviation (sd, 2σ) of n -C₂₃ and n -C₂₉ alkanes, fractionation ϵ between n -alkane and source water and isotopic difference between δD n -C₂₃ and δD n -C₂₉

No.	Sampled material	δD n -C ₂₃	sd ^a	δD n -C ₂₉	sd ^a	δD_{23} – δD_{29}	ϵ n -C ₂₃	ϵ n -C ₂₉
998446	Macrophyte Co Jiana	–191	6				–107	
39	Macrophyte Nam Co	–196	2				–136	
40	Macrophyte Nam Co	–151	34				–88	
41	Algae Nam Co	–176	13				–115	
Mean		–179 ± 20					–111 ± 19	
15	<i>Kobresia schoenoides</i>			–265	2			–163
17	<i>Kobresia schoenoides</i>			–282	2			–182
25	<i>Kobresia schoenoides</i>			–265	1			–162
28	<i>Kobresia schoenoides</i>			–269	1			–167
Mean				–270 ± 8				–168 ± 9
998444	<i>Morina</i> sp. 2005			–218	5			–113
Tibet PB 1	<i>Morina</i> sp. 2004			–207	2			–105
Tibet PB 5	<i>Oxytropis</i> sp. 2004			–190	2			–82
Tibet PB 2	<i>Stipa</i> 2004			–226	4			–122
998442	<i>Stipa</i> sp. 2005			–211	4			–100
Mean	Mean			–211 ± 13				–102 ± 14
Tibet 2	Lake sediment Nam Co	–182	8	–240	6	58	–119	–138
Tibet 3	Lake sediment Nam Co	–165	14	–223	22	58	–101	–119
Tibet 4	Lake sediment Co Jiana	–190	1	–255	3	65	–113	–155
Tibet 7	Lake sediment Nam Co	–181		–275		93	–118	–176
Mean		–179 ± 13		–240 ± 16		68 ± 4	–112 ± 8	–146 ± 24
HZM	Lake sediment Holzmaar	–225	6	–198	1	–27	–187	–154
HZM	<i>Betula Pendula</i>			–169	1			–123

^a Standard deviation.

Table 4

Variation in available fractionation factor ϵ of different studies from terrestrial vegetation, aquatic plant biomass and lake sediments

Material	Enrichment factor ϵ (‰) ^a	Source water δD value (‰)	Reference
Submerged and emerged higher plants	–160	0	Sessions et al. (1999), Sessions (2006)
Lake sediments	–65 to –165		Sauer et al. (2001)
<i>Quercus</i>	–117	–147 to –23	Yang and Huang (2003)
Platanus	–93	–114 to –101	Yang and Huang (2003)
Salix	–144	–114 to –101	Yang and Huang (2003)
C ₃ plants	–117 ± 27	–114 to –101	Chikaraishi and Naraoka (2003)
C ₄ plants	–132 ± 12	–42	Chikaraishi and Naraoka (2003)
CAM plants	–147 ± 10	–42	Chikaraishi and Naraoka (2003)
Fern	–131 ± 6	–42	Chikaraishi and Naraoka (2003)
Aquatic plants (freshwater)	–135 ± 17	–42	Chikaraishi and Naraoka (2003)
Aquatic plants (seaweed)	–155 ± 34	–60	Chikaraishi and Naraoka (2003)
Lake sediments $\epsilon_{(terrestrial)}$	–128 ± 12	–60	Sachse et al. (2004)
Lake sediments $\epsilon_{(aquatic)}$	–157 ± 8	–119 to –41	Sachse et al. (2004)
C ₃ -gymnosperm (<i>Cryptomeria japonica</i>)	–91 to –152	–104 to –6	Chikaraishi et al. (2004)
C ₃ grasses	–165 ± 12	–42	Smith and Freeman (2006)
C ₄ grasses	–140 ± 15	–61	Smith and Freeman (2006)
Deciduous trees	–122	–61	Sachse et al. (2006)
<i>Sphagnum</i> species	–131	–88 to –30	Sachse et al. (2006)
Plant biomass	–118	–88 to –30	Sachse et al. (2006)
Mean ϵ terrestrial plants = –133 ± 16		Mean ϵ aquatic plants = –145 ± 14	

^a The ϵ values for terrestrial vegetation are relative to precipitation water; ϵ values for aquatic plant biomass are relative to ambient lake water.

water saturation conditions in the wetland habitat, evapotranspiration is assumed to be negligible. Thus, $\epsilon_{C_{29}/w}$ values potentially represent the biosyn-

thetic fractionation, which is in the range of observed values (–160‰) for grasses (*Spartina alterniflora*) growing submerged under an unlimited

supply of water (Sessions, 2006). The intermediate $\epsilon_{C_{29}/w}$ values determined for the sedimentary *n*-alkanes indicate that their δD values represent a mixed isotope signal from both sources of terrestrial vegetation. The similarity in $\epsilon_{C_{23}/w}$ values for the surface sediments and the aquatic macrophytes at both lakes, Nam Co and Co Jiana, suggests that the *n*-C₂₃ alkane in the sediments reflects the hydrogen isotope signal of these aquatic plants. In contrast to the $\epsilon_{C_{23}/w}$ and $\epsilon_{C_{29}/w}$ values for the Holzmaar sediments, the fractionation between lacustrine aquatic *n*-alkanes and lake water is smaller than the $\epsilon_{C_{29}/w}$ values at Nam Co and Co Jiana. At the Holzmaar site the apparent isotope fractionation for deciduous tree biomarkers relative to precipitation shows the expected enriched values compared to the biosynthetic fractionation for aquatic organisms due to evapotranspirative enrichment of soil and leaf water. At Nam Co and Co Jiana the sedimentary $\epsilon_{C_{23}/w}$ values, as well as $\epsilon_{C_{23}/w}$ for the aquatic macrophytes, are smaller compared to $\epsilon_{C_{29}/w}$ between terrestrial vegetation and source water.

Yet, understanding of the physiological and biosynthetic mechanisms through the incorporation of hydrogen during *n*-alkane biosynthesis is incomplete, and large variations in fractionation factors are observed for a variety of plant material in different environmental settings, indicating that there is no fixed isotopic fractionation between terrestrial or aquatic plants and their source water (Table 4). Nevertheless, there is agreement that the vegetation type or leaf morphology, as well as biological variables such as the photosynthetic pathway or changes in the isotopic composition of biosynthetic feedstocks, play an important role in determining the degree of enrichment besides environmental parameters such as evaporation in association with relative humidity (Chikaraishi and Naraoka, 2003; Hayes, 2001; Hou et al., 2007; Sachse et al., 2006; Sessions, 2006; Smith and Freeman, 2006). We therefore suggest that the observed $\epsilon_{C_{23}/w}$ and $\epsilon_{C_{29}/w}$ values at the Tibetan lake sites can be considered as fixed for the corresponding vegetation group in this particular ecosystem, although the similarity in $\epsilon_{C_{23}/w}$ and $\epsilon_{C_{29}/w}$ for the dry steppe vegetation is not yet entirely understood.

In addition to the variation in $\epsilon_{C_{23}/w}$ and $\epsilon_{C_{29}/w}$ values, we observed a clear isotopic difference between the δD values of terrestrial (*n*-C₂₉) and aquatic (*n*-C₂₃) lacustrine *n*-alkanes at both Holzmaar and the Tibetan lake sites, strengthening our argument of different biological sources for

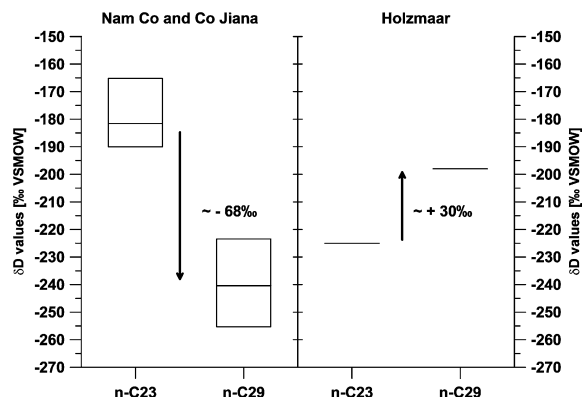


Fig. 8. Isotopic difference between δD from aquatic *n*-alkanes (*n*-C₂₃) and δD from terrestrial *n*-alkanes (*n*-C₂₉).

these components (Fig. 8). Like the isotope fractionation factors, the isotopic difference between these classes of compound shows opposite directions at both lake systems. Whereas the δD values from terrestrial *n*-alkanes are enriched in deuterium by about 30‰ in the Holzmaar sediments compared to δD values from aquatic sources, *n*-C₂₉ is depleted in deuterium in the Tibetan lake sediments and a deuterium enrichment of about 60‰ is observed for *n*-C₂₃. Taking into account the hydrogen sources at both study sites, at Holzmaar the difference between lake and mean inflow water δD values can almost be neglected ($\delta D_{\text{Lake}} = -47‰$ vs. $\delta D_{\text{mean-inflow}} = -55‰$; Table 1), so the lake water and precipitation, as well as inflow water, are in isotopic equilibrium. In contrast, the lake water at Co Jiana is enriched by 30‰ and at Nam Co by even 50‰ relative to the inflow water (Table 1). This significant isotopic difference at Nam Co and Co Jiana indicates the influence of evaporation that resulted in an overall negative water balance at both lakes, that have been gradually shrinking since the last major lake level high stand during the Last Glacial Maximum. The lower enrichment at Co Jiana is ascribed to its smaller size and water volume so that the depletion for lake water during the input of lighter monsoonal rain and melt water has a greater impact on the water and isotope balance.

Whereas mid-European humid climate conditions are present at Holzmaar and evaporation is of minor importance for the lake water balance, the water balance and thus the isotope signatures for Nam Co and Co Jiana in a semi-arid to arid climate setting are driven mainly by the interplay of evaporative enrichment and the depletion through water recharge. The corresponding isotopic differ-

ences between the δD values of lacustrine terrestrial and aquatic *n*-alkanes suggest that the basic hydroclimatic characteristics of a catchment could be preserved in the δD values of sedimentary *n*-alkanes. A positive isotopic difference between terrestrial and aquatic lacustrine *n*-alkane δD values potentially indicates humid climate conditions, with an isotopic enrichment of *n*-alkanes from terrestrial vegetation that is ascribed to evapotranspiration of the soil and leaf water. Semi-arid and arid climate conditions are reflected in a respective negative isotopic difference, where long term isotope enrichment of the lake water results in a corresponding enrichment of *n*-alkane δD values from aquatic sources.

6. Palaeoenvironmental implications

Although our data set for modern lake surface sediments, plant samples and catchment waters is limited, it adds important information on biomarker hydrogen isotopic data and their utility as palaeoenvironmental indicators. The basic statement is that the impact of evaporation results in an isotopic difference between lake water and input water, including precipitation and inflow, that is reflected in an isotopic difference between aquatic and terrestrial *n*-alkanes. In order to apply this isotopic difference as an indicator for the hydroclimatic characteristics of a lake site in terms of humid or arid climate conditions, we used a primary model to estimate evaporation to inflow ratio (*E/I*) values. It is assumed that semi-arid or arid climate conditions are characterized by evaporation amounts that exceed the amount of input, including inflow streams and precipitation, potentially leading to a negative lake water balance ($E/I > 1$) and thus to a long term deuterium enrichment of the lake water relative to the input water. Under humid climate conditions the input exceeds evaporation and results in a positive lake water balance ($E/I < 1$). In order to estimate evaporation to inflow ratio values we used a stable isotope approach as given by

$$E/I = (1 - h)/h \times \delta D_l - \delta D_i / \delta D^\circ - \delta D_l \quad (2)$$

(Gat and Levy, 1978)

with *h* as relative humidity, δD as the isotope value for the lake (l) and inflow water (i), respectively and δD° as the limiting isotopic composition for a desiccating water body without inflow determined, after Craig and Gordon (1965). Applied equations and the input parameters that were inserted into Eq. (2) are given in Table 5.

Initially, the dataset for the measured isotopic signatures of the catchment waters were used to assess the actual evaporation to inflow ratio for Nam Co and Holzmaar (Table 5). Mean annual lake surface temperatures are $\sim 8^\circ\text{C}$ at Nam Co (Xu et al., 2006) and $\sim 12^\circ\text{C}$ at Holzmaar (Moschen et al., 2006). Since data on the isotopic composition of the free atmosphere water vapour over the lake surfaces (δD_A) were not available, δD_A was estimated, based on the mean isotopic composition of local precipitation and $\epsilon_{v/l}$ as the equilibrium fractionation factor between water vapour (v) and liquid (l) (Craig and Gordon, 1965; Table 5).

The *E/I* ratio of 0.07 at Holzmaar suggests that only about 7% of the water flowing into the lake undergoes evaporation, confirming the positive water balance at Holzmaar and the minor impact of evaporation on the lake water. At Nam Co about 75% of the water flowing into the lake undergoes evaporation. This implies that, although evaporation has a significant influence leading to the enrichment of the lake water relative to the inflow, the water balance is positive at present, which is consistent with observations at the Nam Co meteorological station during the last two years (You et al., 2006).

Since the systematics during the incorporation of the hydrogen isotope signal during *n*-alkane biosynthesis are yet not entirely understood and fractionation factors are rather site- and species-specific than constant, we intended to apply the isotopic difference between terrestrial and aquatic *n*-alkane δD values as well as the sedimentary δD values from Nam Co and Holzmaar as input data. Given that the *E/I* ratio is based on relative isotope differences, and assuming an ecosystem-specific apparent fractionation for each lake site that was constant during the past, the sedimentary δD values are supposed to represent the relative changes in their corresponding hydrogen sources.

The input parameters that determine the environmental boundary conditions (relative humidity, mean annual lake surface temperature) were held constant, assuming that variations in the annual mean values on lake surface temperature and relative humidity can be neglected during the timeframe covered by the surface sediments. The results of the *E/I* estimation based on the isotopic difference between δD values from *n*-C₂₃ and *n*-C₂₉ from Holzmaar sediments show a striking similarity to the *E/I* determined with the actual isotope dataset, $E/I = 0.07$ (Table 5). This suggests that the use of

Table 5
Input parameters, underlying calculations and E/I for Nam Co and Holzmaar

		Nam Co actual data	Holzmaar actual data	Nam Co sediment	HZM sediment
Mean annual relative humidity	h	0.52	0.87	0.52	0.87
Mean annual lake surface temperature 77 °C	T	8	12	8	12
Mean δD of input water	δD_i	-122	-54	-246	-198
δD lake water	δD_l	-71	-47	-176	-225
Isotopic difference	$\delta D_{n-C_{23}} - \delta D_{n-C_{29}}$			70	-27
Limiting isotopic composition for a desiccating water body without inflow	$\delta D^o = \delta D_A + \varepsilon/h$ (Craig and Gordon, 1965)	-8.35	-30.63	-132.35	-173.63
Isotopic composition of the free atmosphere water vapour over the lake	$\delta D_A = \delta D_{\text{precipitation}} + \varepsilon_{v/l}$ (Craig and Gordon, 1965)	-213.45	-141.92	-337.45	-284.92
Equilibrium isotope fractionation factor between water vapour (v) and liquid water (l) at the temperature of the lake surface	$\varepsilon_{v/l} = (\alpha_{v/l} - 1) * 10^3$ (Craig and Gordon, 1965)	-91.45	-86.92	-91.45	-86.92
Equilibrium isotope fractionation factor between water vapour (v) and liquid water (l). at the temperature of the lake surface	$\alpha_{v/l}$	0.9085	0.9131	0.9085	0.9131
Equilibrium isotope fractionation factor between liquid water (l) and water vapour (v) at the temperature of the lake surface (experimental data; Majoube, 1971)	$\alpha_{l/v}$	1.10065	1.09520	1.10065	1.09520
Equilibrium fractionation (experimental data for various temperatures; Majoube, 1971)	$\varepsilon_{l/v}^* = (R_{\text{water}}/R_{\text{vapour}}^{-1}) * 10^3$ (Clark and Fritz, 1997)	100.65	95.20	100.65	95.20
Kinetic isotope fractionation ($C_k = 12.5$ for hydrogen)	$\varepsilon_k = (1-h) * C_k$ (Gonfiantini, 1986)	6	1.62	6	1.62
Total isotopic fractionation during evaporation	$\varepsilon_{\text{tot}} = \varepsilon^* + \varepsilon_k$ (Craig and Gordon, 1965)	106.65	96.83	118.55	103.68
Evaporation/Inflow ratio (Gat and Levy, 1978)	$E/I = (1-h)/h * \delta D_l - \delta D_i / \delta D^o - \delta D_l$	0.75	0.07	1.48	0.07

the isotopic difference between aquatic and terrestrial n -alkanes serves as a suitable proxy for estimating the proportion of evaporation from a catchment relative to the inflow. The E/I estimate for Nam Co is based on the mean δD values from the sedimentary n -C₂₃ and n -C₂₉ alkanes determined for the three short core sediments (Tables 3 and 5). The calculated E/I values are remarkably higher than those determined with the actual isotope dataset. Almost 150% (E/I 1.48) of the inflowing water undergoes evaporation, and a negative water balance for Nam Co is suggested, implying that lake level and volume have been reduced during the time covered by the sediments. The discrepancy with the actual evaporation to inflow ratio values is assumed to result from the temporal resolution of the lake surface sediments, since they integrate the environmental conditions of approximately the last 15 years, whereas a stable or slightly positive water balance is only observed for the last two years. These initial estimates of evaporation to inflow ratio values based on the biomarker δD values show that the isotopic difference between aquatic and terrestrial

n -alkane δD values serves as a proxy for the relative isotopic differences between the inflowing water and the lake water itself and thus can be used to quantitatively assess the proportion of inflowing water undergoing evaporation. The comparison with E/I values determined with the actual isotope data from the catchment waters showed that, although a large positive isotopic difference between inflowing water and lake water is an indication of remarkable evaporation and thus semi-arid climate conditions, it does not necessarily imply a negative lake water balance. Furthermore, it has to be stressed that the validity as well as the sensitivity of the input data are essential for the reliability of the E/I estimates. Thus, a sensitivity analysis was carried out to assess the variation in the estimated E/I values with changes in input parameters by $\pm 10\%$ (Table 6). Considering the metrological data, the temperature of the lake surface appears to be the least critical parameter, since a 10% increase results in an increase in E/I by 2.4%. The most critical parameters are the relative humidity (h) and the isotope composition of atmospheric vapour over the lake

Table 6
Changes in E/I ratio (%) of Nam Co for a change (by $\pm 10\%$) in input of parameters based on actual dataset

Parameter	% Change
h	+34/–15
T	+2.5/–2.4
δD_A	+24/–16
δD_i	+50/37
δD_l	+28/–22

surface (δD_A), since 10% positive changes increase E/I by +34% and +24%, respectively (Table 6). Hence, E/I calculations based on sedimentary n -alkane δD values have to account for this uncertainty if they intend to reconstruct the proportion of evaporation during the geological past, where actual environmental data cannot be easily transferred. Finally, the large variations in E/I , in association with changes in the isotope composition of lake water and inflows, imply the sensitivity of these parameters and their significance for the hydroclimatic characteristics of a lake system (Table 6).

7. Conclusions

This investigation of the deuterium content of sedimentary n -alkanes and plant biomass from two contrasting ecosystems, the arid Nam Co catchment and the humid Holzmaar, provides novel insights into the general understanding of the ability of biomarker δD values to record source water δD values.

The explanation of the different fractionation factors in the two different study areas is unclear. In order to use n -alkane hydrogen isotopes from plant biomass as a palaeoclimate proxy, further information is needed, as the apparent fractionation between terrestrial plants and precipitation is controlled by several plant-specific parameters like growth form, photosynthetic pathway and water use strategy, as well as localised site-specific physical conditions such as precipitation, soil moisture or relative humidity.

Here, we suggest using the isotopic difference between n -alkanes from terrestrial and aquatic plants as an indicator for humid and arid climate conditions. After Sachse et al. (2006), an identical water source for terrestrial plants surrounding a lake and aquatic organisms allows the use of the isotopic difference between them as a proxy for terrestrial leaf water deuterium enrichment. This

relationship was established for mid-European humid climate conditions where the evaporation of lake water is less important, because the precipitation amount exceeds the amount of evaporation. Consistent with other lake systems along the European Transect, this enrichment between terrestrial and aquatic n -alkanes is approximately 30‰ on average. Considering the Tibetan lakes, the isotope signals of water sources for terrestrial and aquatic plant biomass are significantly different. The lake water is strongly enriched in deuterium relative to the input water, pointing to exceptional evaporation rates. They are also responsible for a 30‰ higher evapotranspirative enrichment in deuterium in the steppe vegetation relative to the plants from the European Transect. Since the surrounding vegetation consists of steppe grasses and dicots that are highly influenced by evapotranspiration, as well as wetland vegetation that grows under water saturation conditions and thus is assumed not to be influenced by evapotranspiration, the sedimentary terrestrial n -alkanes integrate both isotope signals. Consequently, the long term evaporative enrichment of the lake water is recorded mainly by the aquatic n -alkanes, whereas the isotopic composition of precipitation is reflected in the terrestrial n -alkanes. This results in an isotopic difference between both and indicates the general hydroclimatic characteristics of a lake system. Evaporation to inflow ratio estimations based on the isotopic difference between aquatic and terrestrial n -alkanes showed that: (i) The isotopic difference serves to identify the influence of evaporation and thus to differentiate qualitatively between humid and arid climate conditions; in addition, the comparison of these E/I estimates with E/I values calculated with actual catchment water isotope data gives the following indication: (ii) The proportion of water that undergoes evaporation relative to the inflowing water can be quantitatively assessed, giving the possibility to reconstruct lake water balances in the past.

Acknowledgements

This research is supported by the Deutsche Forschungsgemeinschaft (DFG) Grant GL-262/8 and GL-262/10. We gratefully acknowledge constructive comments from R.D. Pancost, Y. Huang and an anonymous reviewer.

Associate Editor—P.A. Meyers

Appendix A

δ D values of lacustrine and plant biomass *n*-alkanes from Nam Co and Co Jiana

Lab no.	Sampled material	δ D <i>n</i> -C ₁₇ (‰)	Sd (‰)	δ D <i>n</i> -C ₂₁ (‰)	Sd (‰)	δ D <i>n</i> -C ₂₃ (‰)	Sd (‰)	δ D <i>n</i> -C ₂₅ (‰)	Sd (‰)	δ D <i>n</i> -C ₂₇ (‰)	Sd (‰)	δ D <i>n</i> -C ₂₉ (‰)	Sd (‰)	D <i>n</i> -C ₃₁ (‰)	Sd (‰)
998446	Macrophyte Co Jiana					-191	6	-237	3						
39	Macrophyte Nam Co			-209	4	-196	2	-192	2						
40	Macrophyte Nam Co					-151	34	-144	13						
41	Algae Nam Co	-137	12			-176	13	-165	11						
15	<i>Kobresia schoenoides</i>									-250	2	-265	2	-245	2
17	<i>Kobresia schoenoides</i>									-254	35	-282	2	-256	6
25	<i>Kobresia schoenoides</i>									-234	1	-265	1	-254	1
28	<i>Kobresia schoenoides</i>									-210	36	-269	1	-260	2
998444	<i>Morina</i> sp. 2005											-218	5	-205	4
Tibet PB 1	<i>Morina</i> sp. 2004											-207	2	-223	9
Tibet PB 5	<i>Oxytropis</i> sp. 2004											-190	2	-165	12
Tibet PB 2	<i>Stipa</i> 2004											-226	4	-253	1
998442	<i>Stipa</i> sp. 2005									-219	5	-211	4		
				-211	22			-195	18						
Tibet 2	Lake sediment Nam Co					-182	8	-203	4			-240	6	-247	15
Tibet 3	Lake sediment Nam Co			-207	21	-165	14	-173	31	-170	26	-223	22	-213	10
Tibet 4	Lake sediment Co Jiana			-222	8	-190	1	-217	6	-202	14	-255	3	-230	12
Tibet 7	Lake sediment Nam Co					-181	5	-186	9	-180	30	-275	10	-237	2

References

- Arp, G., Thiel, V., Reimer, A., Michaelis, W., Reitner, J., 1999. Biofilm exopolymers control microbialite formation at thermal springs discharging into the alkaline Pyramid Lake, Nevada, USA. *Sedimentary Geology* 126, 159–176.
- Baas, M., Pancost, R., van Geel, B., Damsté, J.S.S., 2000. A comparative study of lipids in *Sphagnum* species. *Organic Geochemistry* 31, 535–541.
- Baier, J., Lucke, A., Negendank, J.F.W., Schleser, G.H., Zolitschka, B., 2004. Diatom and geochemical evidence of mid-to-late Holocene climatic changes at Lake Holzmaar, West-Eifel (Germany). *Quaternary International* 113, 81–96.
- Bray, E.E., Evans, E.D., 1961. Distribution of normal-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* 22, 2–15.
- Burgoyne, T.W., Hayes, J.M., 1998. Quantitative production of H-2 by pyrolysis of gas chromatographic effluents. *Analytical Chemistry* 70, 5136–5141.
- Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD - $\delta^{13}C$ analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* 63, 361–371.
- Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004. Carbon and hydrogen isotopic fractionation during lipid biosynthesis in a higher plant (*Cryptomeria japonica*). *Phytochemistry* 65, 323–330.
- Clark, I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, New York.
- Closs, H., 1979. Die Klimasituation im Regierungsbezirk Trier. *Beiträge zur Trierischen Landeskunde*, 326–377.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Craig, H., Gordon, L.I., 1965. Deuterium and ^{18}O variations in the ocean and the marine atmosphere. In: Tongiorgi, E. (Ed.), *Spoleto Conferences in Nuclear Geology, Stable Isotopes in Oceanographic Studies and Paleotemperatures*. Pisa, pp. 9–130.
- Cranwell, P.A., Eglinton, G., Robinson, N., 1987. Lipids of aquatic organisms as potential contributors to lacustrine sediments 2. *Organic Geochemistry* 11, 513–527.
- Danis, P.A., Masson-Delmotte, V., Stievenard, M., Guillemim, M.T., Daux, V., Naveau, P., von Grafenstein, U., 2006. Reconstruction of past precipitation beta ^{18}O using tree-ring cellulose $\delta^{18}O$ and $\delta^{13}C$: a calibration study near Lac d'Annecy, France. *Earth and Planetary Science Letters* 243, 439–448.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436–468.
- De Wit, J.C., Van der Sraaten, C.M., Mook, W.G., 1980. Determination of the absolute hydrogen isotopic ratio of V-SMOW and SLAP. *Geostandards Newsletter* 4, 33–36.
- De Niro, M.J., Epstein, S., 1977. Mechanism of carbon isotope fractionation associated with lipid-synthesis. *Science* 197, 261–263.
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1324.
- Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An *n*-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Organic Geochemistry* 31, 745–749.
- Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annual Review of Earth and Planetary Sciences* 24, 225–262.
- Gat, J.R., Levy, Y., 1978. Isotope hydrology of inland sabkhas in Bardawil area, Sinai. *Limnology and Oceanography* 23, 841–850.
- Gehre, M., Geilmann, H., Richter, J., Werner, R.A., Brand, W.A., 2004. Continuous flow 2H -/ 1H and ^{18}O / ^{16}O analysis of water samples with dual inlet precision. *Rapid Communications in Mass Spectrometry* 18, 2650–2660.
- Gibson, J.J., Reid, R., Spence, C., 1998. A six-year isotopic record of lake evaporation at a mine site in the Canadian subarctic: results and validation. *Hydrological Processes* 12, 1779–1792.
- Gibson, J.J., Edwards, T.W.D., Birks, S.J., St Amour, N.A., Buhay, W.M., McEachern, P., Wolfe, B.B., Peters, D.L., 2005. Progress in isotope tracer hydrology in Canada. *Hydrological Processes* 19, 303–327.
- Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, P.J.C. (Eds.), *Handbook of Environmental Isotope Geochemistry*, vol. 2. Elsevier, Amsterdam, pp. 113–163.
- Grimalt, J., Albaiges, J., 1987. Sources and occurrence of C_{12} – C_{22} normal-alkane distributions with even carbon-number preference in sedimentary environments. *Geochimica et Cosmochimica Acta* 51, 1379–1384.
- Grimalt, J.O., Dewit, R., Teixidor, P., Albaiges, J., 1992. Lipid biogeochemistry of phormidium and microcoleus mats. *Organic Geochemistry* 19, 509–530.
- Han, J., Calvin, M., 1969. Hydrocarbon distribution of algae and bacteria, and microbiological activity in sediments. *Proceedings of the National Academy of Sciences of the United States of America* 64, 436–437.
- Hayes, J.M., 2001. Fractionation of carbon and hydrogen isotopes in biosynthetic processes. *Stable Isotope Geochemistry* 43, 225–277.
- Hilkert, A.W., Douthitt, C.B., Schluter, H.J., Brand, W.A., 1999. Isotope ratio monitoring gas chromatography mass spectrometry of D/H by high temperature conversion isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry* 13, 1226–1230.
- Hou, J., D'Andrea, W.J., MacDonald, D., Huang, Y., 2007. Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, MA (USA). *Organic Geochemistry* 38, 977–984.
- Huang, Y., Lockheart, M.J., Logan, G.A., Eglinton, G., 1996. Isotope and molecular evidence for the diverse origins of carboxylic acids in leaf fossils and sediments from the Miocene Lake Clarkia deposit, ID, USA. *Organic Geochemistry* 24, 289–299.
- Huang, Y.S., Shuman, B., Wang, Y., Webb, T., 2002. Hydrogen isotope ratios of palmitic acid in lacustrine sediments record late quaternary climate variations. *Geology* 30, 1103–1106.
- Huang, Y.S., Shuman, B., Wang, Y., Webb, T., 2004. Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. *Journal of Paleolimnology* 31, 363–375.
- Kelts, K., Talbot, M.R., 1990. Lacustrine carbonates as geochemical archives of environmental change and biotic–abiotic interactions. In: Tilzer, M.M., Serruya, C. (Eds.), *Large Lakes: Ecological Structure and Function*. Springer Verlag, pp. 288–315.
- Krause, W.J., 1980. Tritium-bilanzierung kleiner einzugsgebiete in der Eifel. Teil 1 – wasserbilanz. *Deutsche Gewässerkundliche Mitteilungen* 24, 2–14.

- Kürschner, H., Herzschuh, U., Wagner, D., 2005. Phytosociological studies in the north-eastern Tibetan Plateau (NW China)—A first contribution to the subalpine scrub and alpine meadow vegetation. *Botanisches Jahrbuch der Systematics* 125, 273–315.
- Lehmkuhl, F., Haselein, F., 2000. Quaternary paleoenvironmental change on the Tibetan Plateau and adjacent areas (Western China and Western Mongolia). *Quaternary International* 65, 121–145.
- Majoube, M., 1971. Fractionation in ^{18}O between ice and water vapor. *Journal de Chimie Physique et de Physico-Chimie Biologique* 68, 625–626.
- Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. *Organic Geochemistry* 34, 261–289.
- Meyers, P.A., Lallier-Verges, E., 1999. Lacustrine sedimentary organic matter records of late quaternary paleoclimates. *Journal of Paleolimnology* 21, 345–372.
- Mingram, J., Schettler, G., Nowaczyk, N., Luo, X.J., Lu, H.Y., Liu, J.Q., Negendank, J.F.W., 2004. The Huguang maar lake – a high-resolution record of palaeoenvironmental and palaeoclimatic changes over the last 78,000 years from South China. *Quaternary International* 122, 85–107.
- Morinaga, H., Itota, C., Isezaki, N., Goto, H., Yaskawa, K., Kusakabe, M., Liu, J., Gu, Z., Yuan, B., Cong, S., 1993. Oxygen-18 and carbon-13 records for the last 14,000 years from lacustrine carbonates of siling-co (lake) in the qinghai-tibetan plateau. *Geophysical Research Letters* 20, 2909–2912.
- Morrill, C., 2004. The influence of Asian summer monsoon variability on the water balance of a Tibetan lake. *Journal of Paleolimnology* 32, 273–286.
- Moschen, R., Lücke, A., Parplies, J., Radtke, U., Schleser, G.H., 2006. Transfer and early diagenesis of biogenic silica oxygen isotope signals during settling and sedimentation of diatoms in a temperate freshwater lake (Lake Holzmaar, Germany). *Geochimica et Cosmochimica Acta* 70, 4367–4379.
- Oehms, M., 1995. Zur Limnologie des Holzmaars. In: Scientific Technical Report 95/16: Das Holzmaar und seine Sedimente. GeoForschungs-Zentrum Potsdam, Manderscheid/Vulkaneifel.
- Ohkouchi, N., Kawamura, K., Taira, A., 1997. Molecular paleoclimatology: reconstruction of climate variabilities in the late Quaternary. *Organic Geochemistry* 27, 173–183.
- Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., Schouten, S., Brinkhuis, H., Damsté, J.S.S., Dickens, G.R., 2006. Arctic hydrology during global warming at the Palaeocene/Eocene thermal maximum. *Nature* 442, 671–675.
- Pendall, E., Betancourt, J.L., Leavitt, S.W., 1999. Paleoclimatic significance of δD and $\delta^{13}\text{C}$ values in pinon pine needles from packrat middens spanning the last 40,000 years. *Palaeogeography, Palaeoclimatology, Palaeoecology* 147, 53–72.
- Rozanski, K., Sonntag, C., Munnich, K.O., 1982. Factors controlling stable isotope composition of European precipitation. *Tellus* 34, 142–150.
- Rozanski, K., Araguasaraguas, L., Gonfiantini, R., 1992. Relation between long-term trends of ^{18}O isotope composition of precipitation and climate. *Science* 258, 981–985.
- Rozanski, K., Johnsen, S.J., Schotterer, U., Thompson, L.G., 1997. Reconstruction of past climates from stable isotope records of palaeo-precipitation preserved in continental archives. *Hydrological Sciences Journal-Journal Des Sciences Hydrologiques* 42, 725–745.
- Sachse, D., Radke, J., Gleixner, G., 2004. Hydrogen isotope ratios of recent lacustrine sedimentary *n*-alkanes record modern climate variability. *Geochimica et Cosmochimica Acta* 68, 4877–4889.
- Sachse, D., Radke, J., Gleixner, G., 2006. δD values of individual *n*-alkanes from terrestrial plants along a climatic gradient – Implications for the sedimentary biomarker record. *Organic Geochemistry* 37, 469–483.
- Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A., Sessions, A.L., 2001. Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. *Geochimica et Cosmochimica Acta* 65, 213–222.
- Schefuss, E., Schouten, S., Schneider, R.R., 2005. Climatic controls on central African hydrology during the past 20,000 years. *Nature* 437, 1003–1006.
- Schmidt, T.C., Zwank, L., Elsner, M., Berg, M., Meckenstock, R.U., Haderlein, S.B., 2004. Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Analytical and Bioanalytical Chemistry* 378, 283–300.
- Schwalb, A., 2003. Lacustrine ostracodes as stable isotope recorders of late-glacial and Holocene environmental dynamics and climate. *Journal of Paleolimnology* 29, 267–351.
- Sessions, A.L., 2006. Seasonal changes in D/H fractionation accompanying lipid biosynthesis in *Spartina alterniflora*. *Geochimica et Cosmochimica Acta* 70, 2153–2162.
- Sessions, A.L., Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochemistry* 30, 1193–1200.
- Shuman, B., Huang, Y.S., Newby, P., Wang, Y., 2006. Compound-specific isotopic analyses track changes in seasonal precipitation regimes in the Northeastern United States at ca 8200 cal yr BP. *Quaternary Science Reviews* 25, 2992–3002.
- Smith, F.A., Freeman, K.H., 2006. Influence of physiology and climate on δD of leaf wax *n*-alkanes from C_3 and C_4 grasses. *Geochimica et Cosmochimica Acta* 70, 1172–1187.
- von Grafenstein, U., Erlenkeuser, H., Trumborn, P., 1999. Oxygen and carbon isotopes in modern fresh-water ostracod valves: assessing vital offsets and autecological effects of interest for palaeoclimate studies. *Palaeogeography, Palaeoclimatology, Palaeoecology* 148, 133–152.
- Williams, W.D., 1991. Chinese and Mongolian saline lakes – a limnological overview. *Hydrobiologia* 210, 39–66.
- Xu, Y., Kang, S., Zhou, S., You, Q., Tian, K., 2006. Characteristics of $\delta^{18}\text{O}$ in waters and the oxygen isotopic equilibrium of lake water in Nam Co basin, Tibetan Plateau. Annual report of Nam Co Monitoring and Research Station for multisphere interactions, vol. 1, pp. 114–121.
- Yang, H., Huang, Y.S., 2003. Preservation of lipid hydrogen isotope ratios in Miocene lacustrine sediments and plant fossils at Clarkia, northern ID, USA. *Organic Geochemistry* 34, 413–423.
- You, Q., Kang, S., Li, C., Li, M., Liu, J., 2006. Features of meteorological parameters at Nam Co Station, Tibetan Plateau. Annual Report of Nam Co Monitoring and Research Station for multisphere interactions, vol. 1, pp. 8–15.

Zhu, D.A., Zhao, X.T., Meng, X.A., Wu, Z.H., Wu, Z.H., Feng, X.Y., Shao, Z.G., Liu, Q.S., Yang, M.L., 2002. Quaternary lake deposits of Nam Co, Tibet, with a discussion of the connection of Nam Co with Ring Co-Jiuru Co. *Acta Geologica Sinica-English Edition* 76, 283–291.

Zhu, D.G., Meng, X.G., Zhao, X.T., Shao, Z.G., Xu, Z.F., Yang, C.B., Ma, Z.B., Wu, Z.G., Wu, Z.H., Wang, J.P., 2004. Evolution of an ancient large lake in the southeast of the northern Tibetan Plateau. *Acta Geologica Sinica-English Edition* 78, 982–992.