

## Carbon Isotope Composition and Geochemical Features of Sediments From Gongga Mountain, China, and Potential Environmental Implications

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Wu Y, Wang T, Liu Y, Ma R and Chen Z (2022) Carbon Isotope Composition and Geochemical Features of Sediments From Gongga Mountain, China, and Potential Environmental Implications. Front. Earth Sci. 10:865575. doi: 10.3389/feart.2022.865575 Using gas chromatography-triple guadrupole tandem mass spectrometry (GC-MS/MS). the soluble organic matter was analyzed for the first time in twenty-two sediment samples from the eastern slopes of the Gongga Mountain, China, at high altitudes between 4,600 and 6,700 m. The C11-C33 n-alkanes and C9-C33 n-alkan-2-ones were identified in these samples. Both compounds were dominated by odd carbon numbers in the long-chain molecules and contained a maximum of n-C<sub>27</sub> or n-C<sub>29</sub>, indicating that the sediments were predominantly of higher plant origin. However, the short-chain n-alkan-2-ones, with a maximum content of n-C17 or i-C18 (phytone, 6, 10, 14-trimethylpentadecan-2-one), did not show a predominance of odd and even numbers, suggesting that they were predominantly derived from bacteria and algae. Therefore, we suggest that the organic matter in Gongga Mountain comes from three sources, i.e. bacteria, algae, and higher plants. Stable carbon isotope ( $\delta^{13}$ C) values ranged from -24.6‰ to -27.3‰, indicating that C<sub>3</sub> plants were the dominant organic input to the sediments and suggesting a relatively colder and drier depositional environment. However, C<sub>4</sub> plants increase sharply at high altitudes of 6,300-6,600 m, suggesting that the paleoclimate of Gongga Mountain became drier and wetter with the increase of altitude.

Keywords: n-alkanes, n-alkan-2-ones, geochemical features, carbon isotope composition, Gongga Mountain

### INTRODUCTION

*N*-alkanes and *n*-alkan-2-ones are abundant in almost all plants and can account for more than 60% of the epidermal lipids. Both of these organic compounds are relatively resistant to degradation after plant decay (Poynter and Eglinton, 1991). These components can show signals of their presence in the sediments (Jansen et al., 2008). Thus, the *n*-alkanes and *n*-alkan-2-ones can be particularly useful as biomarkers for understanding the source of organic matter, and for tracking ecosystem changes and reconstructing palaeo-vegetation (Nichols and Huang., 2007; Andreou and Rapsomanikis 2009; Badewien et al., 2015; Li G. et al., 2018). For example, some indexes of long-chain *n*-alkanes reflect the relative proportion of lower organisms such as bacteria, algae, and higher plants (Crausbay et al., 2014; Wang et al., 2014; Bush and McInerney 2015; Howard et al., 2018). These indexes include the *n*-alkane average chain length (ACL), the ratios of trees to grasses ( $n-C_{29}/n-C_{31}$ ), the ratios of  $\sum n-C_{21-}/\sum n-C_{21+}$  in *n*-alkanes and a carbon preference index (CPI). In addition, the organic carbon

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isotope values ( $\delta^{13}$ C) can be used to estimate the relative contributions of C<sub>3</sub> and C<sub>4</sub> plants, infer paleoclimate changes, and to examine past primary productivity (France-Lanord and Derry 1994). Consequently, we analyzed the biomarkers and the organic carbon isotope values ( $\delta^{13}$ C) of surface sedimens along an elevation transect on the eastern slope of Gongga Mountain, ranging in elevation from 4,600 m to 6,700 m.

Some soil biomarkers may be useful tools for palaeovegetation reconstruction (Didyk et al., 1978; Bai et al., 2020). And while some relevant biomarker studies have previously been done on low elevation soil samples from the Gongga Mountains (Jia et al., 2008; Bezabih et al., 2011; Bai et al., 2011; 2020), the studies on high elevation sediment samples are currently lacking. The reason for this may be due to the fact that sampling becomes much more difficult as the altitude increases. Our study aimed to identify and understand the geochemical characteristics of highaltitude ecosystems in the Gongga Mountain and to reconstruct the local palaeo-vegetatio and track ecosystem changes by measuring the carbon isotope composition and lipid biomarkers in the sediments. Furthermore, in this study, we used lipid biomarkers and  $\delta^{13}$ C analyses to determine how the lipid biomarkers and carbon isotopes can be used to delineate the source of organic matter and related processes.

## SAMPLING AREA, SAMPLES AND METHODS

### Sampling Area and Samples

Gongga Mountain, is the highest peak (7,556 m a.s.l) in the Hengduan Mountains. It is located approximately 30°N and 102°E in the middle and southern section of the Big Snow Mountain Range and on the southeastern edge of the Tibetan Plateau in Sichuan Province, southwest China. It is a unique mountain in western China because it contains both modern low-latitude glacial features and an integrated vertical vegetation distribution ranging from subtropical forests to tundra. Compared with other mountain ranges in China, before the Gongga Mountain, the Gongga Mountain range still has an extensive area of primary coniferous and deciduous forests to an elevation of 4,000 m. With a vertical range of more than 6,300 m along only 11 km of horizontal distance, the eastward slope drops towards the Sichuan Basin in southwestern China. The mean annual temperature is 4°C. The annual rainfall is approximately 1938 mm, and 85% of the rainfall falls during May to October, according to the meteorological station located 3,000 m above sea level (a.s.l) (Alpine Ecosystem Observation and Experiment Station of Gongga Mountain, Chinese Academic of Sciences). The regional climate is characterized by typical monsoon patterns of temperature, precipitation, and evaporation. This region is influenced by both the Pacific and the Indian Ocean meteorological systems, which bring southeasterly and southwesterly monsoons, respectively. There are many special characteristics of the mountain ecosystem and environment in the Gongga Mountain Region, including tropical and subtropical cold-loving plant species (Luo et al., 2015). The hottest months occur well within the rainy season, from May to September, while evaporation peaks during the



sunny, pre-monsoon months (Thomas 1997, 1999). The eastern slope of Gongga Mountain, which is the transitional zone of the first and second step in China, has disparate plant ecosystems at different elevations (Thomas 1999; Zhong et al., 1999). Gongga Mountain is therefore an area with very high biodiversity: approximately 2,500 plant species belonging to 869 genera and 185 families have been identified in this region (Thomas 1999). However, the plant species at high elevations (above the snowline) have not been reported. As a result, selected study area is 4,600-6,700 m above sea level in a typical ecosystem of Gongga Mountain east of the Tibetan Plateau (Figure 1). In June 2012, 22 surface sediment samples (5-10 cm above ground level) were collected from the eastern slope of the Gongga Mountain by removing the layers of snow, ice and litter. The samples were collected over a period of 2 weeks. The altitude of each sampling site was determined by using a GPS unit with an error of  $\pm 10$  m. Samples at each location were taken from three sub-samples that were evenly mixed and bagged. These three sampling locations were collected randomly within an approximate 10 m radius using an electric drill and metal shovel. All samples were wet, and each of them was tightly sealed on site in polyethylene zipper bags. The first bag was sealed in a second, "outer," zipper bag to insure against possible damage and leakage. Bagged samples were frozen immediately after transit to the laboratory.

### **Analytical Methods**

All sediment samples were dried at room temperature and crushed to 100 mesh. Powders were kept frozen at about  $-18^{\circ}$ C until analysis. An aliquot (~250 g) of each sample was Soxhlet-extracted with a mixture of dichloromethane-methanol (93:7, v/v) for 72 h, and then the extracts were separated into saturate, aromatic and polar fractions by a glass chromatographic column packed with activated silica gel and eluted by solvents of increasing polarity. The details of the extraction and separation have been published elsewhere (Wu et al., 2016). The fractions obtained were analyzed using the full scan and the selected ion monitoring (SIM) modes.

TABLE 1   Results of TOC/δ <sup>13</sup> C(‰)	analysis and	d calculated	parameters (	сf
samples at Gongga Mountain.				

Sample#	Altitude (m)	TOC (%)	δ <sup>13</sup> C(‰) (Das)		
GGS-1	6,700	2.57	-25.2		
GGS-2	6,600	2.13	-24.6		
GGS-3	6,500	2.30	-24.4		
GGS-4	6,400	2.08	-24.7		
GGS-5	6,300	3.05	-24.7		
GGS-6	6,200	3.11	-25.1		
GGS-7	6,100	1.34	-25.4		
GGS-8	6,000	2.57	-25.0		
GGS-9	5,900	2.06	-25.2		
GGS-10	5,800	1.46	-24.8		
GGS-11	5,700	2.65	-25.4		
GGS-12	5,600	3.23	-25.8		
GGS-13	5,500	3.35	-26.2		
GGS-14	5,400	3.85	-25.5		
GGS-15	5,300	4.59	-26.1		
GGS-16	5,200	3.91	-26.4		
GGS-17	5,100	5.21	-26.0		
GGS-18	5,000	2.68	-25.8		
GGS-19	4,900	2.87	-25.9		
GGS-20	4,800	3.59	-25.1		
GGS-21	4,700	3.30	-27.3		
GGS-22	4,600	3.77	-26.1		

TOC, total organic carbon.

A GC-MS/MS analysis was performed using a Hewlett-Packard 7890 gas chromatograph (GC) coupled to a Hewlett-Packard 7000B mass selective detector (MSD). The GC was fitted with a HP-5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$ , Agilent, United States), based on a previous study (Wu et al., 2016). The oven temperature was initially 80°C (1 min) and was then increased to 290°C at a rate of 4°C/min and finally held at this temperature for 30 min. Helium was used as the carrier gas at a linear velocity of 28 cm/s, with a GC inlet temperature of 300°C and the injector operating at a flow rate of 0.9 ml/min. The MSD was operated with an ionization energy of 70 eV and a source temperature of 230°C. Data were collected in full-scan mode and scanned from 10 to 550 amu.

Organic carbon isotope analyses are carried out at Oil and Gas Research Center, Northwest Institute of Eco-Environment and Resources (Chinese Academy of Sciences). Firstly, dilute hydrochloric acid was added to sediment sample to remove inorganic carbon, and then the decarbonated and dried sediment sample was analyzed using a Thermo Fisher MAT 253-Flash2000 mass spectrometer. Calibration measurements were performed using a standard reference IAEA-600 ( $\delta^{13}C = -27.77\%$ ), with calculated standard deviations of less than 0.2% per 6 measurements resulting in  $\delta^{13}$ Corg (Coplen et al., 2006).

### RESULTS

## Total Organic Carbon Content and Its Isotopes

The TOC contents of the samples range from 1.34 to 5.21% with an average value of 2.99% (**Table 1**). In addition, the TOC content showed a systematic variation with elevation, peaking in sediments from an elevation of 5,100 m (**Table 1**). The  $\delta^{13}$ C values range from -24.4‰ to -27.3‰ (**Table 1**), indicating that C<sub>3</sub> plants were dominant along the eastern slope of Gongga Mountain (Wei et al., 2015).

## Distribution of Aliphatic Hydrocarbons and Alkanones

The distributions of *n*-alkanes and *n*-alkan-2-ones were measured by mass chromatography of the fragment ions m/z 85 (Figure 2) and m/z 58 (Figure 3). These compounds were identified by comparison of measured mass spectral data and retention indices to published data (George and Jardine 1994; Wu et al., 2012). The aliphatic hydrocarbon fraction consists mainly of *n*-alkanes and isoprenoid alkanes (pristane (Pr) and phytane (Ph)). Straight-chain alkanes are the most abundant hydrocarbons in the extracts (Figure 2). The *n*-alkanes are in the C<sub>11</sub> to C<sub>33</sub> range, with peaks of *n*-C<sub>27</sub> or *n*-C<sub>29</sub>, and the sediment samples studied show a uni-modal characteristic distribution. The odd over even carbon number predominance  $(OEP_{27})$  is significantly greater than 1.0 for all samples, ranging from 3.29 to 6.27. The carbon preference index (CPI<sub>25-31</sub>) ranges from 3.33 to 6.49, and the average chain length (ACL) ranges from 27.37 to 28.33. In samples from elevations of 4,700 m, 5,400 m, 5,800 m, 5,900 m, 6,600 m, and 6,700 m, the Pr content is higher than the Ph content, and the Pr/Ph ratios range from 1.09 to 1.51. However, in other samples, the Ph content is slightly higher than the Pr content, and the Pr/Ph ratios range from 0.66 to 0.94 (Table 2 and Figure 4).

The *n*-alkan-2-ones range from  $C_9$  to  $C_{33}$  and are characterized by bi-modal distributions with a higher relative abundance of the higher-molecular-weight (HMW) homologues, dominated by  $C_{27}$  or  $C_{29}$ , and lower amount of short chain *n*-Alkan-2-ones, dominated by *n*- $C_{17}$  or *i*- $C_{18}$  (phytone, 6,10,14-trimethylpentadecan-2-one). The short chain components show no strong odd/even carbon number preference; however, the long chain components range from *n*- $C_{23}$  to *n*- $C_{33}$ , with a strong odd/even preference.

### DISCUSSIONS

## Vegetation Composition of the Study Area and Depositional Conditions

The  $\delta^{13}$ C values of TOC in soils and sediments reflect the changes of C<sub>4</sub>/C<sub>3</sub> plant input ratios (France-Lanord and Derry 1994; Cayet and Lichtfouse, 2001; Badewien et al., 2015). Typically, C<sub>3</sub> plants have  $\delta^{13}$ C values ranging from -20% to -32%, whereas C<sub>4</sub> plants have  $\delta^{13}$ C values from -9% to -17% (Denies, 1980; Farquhar et al., 1989; Sukumar et al., 1993; Lim et al., 2010; Sun et al., 2012). Yang, (2012) suggested that lower temperature and reduced summer precipitation favoured C<sub>3</sub> over C<sub>4</sub> plant, i.e. C<sub>3</sub> plants dominated in cooler and drier conditions, whereas C<sub>4</sub> plants favoured warmer and wetter climates. To investigate the paleoclimates and paleoenvironments on the east side of the Tibetan Plateau, Southwest China, the  $\delta^{13}$ C values of the organic matter in sediments were determined for the sediments along the



eastern slope of Gongga Mountain. As shown in Table 1 and Figure 4, these values range from -24.6% to -27.4%; the loweraltitude sediments had lower  $\delta^{13}$ C values, while sediments from 6,300–6,600 m had higher  $\delta^{13}$ C values of -24.7‰, -24.7‰, -24.4‰ and -24.6‰, respectively. These results indicate that C<sub>3</sub> plants were likely important contributors to organic compounds in the sediments. Therefore, in general, the climate was probably cold and dry along the eastern slope of Gongga Mountain. The results also showed that the loweraltitude sediments had lower  $\delta^{13}$ C values, suggesting that the more terrigenous C3 plants dominated at lower altitudes. In addition, the  $\delta^{13}$ C values of organic matter in sediments tended to be positive with increasing altitude. From this phenomenon, we speculated whether some amount of C<sub>4</sub> plants could have been present. If C4 plants are present, then a temporary warming and wetting of the palaeoclimate at 6,300-6,600 m may have occurred. (Sukumar et al., 1993; Liu et al., 2005; Xue et al., 2014). However, its cause needs to be further investigated.

The *n*-alkanes were dominated by n-C<sub>27</sub> or n-C<sub>29</sub> with a single peak distribution (**Figure 2**). OEP<sub>27</sub> was significantly greater than 1.0 for all samples (ranging between 3.29 and 6.27). Furthermore, at 4,600, 4,800, 5,200, and 5,500 m, the distribution of *n*-alkanes in the sediments showed a clear odd-numbered dominance, suggesting a dominant contribution from higher plants, but also a small input of algae (Lichtfous et al., 1994). In addition, no significant correlation was found between the Pr/Ph ratio and

altitude. In samples from elevations of 4,700, 5,400, 5,800, 5,900, 6,600 and 6,700 m, the Pr/Ph ratios range from 1.09 to 1.51, indicating weakly oxic depositional conditions. However, in other samples, the Ph content is slightly higher than the Pr content, and the Pr/Ph ratios range from 0.66 to 0.94 (**Table 2** and **Figure 4**). These results are indicative of a suboxic reductive environment (Hughes, Holba, and Dzou. 1995; Rontani et al., 2013).

# Relationship Between $\delta^{13}$ C Values and Altitude, Temperature and Humidity

The change in  $\delta^{13}$ C value of TOC varied between -24.6% and -27.3% from 4,700 m to 6,700 m above sea level on the eastern slope of Gongga Mountain (**Table 1**). Linear regression analysis showed that  $\delta^{13}$ C values of sediments were positively correlated with altitude (**Figure 5**). The changes in  $\delta^{13}$ C value and altitude were characterized by an abrupt fall from 4,600 to 4,700 m, followed by an abrupt increase at 4,800 m. Then, the values were rather stable between 4,900 m and 6,200 m, followed by an moderate increase from 6,300 m to 6,600 m (**Figure 4**, **5**).

The stable carbon isotope values ( $\delta^{13}$ C) of sediments in Gongga Mountain ranged from -24.6‰ to -27.3‰, indicating that C<sub>3</sub> plants were the main organic inputs to the sediments (Vogts et al., 2009). The increase in C<sub>3</sub> plants from low altitude to high altitude in Gongga Mountain was suggested to reflect the influence of decreasing temperature. Thus, the general trend showed a relatively drier and colder sedimentary environment



with the increase of altitude. However, there was a sharp increase of  $C_4$  plants from 4,700 m to 4,800 m, and a mild increase of  $C_4$  plants from 6,300 m to 6,600 m. This phenomenon reflected that there may be a temporary warming trend in the altitude range of 4,700 m to 4,800 m and 6,300 m to 6,600 m. The cause of this phenomenon need to be considered in future studies.

# Molecular Abundance, Distribution, Origin and Potential Significance of *n*-Alkanes

*n*-Alkanes are widely present in plants and other organisms. The source of organic matter can be traced through the distribution characteristics of n-alkanes because different biological sources of n-alkanes possess different distribution characteristics. Previous studies showed that *n*-alkanes from lower organisms range from  $n-C_{15}$  to  $n-C_{20}$ , often with  $n-C_{17}$  or  $n-C_{19}$  as the dominant compounds and without an obvious odd-over-even preference (Eglinton and Hamilton 1967). In contrast, long-chain n-alkanes are mostly derived from epicuticular waxes of leaves from vascular higher plants (Meyers 1997; Fang et al., 2014; Cortina et al., 2016). In addition, woody plants display n-alkane distributions dominated by C227 or C29 n-alkanes, whereas grasses produce distributions dominated by the C<sub>31</sub> n-alkane (Li et al., 2016). Hence, *n*-alkane distribution patterns can be used to estimate changes in vegetation types (Al-Aklabi et al., 2016). Modern organic geochemistry of molecules shows that the ratio  $\sum n-C_{21}/\sum n-C_{21}^+$  reflects the proportion of lower organisms, such as bacteria and algae relative to higher plants (Li G. et al., 2018). In this study, the *n*-alkane carbon numbers range from  $C_{11}$  to  $C_{33}$  with maxima at  $n-C_{23}$  to  $n-C_{31}$  (**Figure 2**) and exhibit a unimodal distribution. The main peaks of unimodal distribution are at  $n-C_{27}$  or  $n-C_{29}$ , and the long-chain *n*-alkanes had odd-carbon-number predominance, indicating that they were mainly derived from terrestrial higher plants. As shown in **Table 2**, the ratio  $\sum n-C_{21}/\sum n-C_{21}^+$  ranged from 0.07 to 0.29 (average 0.64), also suggesting that higher plants were the main source of organic matter to sediments at elevations from 4,600 m to 6,400 m.

The *n*-alkane CPI in sediment is also an indicator of the sources of organic matter (Collister et al., 1994; Routh et al., 2014). Hydrocarbons composed of a mixture of compounds originating from land plant material show a predominance of odd-numbered carbon chains with CPI = 5-10 (Eglinton and Hamilton 1967; Collister et al., 1994; Bi et al., 2005; Duan and Xu 2012), whereas anthropogenic and reworked materials have low CPIs of approximately 1.0 (Bray and Evans 1961; Mille et al., 2007). CPI values close to 1.0 are also thought to indicate a greater input from marine microorganisms and/or recycled organic matter (Bi et al., 2005). High-molecular-weight *n*-alkanes in these sediment samples range from *n*-C<sub>23</sub> to *n*-C<sub>33</sub>, with the most abundant being *n*-C<sub>27</sub> and *n*-C<sub>29</sub>. A clear predominance of odd-carbon-number compounds is exhibited, as indicated by the

Sample /	Altitude	<i>n</i> -Alkane				Isoperiod			<i>n</i> -alkan-one				
	(m)	CPI <sup>a</sup> 25-31	OEP <sup>b</sup> 27	C <sub>21-</sub> / C <sub>21+</sub>	C <sub>29</sub> / C <sub>31</sub>	ACL°	Pr/ Ph	Pr/ nC <sub>17</sub>	Ph/ nC <sub>18</sub>	CPI <sup>a</sup> 25-31	OEP <sup>b</sup> 27	C <sub>21-</sub> / C <sub>21+</sub>	C <sub>29</sub> / C <sub>31</sub>
GGS-1	6,700	4.87	4.67	0.13	4.34	27.69	1.51	0.55	0.34	2.86	3.35	0.12	1.47
GGS-2	6,600	5.07	4.93	0.18	4.04	27.76	1.17	0.48	0.51	3.04	3.63	0.13	1.51
GGS-3	6,500	4.86	4.80	0.16	3.55	27.73	0.67	0.48	0.63	2.89	3.43	0.16	1.42
GGS-4	6,400	5.44	5.03	0.21	3.93	27.86	0.92	0.47	0.45	3.10	3.91	0.20	1.42
GGS-5	6,300	5.34	5.32	0.15	4.17	27.67	0.96	0.42	0.45	2.78	3.40	0.15	1.53
GGS-6	6,200	5.99	5.51	0.10	3.80	27.83	0.84	0.40	0.44	3.07	3.80	0.10	1.49
GGS-7	6,100	3.33	3.29	0.16	4.16	27.37	0.92	0.43	0.51	2.99	3.74	0.25	1.88
GGS-8	6,000	5.37	5.19	0.07	5.52	27.75	0.82	0.49	0.56	3.31	4.15	0.13	1.52
GGS-9	5,900	5.60	5.60	0.06	4.94	27.69	1.55	0.75	0.56	3.15	3.76	0.08	1.51
GGS- 10	5,800	4.79	4.45	0.12	4.35	27.61	1.09	0.54	0.46	3.13	3.83	0.08	1.77
GGS- 11	5,700	4.23	3.80	0.29	3.16	27.64	0.96	0.44	0.50	3.18	4.26	0.22	1.70
GGS- 12	5,600	5.48	5.65	0.16	4.31	27.59	0.86	0.47	0.52	3.80	5.13	0.15	1.97
GGS- 13	5,500	6.23	6.27	0.10	3.26	27.87	0.85	0.65	0.59	3.34	4.11	0.10	1.63
GGS- 14	5,400	4.54	4.41	0.15	3.60	27.56	1.17	0.46	0.47	3.06	3.71	0.12	1.82
GGS- 15	5,300	6.45	6.05	0.16	2.85	28.05	0.68	0.39	0.51	3.68	4.27	0.13	1.61
GGS- 16	5,200	6.36	6.25	0.12	2.96	27.92	0.77	0.43	0.56	3.43	4.43	0.16	1.54
GGS- 17	5,100	5.52	5.28	0.15	2.65	27.80	0.94	0.42	0.48	3.48	4.39	0.12	1.88
GGS- 18	5,000	5.24	5.59	0.08	2.03	27.75	0.69	0.46	0.48	3.43	4.09	0.12	1.38
GGS- 19	4,900	5.45	5.58	0.13	4.30	27.59	0.66	0.45	0.67	3.35	4.13	0.14	1.40
GGS- 20	4,800	6.25	6.02	0.14	1.76	28.08	0.82	0.42	0.55	3.50	4.04	0.28	1.42
GGS- 21	4,700	5.46	4.96	0.10	2.27	28.14	1.15	0.50	0.65	3.47	4.00	0.28	1.42
GGS- 22	4,600	6.49	6.21	0.15	1.92	28.33	0.61	0.45	0.55	3.50	4.02	0.28	1.41

 ${}^{a}CPI_{25-31} = 0.5 \times [(C_{25} + C_{27} + C_{29} + C_{31})/(C_{24} + C_{26} + C_{28} + C_{30}) + (C_{25} + C_{27} + C_{29} + C_{31})/(C_{26} + C_{28} + C_{30} + C_{32})].$ 

 $^{b}OEP_{27} = (C_{27} + 6C_{29} + C_{31})/4(C_{28} + C_{30}).$ 

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

carbon preference index (CPI<sub>25-31</sub>: 3.33-6.49, average: 5.32; OEP<sub>27</sub>: 3.80-6.25, average: 5.22) (Table 2), typical of a terrestrial leaf wax and higher plant source. This strong oddover-even predominance indicates that the source of the *n*-alkanes in the sediments was terrestrial higher plants. On the other hand, the CPI values seem to be related to elevation. For instance, with the exception of sample GGS-7 (6,100 m), the CPI values from low elevation samples were higher than those samples from a high elevation. These results showed that the whole slope of Gongga Mountain was dominated by higher plants and with microbial footprints (Howard et al., 2018). Furthermore, as seen in Table 2, CPI values for samples from lower altitudes below 6,000 m ranged from 4.23 to 6.49 with an average of 5.56, indicating that n-alkanes are more often synthesized by higher plants, while CPI values for samples from higher altitudes above 6,000 m ranged from 3.33 to 5.99 with an average of 4.95, indicating that bacterial fingerprints increase with altitude.

Molecular organic geochemistry has also demonstrated that the  $n-C_{29}/n-C_{31}$  ratio of *n*-alkanes is indicative of the relative proportion of woody plants to grassy plants (Meyers 1997; Ficken et al., 2000; Li G. et al., 2018). The C<sub>29</sub> n-alkanes dominate the sediments and have little variability, indicating that trees dominated Gongga Mountain and that the climate was relatively stable. The ratio of the C<sub>29</sub> n-alkane to C<sub>31</sub> n-alkanes for all samples varied between 4.94 and 1.76, with a relatively wide range and smaller values at lower altitudes (Table 2), indicating a relatively warm and humid climate at lower altitudes. This is due to the fact that as the ratio of C<sub>29</sub>/C<sub>31</sub> becomes smaller, C<sub>31</sub>, which represents grassy plants, gradually increases, indicating that grassy plants multiply vigorously as they prefer a relatively warm and humid climate to grow in. In addition, a high ratio of these alkanes indicates a change from a humid to an arid climate. As shown in **Table 2**, the average ratio of  $n-C_{29}/n-C_{31}$ tends to be high (3.6 > 1) for all samples, indicating that the deposition of the top section between approximately 4,600 m to







6,700 m occurred under relatively continuous humid climate conditions.

Another useful parameter from the *n*-alkane distribution is the average chain length (ACL), which has been suggested to change with plant types. Woody plants display *n*-alkane distributions dominated by the  $C_{27}$  or  $C_{29}$  *n*-alkanes, whereas grasses have distributions dominated by the  $C_{31}$  *n*-alkane (Gamarra and Kahmen 2015; Li et al., 2016). The average ACL is 29.5 for grass, 28.4 for reeds and 27.9 for tree leaves (Duan and Xu 2012). Therefore, grasses usually have high ACL values relatively to those of trees. In our results, samples from elevations of 4,600, 4,700, 4,800, and 5,300 m had ACL values of 28.33, 28.14, 28.08 and 28.05, respectively, while samples from 4,900 m to 6,700 m had ACL values from 27.37 to 27.87 (**Table 2** and **Figure 6**), which are in the range of tree leaves (Duan and Xu, 2012).

indicating that woody plants were the main vegetation. In addition, a plot of  $ACL_{27-31}$  vs. altitude (**Figure 6**) showed that a quadratic relationship exists between these two variables, with lower  $ACL_{27-31}$  values occurring at mid altitudes and higher values occurring at low and high altitudes. The *n*-alkane  $ACL_{27-31}$  values reach a minimum in samples from 6,100 m, and the intermittent decrease in ACL in samples from 6,100 m may indicate a temporal increase in merged C<sub>4</sub> plants. These results also suggest that the region underwent a relatively cold and wet climate because plants in colder/wetter areas have lower  $ACL_{27-31}$  values than those in warmer/drier areas (Zhou et al., 2005; Bush and McInerney 2013). Furthermore, the *n*-alkane mean chain length  $ACL_{27-31}$  ratio gradually decreased and the *n*-alkane (C<sub>29</sub>/C<sub>31</sub>) ratio gradually increased as altitude increased from 4,600 m to 6,100 m (ACL<sub>27</sub>)

33: 27.37-28.33, average: 27.79 and C<sub>29</sub>/C<sub>31</sub>: 1.76-5.52, average: 3.54) (Table 2 and Figure 6), indicating an increase in woody plants, which produce a large proportion of the C<sub>27</sub> and C<sub>29</sub> n-alkanes. This pattern can be best explained in terms of vegetation; that is, woody plants dominate the paleosols, and grasses have less influences, especially near 6,000 m. The increase in the  $C_{29}/C_{31}$  ratio from 4.94 to 5.52 with some oscillations in samples from 5,900 to 6,000 m is possibly caused by a decrease in grasses, which produce large proportions of the C<sub>29</sub> n-alkane (Zhou et al., 2005). In contrast, the  $C_{29}$  *n*-alkanes dominate the sediments from 5,900 to 6,000 m and biomarkers vary with relatively greater amplitudes and at a higher frequency, indicating that woody plants were dominant and that relatively wetter conditions prevailed during these altitudes. This results in a slightly different conclusion than those drawn from other parameters: i.e., the climate became wetter and colder at 6,100 m. The explanation for this discrepancy needs to be further explored.

### Distribution Characteristics and Possible Source of *n*-Alkan-2-ones

*n*-Alkan-2-ones are commonly observed lipid components of sediments from Gongga Mountain. In all samples, the *n*-alkan-2-ones range from C<sub>9</sub> to C<sub>33</sub> and have a bimodal distribution (**Figure 3**). Lower-molecular-weight (LMW) *n*-alkan-2-ones (C<sub>9</sub>-C<sub>21</sub>), which reach maximum values at *n*-C<sub>17</sub> or *i*-C<sub>18</sub>, dominant samples from 4,600 m to 6,700 m, while higher-molecular-weight (HMW) *n*-alkan-2-ones (C<sub>23</sub>-C<sub>33</sub>), with a mode at C<sub>27</sub> or C<sub>29</sub>, dominate in all samples. Their  $\sum n$ -C<sub>21</sub>/ $\sum n$ -C<sub>21+</sub> ratios and the carbon preference indices of the HMW (C<sub>23</sub>-C<sub>33</sub>) *n*-alkan-2-ones (CPI) sensitively reflect the variations in the sediment ecosystem response, also indicating that the organic matter in this sediment was derived from terrestrial herbaceous plants, but was probably reworked by bacteria.

In some studies, *n*-alkan-2-ones that have a close resemblance to the terrigenous *n*-alkane distributions have led several authors to propose that microbial oxidation of *n*-alkanes is the source of *n*-alkan-2-ones, with  $\beta$ -oxidation of fatty acids followed by decarboxylation as an alternate pathway (Volkman et al., 1981; Albaiges, Algaba, and Grimalt 1984; Lehtonen and Ketola 1990; Nichls and Huang 2007). In Gongga Mountain sediment samples, the *n*-alkan-2-one distribution appears to result from the mixing of two populations of compounds: the long chain components (C<sub>23</sub>-C<sub>33</sub>), which have a strong OEP, and the short chain components (C9-C22), which have no OEP (Table 2 and Figure 3). The distribution of n-alkanes in all samples is analogous to that of the n-alkan-2-ones (Figure 2 and Figure 3), with a long-chain alkane OEP and a short-chain alkane with no OEP, indicating that n-alkan-2-ones originated from microbiological subterminal oxidation of n-alkanes (Cranwell, Eglinton, and Robinson 1987; Lehtonen and Ketola 1990). The dominance of the  $C_{29}$  homologue in both the HMW n-alkanes and the n-alkan-2-ones throughout the sediments suggests that the oxidation of *n*-alkanes is the favorable pathway (Chen et al., 2019).

Furthermore, the  $C_{29}/C_{31}$  and  $C_{21}-/C_{21+}$  ratio curves of *n*-alkanes and *n*-alkan-2-ones essentially parallel each other,



with higher values present in samples from 5,700 m to 6,100 m, suggesting the *n*-alkan-2-ones may be formed from the microbial oxidation of the corresponding *n*-alkanes, as previously proposed (Albaiges, Algaba, and Grimalt 1984; Nichls and Huang. 2007; Wu et al., 2012).

In addition, **Figure 7** shows a ternary diagram for the same three *n*-alkanes and *n*-alkan-2-ones ( $C_{27}$ ,  $C_{29}$  and  $C_{31}$ ) from the eastern slope of Gongga Mountain; there are two recognizable clusters in these samples. The *n*-alkanes cluster plots are close to the region that characterizes wood plants. However, the *n*-alkan-2-ones cluster plot near the position characterized by grasslands. This difference can best be explained in terms of vegetation; that is, trees dominate the components of the sediment samples, with some increase in the contribution of grasses during the warm stages.

### CONCLUSION

The *n*-alkanes and *n*-alkan-2-ones were analyzed in sediment samples from Gongga Mountain, Sichuan Basin, on the southeastern edge of the Tibetan Plateau, southwest China. The *n*-alkanes and *n*-alkan-2-ones were from a mixed source of bacteria, algae and terrestrial higher plants, and were mainly derived from terrestrial higher plants.

The C<sub>9</sub>-C<sub>21</sub>/C<sub>23</sub>-C<sub>33</sub> ratios and the carbon preference indices of the HMW (C<sub>23</sub>-C<sub>33</sub>) n-alkan-2-ones (CPI) of the samples sensitively reflect the variation in the sediment ecosystem's response to climate. The CPI and ACL values of *n*-alkanes in sediments from low latitudes were higher than those from high latitudes. The CPI and ACL values for different climate zones can also indicate the variation in the sediment ecosystem's response to climate. The stable carbon  $(\delta^{13}C)$  analyses of the sediments showed that the biomes in the study area were dominated by C<sub>3</sub> plants through paleosol cycles and cold and dry climatic conditions existed in the past.

### DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary material, further inquiries can be directed to the corresponding author.

### **AUTHOR CONTRIBUTIONS**

YW, ZC, and TW contributed ideas and design to the study and engaged in charting. YL and RM performed samples analysis and

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