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Molecular Paleoclimate Reconstructions over the Last 9 ka from a Peat Sequence in South China

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Abstract

To achieve a better understanding of Holocene climate change in the monsoon regions of China, we investigated the molecular distributions and carbon and hydrogen isotope compositions (δ¹³C and δD values) of long-chain n-alkanes in a peat core from the Shiwanqutian (SWGT) peatland, south China over the last 9 ka. By comparisons with other climate records, we found that the δ¹³C values of the long-chain n-alkanes can be a proxy for humidity, while the δD values of the long-chain n-alkanes primarily recorded the moisture source δD signal during 9–1.8 ka BP and responded to the dry climate during 1.8–0.3 ka BP. Together with the average chain length (ACL) and the carbon preference index (CPI) data, the climate evolution over last 9 ka in the SWGT peatland can be divided into three stages. During the first stage (9–5 ka BP), the δ¹³C values were depleted and CPI and Pₐ values were low, while ACL values were high. They reveal a period of warm and wet climate, which is regarded as the Holocene optimum. The second stage (5–1.8 ka BP) witnessed a shift to relatively cool and dry climate, as indicated by the more positive δ¹³C values and lower ACL values. During the third stage (1.8–0.3 ka BP), the δ¹³C, δD, CPI and Pₐ values showed marked increase and ACL values varied greatly, implying an abrupt change to cold and dry conditions. This climate pattern corresponds to the broad decline in Asian monsoon intensity through the latter part of the Holocene. Our results do not support a later Holocene optimum in south China as suggested by previous studies.

Introduction

The Asian monsoon is one of the key components of the global climate system. Monsoon climates, and particularly the summer monsoon-derived rainfall, are crucial to terrestrial ecosystems and human societies in the East Asia [1]. A clear understanding of past changes in monsoonal climate and their drivers, especially during the Holocene, which is closely linked to
human evolution and development, is essential to understand how the terrestrial ecosystems respond to the present climate changes and to predict their future adaptations.

Numerous attempts have been made to explore the evolution of Holocene climate in monsoonal China, however, they display different scenarios. Some studies argued that the Holocene optimum was asynchronous among monsoon regions in China [1,2]. In contrast, some other researches did not support a time-transgressive Holocene optimum in China. For an example, Shi et al. (1992) [3] concluded that the Holocene optimum in China occurred from 8.5 to 3 ka BP. Zhou et al. (2007) [4] reckoned that that the Holocene optimum appeared almost synchronous around 10–5 ka BP across the monsoon regions of China. Similarly, Zhang et al. (2011) [5] suggested that the Holocene climate changes were broadly synchronous across the monsoon regions with Holocene optimum occurring during 10.5–6.5 ka BP. Therefore, more records generated from different sedimentary settings and based on various proxies are needed. Such records, on one hand, can help us draw an overall picture of the climate changes in one certain area; on the other hand, can enable us to make spatial comparisons of the Holocene climate in monsoonal China based on similar archives and proxies, eliminating uncertain factors brought by different archives and proxies.

Over the last two decades, biomarkers have been widely applied in the reconstructions of the paleoenvironmental and paleoclimatic conditions. In particular, n-alkanes have attracted fervent attention, due to their ubiquity, relative ease of extraction and purification from sediments and stronger resistance to microbial degradation [6]. They are increasingly employed as powerful proxies in paleoenvironmental research, especially through the application of compound-specific carbon and hydrogen ratios (e.g. [7–9]). A combination of n-alkane δ13C and δD analyses has been proven to be able to yield particularly useful information on vegetation and hydroclimate (e.g. [10–12]).

Peat deposits are ideal archives for molecular paleoclimate reconstructions in late Quaternary, due to their good capacity to preserve organic matter, successive sedimentation and sensitivity to hydrological oscillations [13,14]. Such deposits consist mainly of organic material, so that molecular paleoclimate proxies, in particular those derived from lipid biomarkers and their compound-specific isotope ratios, are suitable to extract paleoclimatic information [13,14]. Chinese peat deposits from the Holocene have received more and more attention in molecular paleoclimate studies over the last decade. Researchers have investigated peat deposits in northeast China [15–18], southwest China [19–22], central China [23–26], and south China [27, 28] with lipid biomarker approaches. However, studies of n-alkane δ13C and δD values in peat from south China are relatively few.

Here, we reported a molecular paleoclimate record from the Shiwangutian (SWGT) peatland, a previously unstudied peatland in south China. In this study, we investigated the distributions and δ13C and δD values of long-chain n-alkanes from the SWGT peat core over the last 9 ka. The n-alkane records were compared with pollen record from nearby Daping Swamp (~30 km away) [29], n-alkane δD record from Hongyuan peat sequence, southwest China (~1000 km away) [19], stalagmite δ18O (δ18O_carb) record from Dongge Cave situated about 300 km to the southwest [30] and fatty alcohol record from the Dajiuhu peatland, central China (~600 km away) [24] to decipher the paleoclimatic significance of long-chain n-alkane δ13C and δD values and further to assess the paleoclimate changes for the last 9 ka in the SWGT peatland, south China, which can provide new evidence on the climate evolution during the Holocene.

Materials and Methods

Studying site

The SWGT peatland is located in the Chengbu Miao Autonomous County of Hunan Province, bordering the Ziyuan County of Guangxi Zhuang Autonomous Region. This region is affected
by both the East Asian monsoon and Indian monsoon and is featured by a subtropical cool and humid mountain climate. The annual average temperature of this area is 13°C and the annual average precipitation is about 1800 mm [31]. The modern vegetation in this site is dominated by Sphagnum spp. and sedges, together with some bamboo species [31].

Ethics Statement

All necessary permits were obtained for the described field work and were granted by the Administration of Shiwangutian Wetland Nature Reserve of Chengbu County. The field work did not involve endangered or protected species.

Sampling

A 1.4 m long peat core (26°05.20′ N, 110°21.98′ E; 1688 m above sea level) was retrieved in July 2012. Lithology of the SWGT peat core consists of an upper plant debris layer (0–20 cm), a black peat layer (20–128 cm) and a basal white-gray clay layer (128–140 cm) (Fig 1). Peat samples were collected at 2 cm interval. Samples for lipid analyses were from the upper 30–128 cm in this study.

Chronology of the SWGT peat core is based on AMS 14C dating of bulk peat. Calibrated age ranges were obtained using the Calib 7.0 software [32]. The age model is based on linear interpolation of paired calibrated ages.

Lipid extraction and analyses

The freeze-dried peat samples were ground and sieved through a 60-mesh sieve (mesh aperture 0.3 mm). About 1.0 g peat was ultrasonically extracted 6×10 min with dichloromethane/methanol (DCM/MeOH) (9:1, v/v) after adding a mixture of internal standards (androstane, androstanol and cholanic acid). After solvent removal under reduced pressure, the extracts were fractionated into aliphatic, aromatic and polar fractions using silica gel column chromatography with hexane, hexane/DCM (1:1, v/v), DCM/MeOH (1:1, v/v) as the respective elution solvents.

Gas chromatography–mass spectrometry (GC-MS) analysis of the aliphatic fractions was performed on a Hewlett Packard 6890 gas chromatograph interfaced with a Hewlett Packard 5973 mass selective detector in the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences. The chromatograph was equipped with a DB-5 column (30 m×0.25 mm, film thickness 0.25 μm). The oven temperature was programmed from 70°C (held 1 min) and then ramped to 210°C at 10°C min⁻¹ and further increased to 300°C at 3°C min⁻¹ (held 25 min). The identification of n-alkanes was achieved by a combination of GC retention times relative to standards and a mass spectrum library (NIST 08).

The quantification of the aliphatic fractions was performed on a Shimadzu GC 2010 equipped with a flame ionization detector (FID) and a DB-5 column (30 m×0.25 mm, film thickness 0.25 μm) in the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences. The temperature program was identical to that of GC-MS. The absolute abundances were obtained by comparisons of peak areas with those of internal standards and adjusted with the relevant response factors.

Compound-specific hydrogen and carbon isotope analyses

The δ13C values of long-chain n-alkanes were measured on a Finnigan Trace GC coupled to a Finnigan Delta XP isotope ratio mass spectrometer (GC-IRMS) in the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences. Samples were
injected in splitless mode (1 μl), with the injector temperature at 300°C. Separation was achieved by a DB-5MS column (60 m×0.25 mm i.d., film thickness 0.25 μm). The GC oven temperature was initiated at 50°C (held 1 min) and then ramped to 210°C at 10°C/min (held 2 min) and further raised to 300°C at 4°C/min (held 2 min) and finally increased to 310°C at 10°C/min (held 25.5 min). Helium was used as the carrier gas (1.0 ml/min). Instrument performance was checked every four runs using an n-alkane mixture with known δ¹³C values obtained from Arndt Schimmelmann (Indiana University, U.S.A.). Reproducibility for specific compounds was better than 0.5‰ (standard deviation), based on at least duplicate analyses. Results were reported in the δ notation (‰) relative to the Vienna Peedee Belemnite (VPDB) standard.

δD analyses of long-chain n-alkanes were achieved using Trace GC coupled with a Delta V advantage isotope ratio mass spectrometer in the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences. Samples were injected in splitless mode (1 μl), with the injector temperature at 300°C. The GC oven temperature was programmed from 50°C (held 1 min) to 210°C at 10°C/min (held 2 min) and then to 300°C at 6°C/min (held 2 min) and finally to 310°C at 10°C/min (held 25 min). The high temperature conversion (HTC) system was operated at 1400°C and the HTC tube was conditioned with methane. H³⁺ factor was monitored daily, through the measurement period, its values varied around 3.7 and
4.2. To check the system stability, an \( n \)-alkane mixture (\( n \)-C\(_{23}\), \( n \)-C\(_{25}\), \( n \)-C\(_{27}\), \( n \)-C\(_{29}\) and \( n \)-C\(_{31}\) alkane) and the Indiana A4 mixture with known \( \delta D \) values were run between every two samples. Squalane (\( \delta D = 167 \%) \) was used as the internal standard. Reproducibility for specific compounds was better than 5\%, based on at least duplicate analyses. All \( \delta D \) values are reported in the \( \delta \) notation \( (\%) \) relative to the Vienna Standard Mean Ocean Water (VSMOW) standard.

Calculations and statistics

The new time series of \( \delta^{18}O_{\text{carb}} \) record from Dongge Cave were obtained by Matlab R2011b software (The MathWorks Inc., U.S.A.) through cubic spline interpolation method, sharing a common time vector with \( n \)-C\(_{29}\) \( \delta D (\delta D_{C29}) \) record from the SWGT peatland. The correlation analysis between \( \delta D_{C29} \) record from the SWGT peatland and new time series of \( \delta^{18}O_{\text{carb}} \) record from Dongge Cave was performed with SPSS 16.0 software (International Business Machines Co., U.S.A.).

Results

Chronology

Radiocarbon dating results are listed in Table 1 and also shown in Fig 1. Based on the age-model, peaty sediment of the 128–30 cm represents the period from 9 to 0.3 ka BP (Table 1; Fig 1). Generally, the interval from 9 to 2 ka BP displayed much lower sedimentation rates than the period from 2 to 0.3 ka BP (Fig 1).

\( n \)-Alkane distributions

In all peat samples, \( n \)-C\(_{23-33}\) alkanes were present with a strong odd over even predominance (Fig 2), which is indicative of a predominant contribution of higher plants to the peat [33]. The \( n \)-C\(_{25}\) alkane was the most abundant homologue, followed by the \( n \)-C\(_{31}\) alkane (Fig 2). On average, \( n \)-C\(_{29}\) and \( n \)-C\(_{31}\) alkanes accounted for around 40% and 20% of the total \( n \)-alkane concentrations, respectively (Fig 2).

The ACL values of long-chain \( n \)-alkanes fluctuated slightly from 29.1 to 29.3 during 9–5 ka BP (Fig 3). Values remained around 29.0 from 5 to 1.8 ka BP. After that, the ACL values varied dramatically between 28.7 and 29.3 (Fig 3). The CPI values of long-chain \( n \)-alkanes varied between 4.1 and 4.6 from 9 to 1.8 ka BP (Fig 3). They began to increase at 1.8 ka BP and remained around 5.5 afterwards (Fig 3). \( P_{aq} \) values kept relatively low between 0.04 and 0.08

Table 1. Results of the \( ^{14}C \) AMS dating from the SWGT peat core, southern China.

| Sample name | Test organization       | AMS code | Depth (cm) | \( ^{14}C \) (yr BP) | Calibrated age (cal. yr BP) |
|-------------|------------------------|----------|------------|----------------------|-----------------------------|
| GT-4-16     | Beta Analytic, Inc.    | 440017   | 31         | 260 ± 30             | 150–430                     |
| GT-4-25     | Arizona AMS Laboratory | AA99846  | 49         | 1130±40              | 960–1170                    |
| GT-4-35     | Beta Analytic, Inc.    | 341149   | 69         | 1810±30              | 1630–1820                   |
| GT-4-42     | Beta Analytic, Inc.    | 430609   | 83         | 2030±30              | 1900–2100                   |
| GT-4-50     | Arizona AMS Laboratory | AA99847  | 99         | 4130±40              | 4530–4820                   |
| GT-4-55     | Beta Analytic, Inc.    | 341150   | 109        | 6180±30              | 6990–7170                   |
| GT-4-60     | Beta Analytic, Inc.    | 341151   | 119        | 7220±40              | 7960–8160                   |
| GT-4-64     | Arizona AMS Laboratory | AA99848  | 127        | 8070±40              | 8780–9112                   |

All dates shown were obtained from bulk peat using a \( ^{14}C \) accelerator mass spectrometer. Calibrated age ranges were obtained using the Calib 7.0 software with 2\( \sigma \) error intervals [32].

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during 9–1.8 ka BP (Fig 3). They started to increase at 1.8 ka BP and finally reached the peak of 0.2 at 0.3 ka BP (Fig 3).

**Compound-specific carbon and hydrogen isotope compositions of n-alkanes**

The \( \delta^{13}C \) and \( \delta D \) values of \( n-C_{27}, n-C_{29}, n-C_{31} \) alkanes were determined. Due to the relatively low concentrations, some data are not available in the \( n-C_{27} \) and \( n-C_{31} \) alkane isotope records. \( n-C_{27}, n-C_{29} \) and \( n-C_{31} \) alkane \( \delta^{13}C \) (\( \delta^{13}C_{C_{27}}, \delta^{13}C_{C_{29}} \) and \( \delta^{13}C_{C_{31}} \), respectively) values ranged between -36.0‰ and -33.3‰, -35.7‰ and -33.8‰ and -36.7‰ and -34.5‰, respectively, with \( \delta^{13}C_{C_{31}} \) values generally more depleted than \( \delta^{13}C_{C_{27}} \) and \( \delta^{13}C_{C_{29}} \) values (Fig 3). Over the last 9 ka, \( \delta^{13}C_{C_{29}} \) values showed a stronger correlation with \( \delta^{13}C_{C_{27}} \) values (correlation coefficient \( r = 0.93, p < 0.05 \)) than with \( \delta^{13}C_{C_{31}} \) values (\( r = 0.79, p < 0.05 \)).

\( n-C_{27}, n-C_{29} \) and \( n-C_{31} \) alkane \( \delta D \) values (\( \delta D_{C_{27}}, \delta D_{C_{29}} \) and \( \delta D_{C_{31}} \), respectively) varied between -238‰ and -191‰, -241‰ and -191‰ and -226‰ and -186‰, respectively and showed similar covariances (\( r = 0.90, p < 0.05 \)) among each other (Fig 3). Notably, \( \delta D_{C_{31}} \) values were enriched in D relative to \( \delta D_{C_{27}} \) and \( \delta D_{C_{29}} \) values until around 1.8 ka BP (Fig 3). Our study mainly focuses on the isotope compositions of \( n-C_{29} \) alkane as the more concentrated compound may generate a more robust signal during \( \delta^{13}C \) and \( \delta D \) measurements.

In detail, the \( \delta^{13}C_{C_{29}} \) values varied between -35.6‰ and -35.0‰ during 9–5 ka BP (Fig 4). They showed slightly more positive values between -34.7‰ and -35.7‰ during 5–1.8 ka BP (Fig 4). After 1.8 ka BP, \( \delta^{13}C_{C_{29}} \) values exhibited a more positive trend with an amplitude up to 2‰ (Fig 4). \( \delta D_{C_{29}} \) values displayed an overall increasing trend from 9 to 1.8 ka BP with values ranging between -241‰ and -206‰ (Fig 4). \( \delta D_{C_{29}} \) values showed a remarkable increase from -225‰ to -195‰ around 1.8 ka BP (Fig 4). After that, they fluctuated around -200‰ (Fig 4).

**Discussion**

**Interpretations of the n-alkane proxies**

ACL. The ACL values describe the average number of carbon atoms based on the concentrations of long-chain n-alkane homologues [34]. Though humidity and plant types may also
influence \( n \)-alkane ACL values [35, 36], numerous studies explain the variations of \( n \)-alkane ACL values from the perspective of temperature, with larger ACL values indicative of warmer climates and vice versa (e.g. [34, 37–40]). Such an interpretation has been validated in the Dahu peat sequence, south China [28].

\textbf{CPI.} \( n \)-Alkane CPI values express the predominance of odd-numbered over even-numbered \( n \)-alkanes [41]. Higher plants normally have CPI values \( >4 \). \( n \)-Alkanes from bacteria and algae show CPI values around 1 [42, 43]. Degraded or matured organic matter is also
Fig 4. Comparisons of records. (a) Mass accumulation rate of hopanoids in the Dajiuhu peatland [26]. (b) BNA$_{15}$ record from the Dajiuhu peatland [24]. (c) $\delta^{18}$O$_{carb}$ record from Dongge Cave [30]. (d) $\delta^{13}$C$_{C_{31}}$ record from the Hongyuan peat sequence [19]. (e) Ratios of total herb pollen over total tree pollen from the Daping sedimentary sequence [29]. (f) $\delta^{13}$C$_{C_{29}}$ record (this study) and (g) $\delta^{13}$C$_{C_{29}}$ record (this study).

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characterized by low CPI values, due to microbial reworking and cracking, respectively. These processes enable a paleoclimatic interpretation of the CPI under certain conditions. For example, if microbial reworking of peat is suppressed under cold and dry conditions, higher CPI values will be preserved in sediments [6, 44].

P_{aq} Ficken et al. (2000) [45] proposed the P_{aq} index \((C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31})\) n-alkanes to reflect the relative contributions of aquatic macrophytes and terrestrial plants to lake sediments. As Sphagnum species have n-alkane distributions similar to those of aquatic macrophytes [46–48], Nichols et al. (2006) [49] proposed this proxy to reflect the relative abundance of Sphagnum over other bog-forming plants in boreal peatlands. In the SWGT peat core, the P_{aq} values are always < 0.2, which excludes the possibility that Sphagnum species are an important contributor to n-alkanes preserved in this core. During the interval of 1.8–0.3 ka, the increased trend of P_{aq} values suggests that the contribution from Sphagnum species rises a little during this interval. In present, Sphagnum species and vascular species dominate in the SWGT peatland.

δ^{13}C values of long-chain n-alkanes. Sedimentary plant wax δ^{13}C values are often used to determine relative contributions of plants with different photosynthetic pathway, i.e. C_{3} and C_{4} plants [50, 51]. The CO_{2} fixation pathways used by most terrestrial plants yield distinct n-alkane δ^{13}C values, which range from -28‰ to -40‰ in C_{3} plants and -17‰ to -25‰ in C_{4} plants [50, 51]. Peatlands are waterlogged conditions, which do not favor the growth of C_{4} plants. In the SWGT peat core, the δ^{13}C signatures of long chain n-alkanes revealed an overwhelming predominance of C_{3} plants. In addition, the consistent patterns of n-alkanes in the whole core do not support that vegetation changes played an important factor on the fluctuations of n-alkane δ^{13}C values in SWGT. Previous studies have demonstrated that δ^{13}C values from peat organic matter in the monsoon regions of China can be an indicator of regional relative humidity (RH) [5, 16, 52]. Under relatively dry conditions, peat-forming vascular plants can close their stomata to reduce leaf evapotranspiration and prevent the excessive loss of water. This will also make less CO_{2} enter into the leaves through the stomata, which will lead to weaker discrimination against^{13}CO_{2} and result in less depleted δ^{13}C values [53, 54]. As such, we interpret n-alkane δ^{13}C values from SWGT peatland as a proxy for RH, with more positive δ^{13}C values under dry climate.

δD values of long-chain n-alkanes. Globally, sedimentary plant wax δD values reliably track the precipitation δD values [55]. In addition, soil water evaporation and leaf transpiration can modify the primary signal, especially in arid environments [56, 57]. Furthermore, biosynthetic fractionation between source water and plant wax varies greatly among different life forms [57] and is not necessarily constant even for the same plant species [58]. Because the magnitudes of these influencing factors in different environments are not well constrained, the interpretation of leaf wax δD values often depends on site specific conditions. On the other hand, sedimentary accumulations of plant waxes tend to average and smoothen these effects which take place on the level of individual plants, enabling the use of plant wax δD records as robust paleohydrological records [55].

During 9 to 1.8 ka BP, the δD_{C29} values exhibited a general more positive trend in the SWGT peat core, which is coherent with the δD_{C31} record from the Hongyuan peat core in southwest China [19] (Fig 4). Furthermore, our δD_{C29} record and δ^{18}O_{carb} record from the nearby Dongge Cave [30] showed a significant correlation during this period \((r = 0.76, p < 0.05)\) (Fig 5) indicating a common driver of variability. Stalagmite δ^{18}O records in China are thought to primarily reflect isotope composition of the moisture source [59]. Therefore, the δD_{C29} values in our record are considered to primarily record moisture source δD signals, which is in agreement with the previous studies in other localities in the monsoonal region of China [19, 60]. Due to the close proximity of these two records and their apparent similarity,
we can assume that both sites received moisture from the same source. This allows us to evaluate moisture source $\delta D$ and $\delta^{18}O$ values in concert. During the period from 9.0 and 1.8 ka, the regression function of $\delta D_{C29}$ and $\delta^{18}O_{carb}$ values showed a slope of 9.3, which is slightly steeper than the slope of the modern regional meteoric water line ($\delta D = 8.9 \times \delta^{18}O + 15.5$) in the nearby Guilin City (~100 km away) [61]. This may result from the potential effect of evapotranspiration on the $\delta D$ values of leaf wax $n$-alkanes (which would not act upon stalagmite $\delta^{18}O$ values).

However, during the period from 1.8 to 0.3 ka BP, the correlation between $\delta D_{C29}$ values and $\delta^{18}O_{carb}$ values was absent (Fig 5), with values falling above the regression line from the previous period (Fig 4). This may arise from an enhanced influence of evapotranspiration on leaf wax $\delta D$ signatures [57] in drier conditions. Besides, an influence of vegetation changes on $\delta D$ values is reflected by the similar $\delta D_{C27}$, $\delta D_{C29}$ and $\delta D_{C31}$ values during this interval, which are not observed during 9–1.8 ka BP (Fig 4). This vegetation effect is also suggested by $P_{aq}$ values, which imply an increasing input of *Sphagnum* during this interval. *Sphagnum* tends to take up the surface water while the vascular plants make use of deeper water through root system. Therefore, the $n$-alkane $\delta D$ values of *sphagnum* may be more positive than those of vascular plants growing on the same site [62]. Another possibility is a change to more arid/warm moisture source.

**Paleoclimate changes in SWGT over the last 9 ka**

Based on our new biomarker and stable isotope records from the SWGT peat core, the climate evolution over the last 9 ka can be divided into three stages.

During the first stage (9–5 ka BP), more negative $\delta^{13}C_{C29}$ values reveal a wet condition (Fig 4). Higher ACL values agree with the higher temperatures in the Dajiuhu record, central China [24] (Figs 3 and 4). Lower CPI values imply wet and warm climate (Fig 3). Quite low $P_{aq}$ values may be indicative of little contribution from *Sphagnum* (Fig 3). Together, they reveal that this period is featured by warm and wet climate. Such a period of higher temperature and
precipitation broadly coincides with the Holocene optimum reported from the pollen data from the nearby Daping Swamp (8.2–4.6 ka BP; [29, 63]), and the Dahu peat deposit (26°46′N, 119°02′E; 1007 m a.s.l.) (~9–6 ka BP; [28]), and Gantang peat (31°29′N, 109°59′E; 1750 m a.s.l.) (8.2–4 ka BP; [64]). Also, our results do not support the deduction that the Holocene optimum occurred at ~3 ka in south China [1].

During the second stage (5–1.8 ka BP), the less negative δ13CC29 values imply a shift to a drier climate (Fig 4). CPI and \( P_{aq} \) values showed few changes (Fig 3). The decreased ACL values followed the pattern of temperature changes in Dajiuhu [24], suggesting lower temperatures (Figs 3 and 4). We consider the climate during this stage as relatively cool and dry. This is supported by the pollen record from the Daping Swamp, which suggests a shift to cool and dry climate at 4.5 ka BP [29, 63] (Fig 4). A decrease in moisture during this period has been widely reported in various areas in China, India and Africa and has been considered as a crucial cause of widespread cultural collapse in low-latitude regions [9, 65–68].

After 1.8 ka BP, both \( \delta D_{C29} \) and \( \delta^{13}C_{C29} \) values showed marked positive excursions, probably linked with dry climate (Fig 4). The ACL values on average displayed lower values, agreeing with the lower temperatures in Dajiuhu [24] (Figs 3 and 4). The CPI values increased greatly, which is indicative of cold and dry climate (Fig 3). The higher \( P_{aq} \) values suggest more contribution from Sphagnum due to the cool or/wet condition (Fig 3). Together, they indicate an abrupt change to colder and drier climate from 1.8 ka BP onwards. The bulk dry density in the nearby Daping peat deposit recorded an abrupt decrease at 1.7 ka [63]. Calcite oxygen isotope composition from Dongge Cave stalagmite DA inferred a weak monsoon interval centered at 1.6 ka [69]. Such a sudden change to dry climate has also been reported from Lake Huguangyan [70]. However, we cannot rule out the possible influence from human activity on the environmental change around 1.8 ka BP, as agriculture developed rapidly in southern China from approximately 2 ka BP to present [67, 71]. Besides, the influence from root percolation on the upper peat layer is possible.

Comparing with the first and second stages, the interval between 1.8 and 0.3 ka has a much higher sedimentation rate (Fig 1). The alkane proxies deduced cooler and drier climate during 1.8–0.3 ka would constrain microbial degradation and facilitate organic matter accumulation. In addition, the vegetation types would also have an influence on the degradation. Sphagnum species generally have a slow decay rate than vascular peat-forming plants [72]. It is puzzling that alkane proxies particularly ACL and \( P_{aq} \) show remarkable fluctuations during 1.8–0.3 ka. Future work is required to testify the possible causes for such a large and frequent change of alkane ratios in this peat core under a drier and cooler climate during 1.8–0.3 ka.

Our record reveals a warm and wet period from 9 to 5 ka BP, followed by a transition of a relatively cool and dry condition from 5 to 1.8 ka BP, and turned to cold and dry condition from 1.8 ka BP onwards. This climate pattern corresponds to the broad decline in Asian Monsoon intensity through the latter part of the Holocene, which is linked with the orbitally induced lowering of Northern Hemisphere summer solar insolation and the associated southward migration of the mean position of Intertropical Convergence Zone [73, 74]. Our results do not support the assertion that the Holocene optimum occurred around 3 ka BP in south China [1].

**Conclusions**

We analyzed the distributions and the \( \delta^{13}C \) and \( \delta D \) values of long-chain \( n \)-alkanes in a peat core from the SWGT peatland, south China over the last 9 ka. With these alkane ratios, climate evolution during the last 9 ka in the SWGT peatland can be divided into three stages. The first stage (9–5 ka BP) was warm and wet, which is regarded as the Holocene optimum. The second
stage (5–1.8 ka BP) witnessed a shift to relatively cool and dry climate. During the third stage (1.8–0.3 ka BP), an abrupt change to drier and colder condition occurred. This climate pattern corresponds to the broad decline in Asian Monsoon intensity through the latter part of the Holocene. Our results do not support the assertion that the Holocene optimum occurred later in south China.

Supporting Information
S1 Table. Total concentrations (μg/g) and ACL, CPI and $P_{aq}$ values of $n$-alkanes in the Shiwangutian peat core.

S2 Table. δ$^{13}$C values of $n$-alkanes in the Shiwangutian peat core.

S3 Table. δD values of $n$-alkanes in the Shiwangutian peat core.

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Author Contributions
Conceived and designed the experiments: XW XH.
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