

Hydrogen isotopic composition of plant leaf wax in response to soil moisture in an arid ecosystem of the northeast Qinghai-Tibetan Plateau, China

Yuan YAO^{1,2}, WeiGuo LIU^{1,2*}

¹ School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China;

² State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

Abstract: The hydrogen isotopic composition of plant leaf wax (δD_{wax}) is used as an important tool for paleohydrologic reconstruction. However, the understanding of the relative importance of environmental and biological factors in determining δD_{wax} values still remains incomplete. To identify the effects of soil moisture and plant physiology on δD_{wax} values in an arid ecosystem, and to explore the implication of these values for paleoclimatic reconstruction, we measured δD values of soil water (δD_{water}) and δD_{wax} values in surface soils along two distance transects extending from the lakeshore to wetland to dryland around Lake Qinghai and Lake Gahai on the northeast Qinghai-Tibetan Plateau. The results showed that the δD_{water} values were negatively correlated with soil water content (SWC) ($R^2=0.9166$), and ranged from -67‰ to -46‰ with changes in SWC from 6.2% to 42.1% in the arid areas of the Gangcha (GCh) and Gahai (GH) transects. This indicated that evaporative D-enrichment in soil water was sensitive to soil moisture in an arid ecosystem. Although the shift from grasses to shrubs with increasing aridity occurred in the arid area of the GH transect, the δD_{wax} values in surface soils from the arid areas of the two transects still showed a negative correlation with SWC ($R^2=0.6835$), which may be due to the controls of primary evaporative D-enrichment in the soil water and additional transpirational D-enrichment in the leaf water on the δD_{wax} values. Our preliminary research suggested that δD_{wax} values can potentially be applied as a paleo-humidity indicator on the northeast Qinghai-Tibetan Plateau.

Keywords: hydrogen isotope; D-enrichment; soil water content; northeast Qinghai-Tibetan Plateau

Citation: Yuan YAO, WeiGuo LIU. 2014. Hydrogen isotopic composition of plant leaf wax in response to soil moisture in an arid ecosystem of the northeast Qinghai-Tibetan Plateau, China. *Journal of Arid Land*, 6(5): 592–600. doi: 10.1007/s40333-014-0005-9

The hydrogen isotopic composition of plant leaf wax (δD_{wax}) preserved in natural archives over geological timescales has been increasingly used as a promising paleohydrological proxy. Environmental water, as the ultimate hydrogen source of plant leaf wax, is considered as the primary controlling factor of δD_{wax} values (Sachse et al., 2012). In large spatial scales, the fundamental control on δD_{wax} values is the hydrogen isotopic composition of precipitation (Hou et al., 2008; Liu and Yang, 2008; Tipple and Pagani, 2013). Given that the apparent hydrogen isotopic fractionation between source water and plant leaf wax ($\epsilon_{wax/water}$) inte-

grates transpirational D-enrichment in leaf water with biosynthetic fractionation, and some processes that control on δD_{wax} values are not well understood (Sachse et al., 2006, 2009; Smith and Freeman, 2006; Yang and Leng, 2009; Polissar and Freeman, 2010; McInerney et al., 2011), the effects of environmental and biological factors on δD_{wax} values are still being investigated in recent decades.

In general, δD_{wax} values of C_4 grasses are slightly more positive than those of C_3 grasses (Bi et al., 2005; Smith and Freeman, 2006). However, the δD_{wax} values are considerably affected by plant life forms (e.g. tree,

*Corresponding author: WeiGuo LIU (E-mail: liuwg@loess.llqg.ac.cn)

Received 2013-07-23; revised 2013-11-17; accepted 2013-12-06

© Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Science Press and Springer-Verlag Berlin Heidelberg 2014

shrub and grass) rather than by plant photosynthetic pathway (C_3 vs. C_4) in northwestern China (Liu et al., 2006a) and in northeastern USA (Hou et al., 2007a). Interspecies variability in $\varepsilon_{\text{wax/water}}$ within growth forms also has significant variations that may be related to the differences in plant physiology, biochemistry and the timing of leaf wax synthesis (Chikaraishi and Naraoka, 2007; Hou et al., 2007a; Feakins and Sessions, 2010; Sachse et al., 2010, 2012). In addition, evapotranspiration (soil water evaporation and leaf water transpiration), which is controlled by environmental factors (e.g. temperature and humidity), drives D-enrichment in leaf water (Yapp and Epstein, 1982; Leaney et al., 1985; Yakir et al., 1990) and the signal can be recorded by δD_{wax} values (Kahmen et al., 2013a). Humidity, particularly in arid ecosystems, has an important role in determining δD_{wax} values through D-enrichment by evapotranspiration (Smith and Freeman, 2006). Liu and Huang (2005) showed that the changes in δD_{wax} values in a paleosol profile are strongly consistent with those in aridity on the Chinese Loess Plateau.

The combined effects of environmental and biological factors on δD_{wax} values have recently been studied to determine their relative importance in the distribution of δD_{wax} signature. Enhanced D-enrichment with increasing aridity is partially countered by shifts in vegetation types across a large gradient of humidity and vegetation composition in southwestern USA (Hou et al., 2008). Plant physiology may exert a greater effect on δD_{wax} values of grasses than environmental conditions (McInerney et al., 2011). Wang et al. (2013a) found that the δD_{wax} values of C_{31} and C_{33} n-alkanes from a marine sediment core in the southwestern part of the Indian Ocean respond to the changes in C_3/C_4 vegetation. Whereas the simulated global patterns of D-enrichment in leaf water revealed that δD_{wax} values could reflect evapotranspirational signal in arid or temperate regions (Kahmen et al., 2013b).

Therefore, determining the relative importance of environmental and biological factors controlling on δD_{wax} values is important to examine the use of the values as a paleoclimatic proxy. In this study, we measured the δD values of soil water (δD_{water}) and δD_{wax} values in surface soils along two distance transects extending from the lakeshore to wetland to dryland around Lake Qinghai and Lake Gahai, to further

understand the controlling factors and the implication of δD_{wax} values for paleoclimatic reconstruction in the arid ecosystem.

1 Study area and methods

1.1 Study area and samples

We collected soil water and surface soil samples around Lake Qinghai and Lake Gahai in the northeast Qinghai-Tibetan Plateau (Fig. 1). Lake Qinghai ($36^{\circ}32'–37^{\circ}15'N$, $99^{\circ}36'–100^{\circ}47'E$; 3,200 m asl), the largest inland brackish lake in China, is characterized by an arid and semi-arid climate with a mean annual precipitation of 400 mm and a 10-year (1994–2004) mean summer temperature of $11.4^{\circ}C$ (Henderson et al., 2003; Liu et al., 2008). Influenced by the East Asian summer monsoon, the Indian summer monsoon, the winter monsoon and the westerly jet stream, the region is highly sensitive to global climate change (An et al., 2000). Although summer has the highest precipitation, the potential evaporation (800–1,200 mm) greatly exceeds precipitation in the lake (Liu et al., 2006b). Lake Gahai ($37^{\circ}08'N$, $97^{\circ}33'E$), a closed-basin lake in the northeast Qaidam Basin, is fed mostly by groundwater with no permanent inflow streams (Wang and Dou, 1998). Mean annual precipitation and mean summer temperature at nearby Delingha climate station (2,928 m asl), ca. 25 km north of Gahai, is about 160 mm and $15.6^{\circ}C$, respectively. The mean annual potential evaporation is approximately 2,000 mm based on the average value for the period of 1971–2000 (Zhao et al., 2008).

Soil water and surface soil samples in the upper soil layer of 5 cm along two transects were collected in the summer of 2012 (Fig. 1 and Table 1). The Gangcha (GCh) transect ($37^{\circ}11'18''–37^{\circ}12'15''N$, $100^{\circ}06'41''–100^{\circ}06'51''E$) was in the north of Lake Qinghai within Gangcha county. Six soil water and surface soil samples from this transect were collected at a distance of ca. 0, 150, 225, 1,100, 1,700 and 1,700 m from the lakeshore, respectively. The Gahai (GH) transect ($37^{\circ}09'33''–37^{\circ}09'37''N$, $97^{\circ}33'48''–97^{\circ}34'14''E$) was in the northeast of Lake Gahai. Seven soil water and surface soil samples from this transect were collected at a distance of ca. 5, 55, 170, 300, 500, 600 and 700 m from the lakeshore, respectively. All samples were frozen and stored on dry ice in the field and then kept at $-20^{\circ}C$ in the laboratory until analysis.

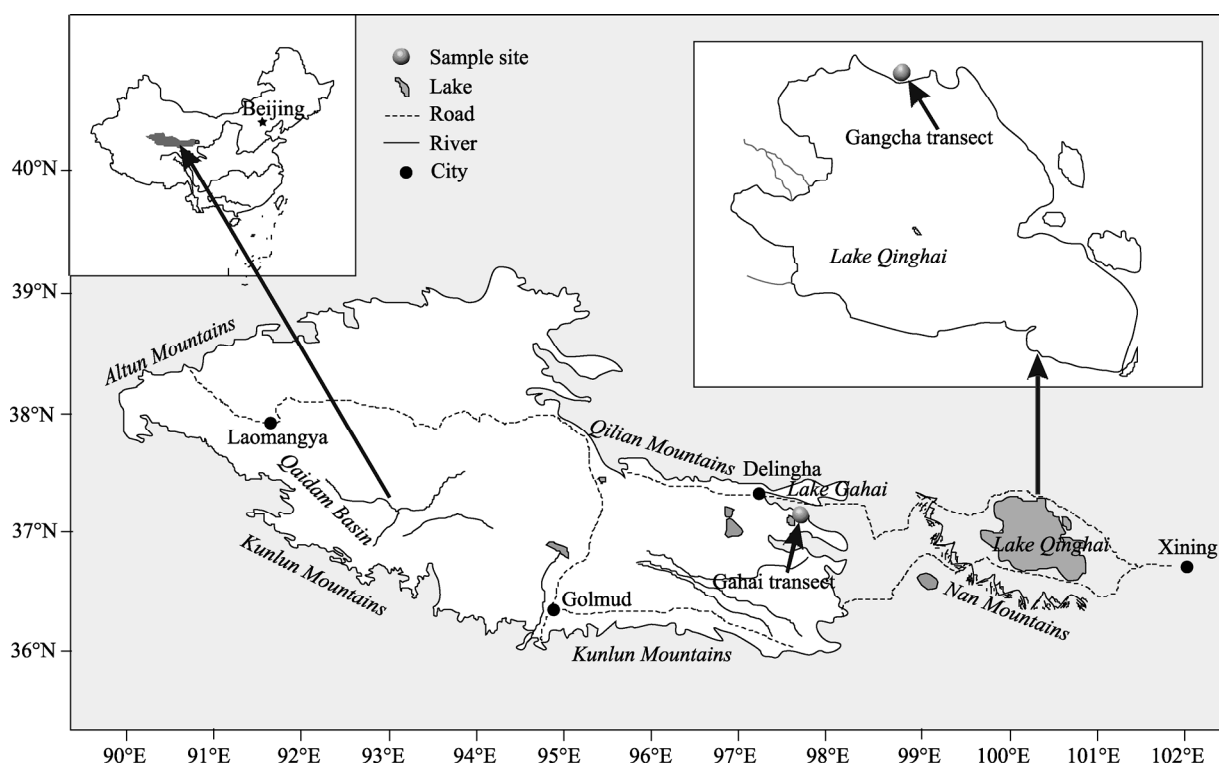


Fig. 1 Map of the Lake Qinghai and Lake Gahai on the northeast Qinghai-Tibetan Plateau, China

Table 1 SWC, δD_{water} , δD_{wax} of C_{31} n-alkane and $\epsilon_{\text{wax/water}}$ in the Gangcha (GCh) and Gahai (GH) transects

Sample number	Distance from the lakeshore (m)	Plant type	SWC (%)	δD_{water} (‰)	δD_{wax} of C_{31} n-alkane (‰)	$\epsilon_{\text{wax/water}}$ (‰)
GCh12-2	0	Grass	58.0	-45	-194	-156
GCh12-3	150	Grass	51.9	-49	-192	-150
GCh12-4	225	Grass	48.8	-40	-181	-147
GCh12-5	1,100	Grass	42.1	-67	-204	-147
GCh12-6-1	1,700	Grass	26.1	-59	-192	-142
GCh12-6-2	1,700	Grass	39.1	-64	-200	-145
GH12-1	5	Fern	17.3	-48	-167	-124
GH12-2	55	Fern grass	15.9	-50	-193	-150
GH12-3	170	Fern grass	15.7	-50	-192	-150
GH12-4	300	Grass	17.9	-50	-199	-157
GH12-6	500	Shrub	16.4	-52	-170	-125
GH12-7	600	Shrub	15.9	-46	-163	-123
GH12-8	700	Shrub	6.2	-47	-158	-117

Note: SWC, Soil water content; δD_{water} , δD values of soil water; δD_{wax} , hydrogen isotopic composition of plant leaf wax; $\epsilon_{\text{wax/water}}$, apparent hydrogen isotopic fractionation between source water and plant leaf wax.

1.2 Analytical methods

1.2.1 Soil water content (SWC) analysis

SWC was obtained by measuring soil sample weight before and after freeze drying.

1.2.2 Extraction and purification of n-alkanes

Soil samples were freeze-dried and grounded using an

agate mortar and pestle, and then sieved through a 100-mesh screen and homogenized. Methods for extraction, fractionation and purification of lipids were similar to those described by Zhang and Liu (2011). About 5 g sieved soil materials were extracted ultrasonically (3×20 min) with dichloromethane (DCM) and methanol (9:1, v/v). The solvent was then

removed with a N₂ stream. The n-alkane fractions were obtained by eluting the total extracts on a silica gel flash column (100–200 mesh silica gel) using hexane.

1.2.3 Gas chromatography

The n-alkanes were identified by comparing the retention times defined by Gas chromatography (GC) analysis of a mixed n-alkanes standard. GC was performed using an Agilent 6890 GC with a HP1-ms column (60-m height, 0.32-mm inner diameter and 0.25-μm film thickness) and a flame ionization detector. The samples were injected in split mode, with a GC inlet temperature of 310°C and a flow rate of 1.2 mL/min. The oven temperature program was 40°C (1 min) to 150°C at 10°C/min and then to 310°C (20 min) at 6°C/min. GC analysis was carried out at the stable isotope laboratory of the Institute of Earth Environment, Chinese Academy of Sciences.

1.2.4 Hydrogen isotope analysis

Hydrogen isotope ratio of individual n-alkanes was analyzed using GC-thermal conversion-isotope ratio mass spectrometry (GC-TC-IRMS). A Thermo Trace Ultra GC was used along with a high temperature H/D pyrolysis reactor connected online to a Thermo Delta V Advantage isotope ratio mass spectrometer. Compounds separated with GC column (identical temperature program and GC column with an Agilent 6890 GC used for GC analysis) were converted to H₂ by a pyrolysis reactor at 1,450°C, and then H₂ was introduced into the mass spectrometer. H₃ factors were calculated daily using the same H₂ reference gas. The precision of isotopic measurements of H₂ reference gas after H₃ factor correction was 1‰ or better. Analytical error was <3‰ for samples. Compound specific hydrogen isotope analysis was carried out at the stable isotope laboratory of the Institute of Earth Environment, Chinese Academy of Sciences.

Hydrogen isotope ratio of soil water was analyzed using Isotope Water Analyzer (IWA) (LGR IWA-35EP) at the School of Environmental Science and Engineering, Chang'an University. The δD_{water} values were normalized to VSMOW using lab standards. The average precision of the δD_{water} measurements was <0.3‰.

The apparent hydrogen isotopic fractionation between soil water and plant leaf wax (ε_{wax/water}) was calculated as Eq. 1:

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

2 Results and discussion

2.1 Effect of soil moisture on δD_{water}

In an arid ecosystem where there is a significant D-enrichment in soil water towards the surface (Allison, 1982; Barnes and Allison, 1983; Tang and Feng, 2001), humidity plays an important role in determining δD_{water} values by evaporation (Smith and Freeman, 2006; Hou et al., 2008; McInerney et al., 2011). In the present study, we selected two natural transects extending from the lakeshore to wetland to dryland around Lake Qinghai and Lake Gahai with a considerable difference in SWC (6.2% to 42.1%). They provide ideal locations for investigating the effect of soil moisture on hydrogen isotopic compositions. Unfortunately, the δD_{water} values had a weak positive correlation ($R^2=0.4054$) with SWC in the GCh transect, and a poor negative correlation ($R^2=0.1827$) with SWC in the GH transect (Figs. 2a and b). This result is potentially due to the effect of lake water on δD_{water} values from the lakeshore and wetland in which soil water derives from a mixture of lake water and precipitation. In arid lake areas (e.g. Lake Gahai in the Qaidam Basin and Lake Qinghai) where evaporation exceeds precipitation (Liu et al., 2006b), lake water is more D-enriched than precipitation due to strong evaporation (Mügler et al., 2008; Xia et al., 2008; Aichner et al., 2010). Duan and Xu (2012) reported that δD_{water} values from Lake Qinghai with a mean value of 4.7‰ were obviously more positive than those from the river water with a mean value of −45.3‰. Potential evaporation (800–1,200 mm) greatly exceeds precipitation (400 mm) in the Lake Qinghai (Liu et al., 2006b), resulting in obvious D-enrichment of lake water relative to river water. We observed that δD_{water} values (average value of −45‰) from the lakeshore and wetland (within 225 m from the lakeshore) were more positive than those (average value of −63‰) from the dryland (225 m beyond the lakeshore) in the GCh transect (Table 1). Therefore, some lake water inputted into the lakeshore and the wetland, resulting in a poor correlation between the δD_{water} values and SWC.

To reduce the effect of lake water on δD_{water} values and further investigate the sensitivity of δD_{water} values to soil moisture, we analyzed the relationship between SWC and δD_{water} values in the arid areas of the GCh

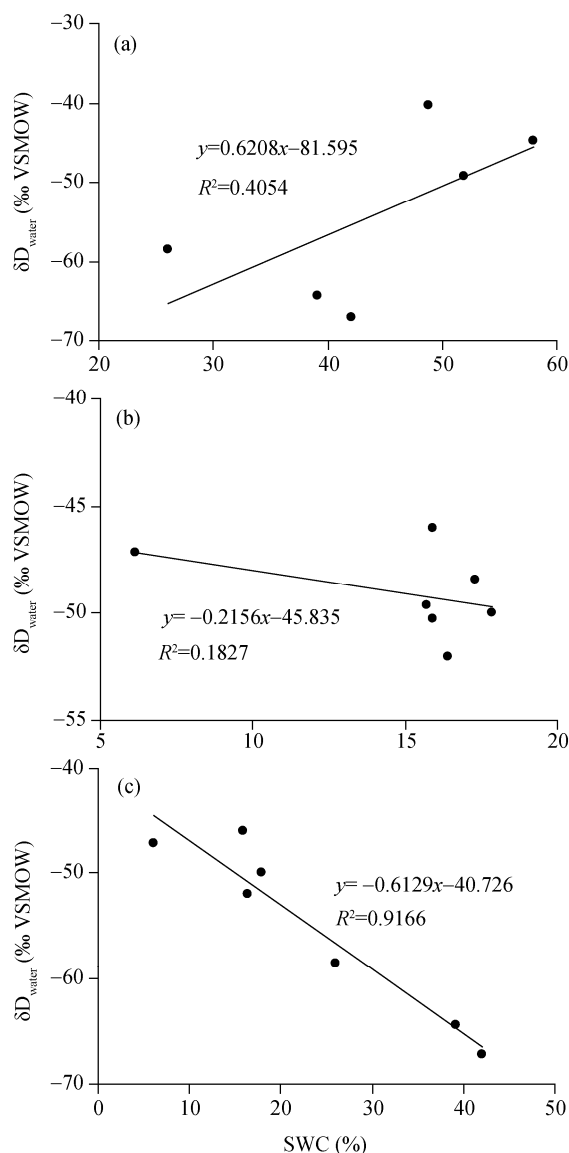


Fig. 2 Correlations between δD_{water} values and soil water content (SWC) in the GCh transect (a), GH transect (b) and arid areas of the GCh and GH transects (c)

and GH transects (225 m beyond the lakeshore). The δD_{water} values were significantly negatively correlated with SWC ($R^2 = 0.9166$; Fig. 2c), indicating that soil moisture exerts a major control on δD_{water} values in the arid areas. The negative correlation may be due to enhanced evaporative D-enrichment in soil water with decreasing SWC (Smith and Freeman, 2006; McInerney et al., 2011). The δD_{water} values also showed a large variation from -67‰ to -46‰ with changes in SWC (6.2%–42.1%), suggesting that evaporative D-enrichment in soil water is sensitive to soil moisture in the arid areas. This observation is consistent with those from previous studies (Smith and Freeman, 2006;

Hou et al., 2008; McInerney et al., 2011), but contradicts the conclusion of Feakins and Sessions (2010). Feakins and Sessions (2010) measured the δD_{water} values of tree xylem as a direct proxy of δD_{water} values in southern California and found that little change existed in soil water D-enrichment. We speculated that deep-rooted sampled trees absorb more deep soil water that is more D-depleted relative to surface soil at a certain depth range due to decreased evaporation, and uptake of the D-depleted soil water may be the major cause of the little change in soil water D-enrichment.

2.2 Effect of soil moisture on δD_{wax} values in surface soils

In our study, the GCh transect is dominated by single-species grasses at all sample sites, whereas there are obvious shifts in vegetation types, from ferns to grasses to shrubs, along the aridity gradient in the GH transect. These characteristics allowed us to assess the relative effect of plant physiology and soil moisture on hydrogen isotopic signatures of plant leaf wax in surface soils. In this study, we focused on the δD_{wax} values of C_{31} n-alkane as the representative isotope values of higher terrestrial plants, because C_{31} n-alkane had the highest concentration of the long-chain n-alkanes in most of our samples. Considering the effect of lake water on δD_{water} values from the lakeshore and wetland, we analyzed the δD_{wax} values of C_{31} n-alkane from surface soils in the arid areas of the GCh and GH transects.

The δD_{wax} values in surface soils were negatively correlated with SWC ($R^2 = 0.6835$; Fig. 3), indicating that soil moisture exerts a significant effect on δD_{wax}

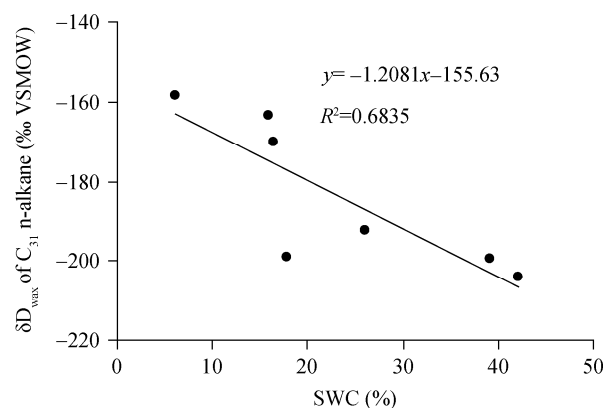


Fig. 3 Correlation between δD_{wax} values of C_{31} n-alkane in surface soils and SWC in the arid areas of the GCh and GH transects

values in surface soils despite the shifts in vegetation types in the GH transect. Nevertheless, soil moisture may have an indirect effect on δD_{wax} values in surface soils in this study. In the arid area of the GH transect, the shift from grasses to shrubs can result in more positive δD_{wax} values in surface soils along the GH transect, because shrubs have higher δD_{wax} values than grasses at the same site (Liu et al., 2006a; Hou et al., 2007a).

In order to understand how soil moisture affects the δD_{wax} values in surface soils in our study, we examined and discussed soil water evaporation, leaf water transpiration and plant physiology as below.

First, the δD_{wax} values in surface soils were positively correlated with the δD_{water} values ($R^2=0.6355$; Fig. 4), indicating that soil water, as the ultimate source water of higher terrestrial plants, exerts the primary control on δD_{wax} values. This observation was supported by previous studies that δD values of precipitation as the first order of control are recorded by δD_{wax} signals in large spatial scales (Hou et al., 2008; Liu and Yang, 2008; Tipple and Pagani, 2013). The δD_{water} values were also significantly negatively related to SWC in the arid areas of the GCh and GH transects due to enhanced evaporative D-enrichment in soil water with increasing aridity (Fig. 2c). Therefore, we suggested that the evaporative D-enrichment in soil water, which is controlled by soil moisture, plays an important role in determining δD_{wax} values, and this significant evaporation signal is recorded by δD_{wax} values in surface soils.

Second, transpiration can drive D-enrichment in leaf water with increasing aridity (Yapp and Epstein, 1982; Leaney et al., 1985; Yakir et al., 1990), which has an additional critical effect on δD_{wax} values (Smith and Freeman, 2006; Feakins and Sessions, 2010). The apparent hydrogen isotopic fractionation between soil water and plant leaf wax ($\epsilon_{\text{wax/water}}$) depends on both environmental and biological factors (Sessions, 2006; Liu and Yang, 2008; Sachse et al., 2009; Yang et al., 2011). Since there is no shift in vegetation types in the GCh transect, $\epsilon_{\text{wax/water}}$ values could reflect variation in the leaf water transpiration. As shown in Fig. 5, $\epsilon_{\text{wax/water}}$ values showed a significant negative correlation with SWC ($R^2=0.8245$), and a greater $\epsilon_{\text{wax/water}}$ values from plant (less hydrogen isotopic fractionation between plant leaf wax and source water) resulted

from more transpirational D-enrichment in leaf water (Sachse et al., 2009). Theoretically, a site with lower SWC provides a drier growing environment for plants, and the changes in SWC reflect significant changes in moisture around plants growing on the soils in the two transects. Decreasing SWC therefore leads to increasing $\epsilon_{\text{wax/water}}$ values through transpirational D-enrichment in leaf water, and the transpiration signal will be recorded by δD_{wax} values together with evaporation. A study of the model predictions revealed that evaporation and transpiration were highly sensitive to change in aridity, especially in an arid area, thus important information about aridity was recorded by δD_{wax} values (Smith and Freeman, 2006). Both the climate chamber experiment and the observational study along climate gradient in northern Australia also provided strong evidences on the significant effect of evapotranspirational D-enrichment on δD_{wax} values (Kahmen et al., 2013a, b).

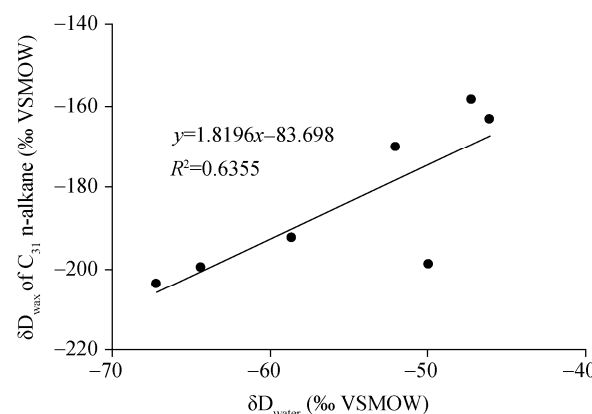


Fig. 4 Correlation between δD_{wax} values of C_{31} n-alkane in surface soils and δD_{water} values in the arid areas of the GCh and GH transects

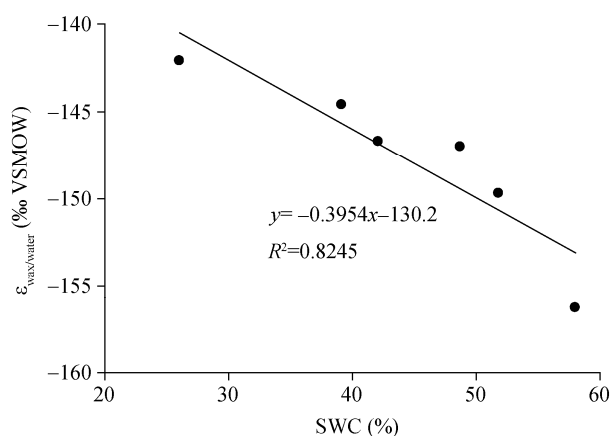


Fig. 5 Correlation between $\epsilon_{\text{wax/water}}$ values and SWC in the GCh transect

The slope of the relationship between $\epsilon_{\text{wax/water}}$ values and SWC in the GCh transect (-0.3954 ; Fig. 5) was larger than that between δD_{water} values and SWC in the arid areas of the GCh and GH transects (-0.6129 ; Fig. 2c), suggesting that soil water evaporation is more sensitive to soil moisture than leaf water transpiration for grasses. This result further demonstrated that evaporation is more important than transpiration in determining the δD_{wax} values, which is consistent with the finding from McInerney et al. (2011), who found that soil evaporation correlating with humidity affected δD_{wax} values rather than leaf transpiration for C_3 and C_4 shallow-rooted grasses. By contrast, deep-rooted shrubs and trees from an arid ecosystem in southern California did not show significant evaporative D-enrichment in soil water by comparing stem water and precipitation; instead, transpiration signal was recorded by δD_{wax} values (Feakins and Sessions, 2010). The contradicting results may be attributed to the distinct physiological characteristics of different plant life forms.

A significant difference in δD_{wax} values was also observed among different vegetation types (Liu et al., 2006a; Hou et al., 2007a), which may be attributed to the different physiological characteristics, such as leaf stomatal conductance (Pedentchouk et al., 2008), venation pattern (Helliker and Ehleringer, 2000) and hydraulic system (Hou et al., 2007b). Hou et al. (2008) found that the effect of humidity on evapotranspirational D-enrichment in leaf water was partially countered by the opposing influence of vegetation changes. McInerney et al. (2011) also suggested that plant physiology had a higher effect on δD_{wax} values than evapotranspiration for grasses. In the GH transect, the $\epsilon_{\text{wax/water}}$ values were weakly negatively correlated with SWC ($R^2=0.2555$; Fig. 6), potentially because the enhanced transpirational D-enrichment in leaf water with increasing aridity was hindered by the influence of shifts in vegetation types. Therefore, a vegetation type may be a more important factor in determining δD_{wax} value compared with transpiration.

In summary, although there was the shift in vegetation types in the arid area of the GH transect with increasing aridity, the δD_{wax} values in surface soils can still respond to soil moisture because the moisture exerted a primary control on δD_{water} values which determined the δD_{wax} values in surface soils in our study.

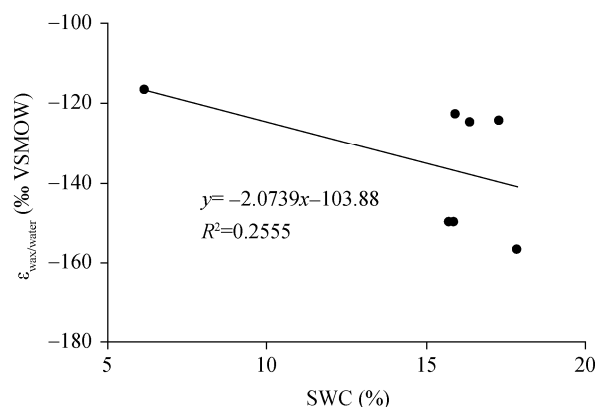


Fig. 6 Correlation between $\epsilon_{\text{wax/water}}$ values and SWC in the GH transect

2.3 Implication for paleo-humidity variation

Previous studies found that δD_{wax} values can reconstruct paleo-humidity in different sedimentary archives (Liu and Huang, 2005; Schefuß et al., 2005; Wang et al., 2013b). A record of δD_{wax} values from a loess profile spanning the last 130 ka on the Chinese Loess Plateau showed that the changes in δD_{wax} values were strongly consistent with changes in aridity (Liu and Huang, 2005). In a 20-ka record of δD_{wax} values from a marine sediment core close to the Congo River, the δD_{wax} values were explained to be indicating wetter (more negative δD_{wax} values) or drier (more positive δD_{wax} values) conditions (Schefuß et al., 2005).

Lake Qinghai or Lake Gahai sediments, ideal vehicle for paleoenvironmental research, generally integrated both environmental and ecological information over geological timescales. During the periods of drought, the drier climate resulted in higher δD_{wax} values partly due to enhanced evapotranspirational D-enrichment in leaf water (Liu and Huang, 2005). In addition, the shifts in vegetation types were controlled by the changes in humidity on the northeast Qinghai-Tibetan Plateau (Herzschuh et al., 2009). Chenopodiaceae shrubs were more abundant during drier periods than wetter periods on the northeast Qinghai-Tibetan Plateau (Zhao et al., 2008) and had higher δD_{wax} values than grasses (Liu et al., 2006a; Hou et al., 2007a). Thus a drier climate resulted in higher δD_{wax} values while a wetter climate resulted in lower δD_{wax} values due to the combined effects of shifts in vegetation types (grasses and shrubs) controlled by humidity and evapotranspiration. Wang et al. (2013b) suggested that δD_{wax} values from the

sediment profile were mainly controlled by vegetation types (grasses and shrubs) which depended on moisture, and they also reconstructed regional changes in moisture in 1,700 years on the northeast Qinghai-Tibetan Plateau. In our study, evaporative D-enrichment in soil water controlled by moisture was identified as the primary control on the δD_{wax} values rather than the shifts in vegetation types (grasses and shrubs) in the arid areas of the GCh and GH transects. In conclusion, we suggested that δD_{wax} values can be used as a paleo-humidity indicator although the shifts in vegetation types (grasses and shrubs) ever existed on the northeast Qinghai-Tibetan Plateau.

3 Conclusions

From the investigation of δD_{water} and δD_{wax} values in surface soils along two distance transects extending from the lakeshore to wetland to dryland around Lake Qinghai and Lake Gahai, we found that δD_{water} values were negatively correlated with SWC, and were sensitive to soil moisture in the arid areas of the GCh and GH transects. The δD_{wax} values in surface soils were also negatively correlated with SWC in the arid areas of the GCh and GH transects, indicating that the δD_{wax} values can respond to the changes in soil moisture in our study.

A significant positive relationship between δD_{water} values and δD_{wax} values in surface soils was observed, suggesting that evaporative D-enrichment in soil water was the primary control on the δD_{wax} values. The additional transpirational D-enrichment in leaf water likewise showed a strong negative correlation with SWC, and this signal can be recorded by δD_{wax} values together with evaporation as a result of changes in soil moisture. We suggested that the δD_{wax} values of lake sediments on the northeast Qinghai-Tibetan Plateau where shifts in vegetation types (grasses and shrubs) ever existed can be used as a paleo-humidity indicator.

Acknowledgements

This research was supported by the National Basic Research Program of China (2013CB955901) and the National Natural Science Foundation of China (41073018). We thank HuanYe WANG and YuXin HE for their help with sample collection. We are very grateful to Zheng WANG and YunNing CAO for their help with GC and GC-TC-IRMS analyses. We also appreciate two anonymous reviewers and the editors for their helpful comments.

References

- Aichner B, Herzsuh U, Wilkes H, et al. 2010. δD values of n-alkanes in Tibetan lake sediments and aquatic macrophytes: A surface sediment study and application to a 16 ka record from Lake Koucha. *Organic Geochemistry*, 41: 779–790.
- Allison G B. 1982. The relationship between ^{18}O and deuterium in water in sand columns undergoing evaporation. *Journal of Hydrology*, 55: 163–169.
- An Z S, Porter S C, Kutzbach J E, et al. 2000. Asynchronous Holocene optimum of the East Asian monsoon. *Quaternary Science Reviews*, 19: 743–762.
- Barnes C J, Allison G B. 1983. The distribution of deuterium and ^{18}O in dry soil: 1. Theory. *Journal of Hydrology*, 60: 141–156.
- Bi X H, Sheng G Y, Liu X H, et al. 2005. Molecular and carbon and hydrogen isotopic composition of n-alkanes in plant leaf waxes. *Organic Geochemistry*, 36: 1405–1417.
- Chikaraishi Y, Naraoka H. 2007. $\delta^{13}\text{C}$ and δD relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. *Organic Geochemistry*, 38: 198–215.
- Duan Y, Xu L. 2012. Distributions of n-alkanes and their hydrogen isotopic composition in plants from Lake Qinghai (China) and the surrounding area. *Applied Geochemistry*, 27: 806–814.
- Feakins S J, Sessions A L. 2010. Controls on the D/H ratios of plant leaf waxes in an arid ecosystem. *Geochimica et Cosmochimica Acta*, 74: 2128–2141.
- Helliker B R, Ehleringer J R. 2000. Establishing a grassland signature in the veins: ^{18}O in the leaf water of C_3 and C_4 grasses. *Proceedings of the National Academy of Sciences of the United States of America*, 97: 7894–7898.
- Henderson A C G, Holmes J A, Zhang J W, et al. 2003. A carbon and oxygen-isotope record of recent environment change from Lake Qinghai, NE Tibetan Plateau. *Chinese Science Bulletin*, 48: 1463–1468.
- Herzsuh U, Kramer A, Mischke S, et al. 2009. Quantitative climate and vegetation trends since the late glacial on the northeastern Tibetan Plateau deduced from Koucha Lake pollen spectra. *Quaternary Research*, 71: 162–171.
- Hou J Z, D'Andrea W J, MacDonald D, et al. 2007a. Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). *Organic Geochemistry*, 38: 977–984.
- Hou J Z, D'Andrea W J, MacDonald D, et al. 2007b. Evidence for water use efficiency as an important factor in determining the δD values of tree leaf waxes. *Organic Geochemistry*, 38: 1251–1255.
- Hou J Z, D'Andrea W J, Huang Y S. 2008. Can sedimentary leaf waxes record D/H ratios of continental precipitation? Field, model, and experimental assessments. *Geochimica et Cosmochimica Acta*, 72: 3503–3517.
- Kahmen A, Schefuß E, Sachse D. 2013a. Leaf water deuterium enrichment shapes leaf wax n-alkane δD values of angiosperm plants I: Experimental evidence and mechanistic insights. *Geochimica et Cosmochimica Acta*, 111: 39–49.
- Kahmen A, Hoffmann B, Schefuß E, et al. 2013b. Leaf water deuterium enrichment shapes leaf wax n-alkane δD values of angiosperm plants

- II: Observational evidence and global implications. *Geochimica et Cosmochimica Acta*, 111: 50–63.
- Leaney F W, Osmond C B, Allison G B, et al. 1985. Hydrogen-isotope composition of leaf water in C_3 and C_4 plants: its relationship to the hydrogen-isotope composition of dry matter. *Planta*, 164: 215–220.
- Liu W G, Huang Y S. 2005. Compound specific D/H ratios and molecular distributions of higher plant leaf waxes as novel paleoenvironmental indicators in the Chinese Loess Plateau. *Organic Geochemistry*, 36: 851–860.
- Liu W G, Yang H, Li L W. 2006a. Hydrogen isotopic compositions of n-alkanes from terrestrial plants correlate with their ecological life forms. *Oecologia*, 150: 330–338.
- Liu W G, Yang H. 2008. Multiple controls for the variability of hydrogen isotopic compositions in higher plant n-alkanes from modern ecosystems. *Global Change Biology*, 14: 2166–2177.
- Liu W G, Liu Z H, Fu M Y, et al. 2008. Distribution of the C_{37} tetra-unsaturated alkenone in Lake Qinghai, China: a potential lake salinity indicator. *Geochimica et Cosmochimica Acta*, 72: 988–997.
- Liu Z H, Henderson A C G, Huang Y S. 2006b. Alkenone-based reconstruction of late-Holocene surface temperature and salinity changes in Lake Qinghai, China. *Geophysical Research Letters*, 33, L09707. doi: 10.1029/2006GL026151.
- McInerney F A, Helliker B R, Freeman K H. 2011. Hydrogen isotope ratios of leaf wax n-alkanes in grasses are insensitive to transpiration. *Geochimica et Cosmochimica Acta*, 75: 541–554.
- Mügler I, Sachse D, Werner M, et al. 2008. Effect of lake evaporation on δD values of lacustrine n-alkanes: A comparison of Nam Co (Tibetan Plateau) and Holzmaar (Germany). *Organic Geochemistry*, 39: 711–729.
- Pedentchouk N, Sumner W, Tipple B, et al. 2008. $\delta^{13}C$ and δD compositions of n-alkanes from modern angiosperms and conifers: An experimental set up in central Washington State, USA. *Organic Geochemistry*, 39: 1066–1071.
- Polissar P J, Freeman K H. 2010. Effects of aridity and vegetation on plant-wax δD in modern lake sediments. *Geochimica et Cosmochimica Acta*, 74: 5785–5797.
- 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.
- Sachse D, Kahmen A, Gleixner G. 2009. Significant seasonal variation in the hydrogen isotopic composition of leaf-wax lipids for two deciduous tree ecosystems (*Fagus sylvatica* and *Acer pseudoplatanus*). *Organic Geochemistry*, 40: 732–742.
- Sachse D, Gleixner G, Wilkes H, et al. 2010. Leaf wax n-alkane δD values of field-grown barley reflect leaf water δD values at the time of leaf formation. *Geochimica et Cosmochimica Acta*, 74: 6741–6750.
- Sachse D, Billault I, Bowen G J, et al. 2012. Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annual Review of Earth and Planetary Sciences*, 40: 221–249.
- Schefuß E, Schputen S, Schneider R R. 2005. Climatic controls on central African hydrology during the past 20,000 years. *Nature*, 437: 1003–1006.
- Sessions A L. 2006. Seasonal changes in D/H fractionation accompanying lipid biosynthesis in *Spartina alterniflora*. *Geochimica et Cosmochimica Acta*, 70: 2153–2162.
- 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.
- Tang K L, Feng X H. 2001. The effect of soil hydrology on the oxygen and hydrogen isotopic compositions of plants' source water. *Earth and Planetary Science Letters*, 185: 355–367.
- Tipple B J, Pagani M. 2013. Environmental control on eastern broadleaf forest species' leaf wax distributions and D/H ratios. *Geochimica et Cosmochimica Acta*, 111: 64–77.
- Wang S M, Dou H S. 1998. Chinese Lake. Beijing: Science Press, 493–494.
- Wang Y V, Larsen T, Leduc G, et al. 2013a. What does leaf wax δD from a mixed C_3/C_4 vegetation region tell us? *Geochimica et Cosmochimica Acta*, 111: 128–139.
- Wang Z, Liu W G, Liu Z H, et al. 2013b. A 1700-year n-alkanes hydrogen isotope record of moisture changes in sediments from Lake Sugan in the Qaidam Basin, northeastern Tibetan Plateau. *The Holocene*, doi: 10.1177/0959683613486941.
- Xia Z H, Xu B Q, Mügler I, et al. 2008. Hydrogen isotope ratios of terrigenous n-alkanes in lacustrine surface sediment of the Tibetan Plateau record the precipitation signal. *Geochemical Journal*, 42: 331–338.
- Yakir D, Deniro M J, Gat J R. 1990. Natural deuterium and O-18 enrichment in leaf water of cotton plants grown under wet and dry condition: evidence for water compartmentation and its dynamics. *Plant, Cell & Environment*, 13: 49–56.
- Yang H, Leng Q. 2009. Molecular hydrogen isotope analysis of living and fossil plants: Metasequoia as an example. *Progress in Natural Science*, 19: 901–912.
- Yang H, Liu W G, Leng Q, et al. 2011. Variation in n-alkanes δD values from terrestrial plants at high latitude: Implications for paleoclimate reconstruction. *Organic Geochemistry*, 42: 283–288.
- Yapp C J, Epstein S. 1982. A reexamination of cellulose carbon-bound hydrogen δD measurements and some factors affecting plant-water D/H relationships. *Geochimica et Cosmochimica Acta*, 46: 955–965.
- Zhang P, Liu W G. 2011. Effect of plant life form on relationship between δD values of leaf wax n-alkanes and altitude along Mount Taibai, China. *Organic Geochemistry*, 42: 100–107.
- Zhao Y, Yu Z C, Chen F H, et al. 2008. Sensitive response of desert vegetation to moisture change based on a near-annual resolution pollen record from Gahai Lake in the Qaidam Basin, northwest China. *Global and Planetary Change*, 62: 107–114.