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Hydrogen isotopic compositions of long-chain leaf wax *n*-alkanes in Lake Qinghai sediments record palaeohydrological variations during the past 12 ka

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ABSTRACT

Lake Qinghai, the largest saltwater lake in China, is located on the northeastern Qinghai-Tibetan Plateau. The lake sediments record the climatic variation and response to global climate change on the plateau. Numerous studies of the lake have been conducted, but various opinions remain regarding the palaeoclimatic conditions for the lake since the Last Glacial Maximum, especially the palaeohydrological conditions for the northeastern plateau in the early Holocene. Here, we discuss the hydrogen isotopic composition (δD) of long-chain leaf wax *n*-alkanes for studying the hydrological changes in the lake since the Holocene. The results show that, on the northeastern Qinghai-Tibetan Plateau, C_{31} δD values were quite negative (avg. −202 ± 4‰) in the early Holocene (8–12 ka), indicating a strong monsoon and greater precipitation during that period. During 8–4 ka, C_{31} δD values gradually became more positive, indicating that the monsoon gradually weakened and precipitation gradually decreased. The C_{31} δD values were more positive in the late Holocene, with a mean value of −186 ± 3‰, showing that the regional monsoon weakened and the amount of precipitation was low. In addition, C_{31} δD values indicated large amounts of precipitation in the early Holocene, but the C_{29} δD values during the same period were significantly more positive than C_{31} due to a large contribution from aquatic plants. Therefore, the water level of the lake was low in this period, which could be related to strong evaporation of the lake water because of the high temperature in the early Holocene. Our study clarifies the changes in the monsoon and precipitation in the northeastern Qinghai-Tibetan Plateau and it provides a new estimate of the water level variation in Lake Qinghai in the early Holocene.

1. Introduction

The Qinghai-Tibetan Plateau is the highest plateau in the world and it is sensitive to the Asian monsoon and global environmental change (An et al., 2000). In past decades, a number of studies of palaeoenvironmental changes in the area have been conducted (e.g. An et al., 2001; Currie et al., 2005; DeCelles et al., 2007; Polissar et al., 2009; Henderson et al., 2010; Wischnewski et al., 2011; He et al., 2013; Zhuang et al., 2014). Numerous lakes are present on the plateau, and their sediments contain records of the hydrology and vegetation changes in the catchment. Climate change information can be extracted from the lake sediments due to their characteristics of continuous deposition, high deposition rate, high resolution and abundant information (Zhang and Wang, 1999). Lake Qinghai is the largest on the Qinghai-Tibetan Plateau and it is influenced by westerlies and the Asian monsoon (An et al., 2012). Such large lakes are influenced not only by catchment climate signals but also by regional climate changes and are therefore excellent archives for preserving palaeoclimatic information (Henderson and Holmes, 2009). Hence, the lake has attracted a large amount of palaeoenvironmental research.

Palaeoclimatic studies of Lake Qinghai have demonstrated that the monsoon was strong and the precipitation was high in the early Holocene and that the monsoon gradually weakened and the precipitation decreased during the mid- to late Holocene (e.g., Shen et al., 2005; Liu et al., 2007, 2014; An et al., 2012; Jin et al., 2015). The monsoon was stronger in the early Holocene, and temperature and precipitation were also higher in the same period. Studies have

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suggested a high water level in Lake Qinghai in the early Holocene (e.g., Thomas et al., 2016), but other studies have demonstrated that the lake had a low water level during this period (e.g., Zhang et al., 1994; Yu and Kelts, 2002; Liu et al., 2013, 2015; Li and Liu, 2014; Wang et al., 2014; Chen et al., 2016). Therefore, it was necessary to clarify the early Holocene climatic and hydrological conditions from Lake Qinghai records.

n-alkanes can be well preserved in environmental media, forming a reliable record of climate change (Sessions et al., 2004; Sachse et al., 2006; Eglinton and Eglinton, 2008). The *n*-alkane δD values of terrestrial plants record the variation in meteoric water δD values (Sachse et al., 2006; Liu and Yang, 2008; Rao et al., 2009; Xie et al., 2012; Feakins et al., 2016), and the *n*-alkane δD values of aquatic plants record lake water δD values (Duan and Xu, 2012; Duan et al., 2014; Liu et al., 2016). Therefore, δD values have been widely used for palaeohydrological reconstruction of Qinghai-Tibetan Plateau lakes, such as Lake Kala Kule (Aichner et al., 2015), Lake Sugan (Wang et al., 2013), Lake Hurleg (He et al., 2016), Lake Genggahai (Rao et al., 2016), Paru Co (Bird et al., 2014), Dagze Co (Li et al., 2015), Nam Co (Mügler et al., 2010; Günther et al., 2015) and Tangra Yumco (Günther et al., 2016). However, for Lake Qinghai, few Holocene δD records have been reported, and only the δD values of long chain alkanoic acids have been analysed. Namely, Thomas et al. (2016) analysed the δD values of C_{28} alkanoic acids in the sediments of the lake since ca. 30 ka to evaluate the changes in the main moisture sources in the region. Hence, it was necessary to analyse the *n*-alkane δD values in the sediments of the lake during the Holocene. Lacustrine sediment *n*-alkanes often have multiple sources, including terrestrial plants, aquatic plants and lower organisms (Gao et al., 2011; Rao et al., 2014), and recent studies have indicated that aquatic plants have a large contribution to the long chain *n*-alkanes in the lake sediments (Aichner et al., 2010a; Liu et al., 2015, 2016; Liu and Liu, 2016). For example, Liu et al. (2015, 2016) found that there are a large number of submerged plants distributed in shallow lake areas and that the long chain *n*-alkanes produced by these plants had a significant influence on the C_{27} and C_{29} *n*-alkanes in lake sediments. In contrast, C_{31} was found to be derived mainly from terrestrial plants (Liu et al., 2015, 2016). Therefore, the δD values of individual long chain *n*-alkanes in a core from Lake Qinghai can reflect changes in different plant types and in the δD values of their water sources.

We analysed the hydrogen isotopic composition of C_{29} and C_{31} over the past 12 ka in the 1F core from Lake Qinghai. The purpose was to provide evidence for the palaeohydrological changes during the Holocene in the lake area and to further analyse the water level variation in Lake Qinghai during the early Holocene. The results also provide a basis for detailed understanding of applying compound specific *n*-alkanes for palaeoclimatic reconstruction in the Lake Qinghai region and the northeastern Qinghai-Tibetan Plateau.

2. Study site

Lake Qinghai (36°32′–37°15′N, 99°36′–100°47′E) is the largest inland brackish lake in China and has an average elevation of 3194 m. It covers an area of ca. 4400 km^2, has a maximum water depth of 27 m, an average water depth of 21 m, and it is surrounded by mountains, such as Datongshan, Riyueshan and Nanshan (Liu et al., 2011). The average regional annual temperature is 1.2 °C, with high temperatures of 10.4–15.2 °C in July (Jin et al., 2010), and the mean annual precipitation is ca. 400 mm, which is concentrated from June to September. The annual average evaporation is ca. 800 mm, which greatly exceeds the amount of precipitation (Colman et al., 2007). The lake has an average salinity of 14.1 g/l and water supplied mainly by the Buha, Heima and Shaliu Rivers. Several small lakes (e.g., Lake Gahai, Lake Erhai and Haiyan Bay) formed in the vicinity of Lake Qinghai as the lake level decreased (Liu et al., 2008). Among these satellite lakes, Lake Erhai is a freshwater lake owing to the inflow of the Daotang River, and Lake Gahai contains higher salinity than Lake Qinghai due to limited freshwater sources (Liu et al., 2008, 2009). The terrestrial vegetation in the Lake Qinghai catchment is mainly mountainous shrubs and alpine meadows (Colman et al., 2007), most of which are C_3 plants (Liu et al., 2015). For aquatic plants in the lake, the shallow areas (<10 m) are dominated mainly by *Potamogeton L.* and *Ruppia L.*, while the deep areas are covered mainly by *Cladophora* (Liu et al., 2013, 2015).

3. Material and methods

3.1. Material

The 1F core from Lake Qinghai was drilled in 2005 (Fig. 1) using the ICDP GLAD800 drilling system with the support of the International Continental Drilling Programme (ICDP). The age model for the core was based on accelerator mass spectrometry (AMS) ^{14}C dates, including 52 bulk (total organic carbon, TOC), 6 Ruppiaceae seeds, and 7 plant residue samples (An et al., 2012; Zhou et al., 2014). The core covers the climate change history since the Last Glacial Maximum, and the uppermost 5.0 m are composed mainly of silty clay or clays with horizontal bedding, and they have a high content of carbonate (40–60%) and TOC (avg. 4.6%; An et al., 2012). The subsamples from the upper 5.15 m, covering ca. 12 ka (An et al., 2012), were analysed here. The core was sampled at 1 cm intervals, and subsamples of the sediment were taken at 5 cm intervals for hydrogen isotopic analysis.

3.2. Methods

The samples were freeze-dried in the laboratory. Dried sediment (ca. 2–3 g) was extracted with dichloromethane (DCM) and methanol (MeOH) (9:1, v/v). The extracts were dried under N_2 in a water bath. The saturated hydrocarbon fraction was isolated using silica column chromatography (100–200 mesh) via hexane elution.

Quantification was performed using an Agilent 6890 gas chromatography (GC) instrument (Agilent HP-1ms column: 60 m × 0.32 mm i.d., 0.25 μm film thickness) and flame ionization detection, based on previous studies (Liu et al., 2006; 2015). Briefly, the sample was injected in split mode, with the GC inlet at 310 °C and a flow rate of 1.2 ml/min. The oven temperature was initially 40 °C (1 min) and increased to 150 °C at 10°C/min and then to 315 °C (held 20 min) at 6 °C/min. Individual *n*-alkane peak areas were compared with external standards with known amounts of individual *n*-alkanes.

The hydrogen isotopic composition of individual *n*-alkanes was determined using a Delta-V isotope ratio mass spectrometry (IRMS) instrument (Thermo Finnigan). The *n*-alkanes were converted to H via a high-temperature pyrolysis reactor at 1430 °C. The H^3+ factor was calculated daily using the same H_2 reference gas. Mixed laboratory standards of *n*-alkanes (C_{21}, C_{25}, C_{27}, C_{29}, C_{31}, and C_{33}) were measured after every five injections, and the standard deviation of the δD values for the *n*-alkane standards was generally <3‰ (Cao et al., 2012; Liu et al., 2012). All reported δD values (‰) are relative to Vienna Standard Mean Ocean Water (VSMOW).

The *Paq* index, a proxy for evaluating the contribution of *n*-alkanes from submerged/floating aquatic plants relative to emergent and terrestrial plants (Ficken et al., 2000), was calculated as follows:

$$Paq = (C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31}).$$