A potential suite of climate markers of long-chain *n*-alkanes and alkenones preserved in the top sediments from the Pacific sector of the Southern Ocean

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Abstract

Investigation of organic compounds in marine sediments can potentially unlock a wealth of new information in these overlooked climate archives. Here we present pilot study results of organic geochemical features of long-chain *n*-alkanes and alkenones and individual carbon isotope ratios of long-chain *n*-alkanes from a newly collected, approximately 8-meter long, Pleistocene age sediment core, located in the far reaches of the Pacific sector of the Southern Ocean. We initially analyzed a suite of organic compounds in the core, and the results show abundant long-chain *n*-alkanes (C_{29}-C_{35}) with predominant odd-over-even carbon preference, which suggests an origin of terrestrial higher plant waxes via long range transport of dust, possibly from Australia and New Zealand. The $\delta^{13}C$ values of the C_{31} *n*-alkane range from -29.4 to -24.8‰, in which the higher $\delta^{13}C$ values suggest more contributions from C_4 plants waxes. In the analysis, we found that the mid-chain *n*-alkanes (C_{23}-C_{25}) have small odd-over-even carbon preference, suggesting that they were derived from marine non-diatom pelagic phytoplankton and microalgae, and terrestrial sources. Furthermore, the C_{26} and C_{28} with lower $\delta^{13}C$ values (~ -34‰) indicate an origin from marine chemoautotrophic bacteria. We found that the abundances of tetra-unsaturated alkenones ($C_{37:4}$) in this Southern Ocean sediment core ranges from 11-37%, perhaps a marker of low sea surface temperature (SST). The results of this study strongly indicate that the $\delta^{13}C$ values of long-chain *n*-alkanes and U^{k}_{37} index are potentially useful to reconstruct detailed history of C_3/C_4 plants and SST change in the higher latitudes of the Southern Ocean.

Keywords: Southern Ocean; Pacific Ocean; *n*-alkane; carbon isotopic; SST; U_{37}^{k}

1. Introduction

The Southern Ocean plays an important role in global climate and carbon cycle related to westerly winds and the Antarctic Circumpolar Current (ACC, Fischer et al. 2010; Marshall and Speer 2012). Mid-latitude westerly winds are important in transporting mineral dust from the continent of Australia and New Zealand to the South Pacific sector of the Southern Ocean (Lamy et al. 2014). The location and intensive change of the westerly winds and ACC directly control the exchange of heat, salt, nutrients and freshwater between low and high latitudes (Pahnke and Zahn 2005; Toggweiler and Russell 2008; Shevenell et al. 2011; Toyos et al. 2020). Thus, environmental fluctuations in the Southern Ocean play a vital role in global climate change.

Well preserved organic matter in marine sediments is a direct indicator of environmental conditions at the time of sedimentation and thus is important for paleo-environmental studies (Meyers and Ishiwatari 1993). Among these, lipid organic biomarkers have been widely used to reconstruct past environmental and climatic conditions in oceans and lakes (Eglinton and Eglinton 2008; Holtvoeth et al. 2019). Long-chain *n*-alkanes (C_{25}-C_{35}) are important components of the epicuticular wax in higher terrestrial plants, and these *n*-alkanes are eroded from leaf surfaces and soil by winds and then transported to the Southern Ocean (Bendle et al. 2007; Martínez-Garcia et al. 2009, 2011; Lamy et al. 2014; Jaeschke et al. 2017). Short- and mid-chain lengths have been reported as the major components of *n*-alkanes in the surface ocean sediments around Antarctica, carbon preference index (CPI) and specific-compound carbon isotopic values have also been reported to be mainly derived from phytoplankton and bacteria (Harada et al. 1995; Bubba et al. 2004). Relatively higher carbon isotopic values of C_{31} *n*-alkane in the surface sediments from the Australian sector of the Southern Ocean suggest significant contributions of C_4 higher vascular plant waxes or conifer resin (Ohkouchi et al. 2000). Altered or recycled material mixed with modern marine input is also an important source for long-chain *n*-alkanes with low CPI values in ocean sediments in the Ross Sea region (Kvenvolden et al. 1987; Venkatesan 1988; Duncan et al. 2019). Although the high latitude of the Southern Ocean is usually considered to be little influenced by river and continent soils, based on above results, the sources of *n*-alkanes in the ocean sediments are thought to be complex, thus their eco-environmental implications are still being explored.

A subtropical to polar SST gradient has been related to the position and intensity of the westerly winds and ACC in the Southern Ocean (Lamy et al. 2010; Kohfeld et al. 2013). Therefore, quantitative SST records from the past are essential for evaluating the importance of the Southern Ocean for the global climate. However, the most widely used organic geochemical SST index, alkenone paleothermometry, has

only rarely been employed in high latitudes of the Southern Ocean. The U^{k}_{37} = ([$C_{37:2}$ − $C_{37:4}$] / [$C_{37:2}$ + $C_{37:3}$ + $C_{37:4}$]) index has been proposed to quantify the degree of alkenone unsaturation (Brassell et al. 1986), which is a function of SST. Because trace of $C_{37:4}$ is often absent in open ocean sediments when SSTs are higher than 12˚C (Prahl and Wakeham 1987), the index was simplified to $U^{k'}_{37}$ = ([$C_{37:2}$] / [$C_{37:2}$ + $C_{37:3}$]). In recent decades, the $U^{k'}_{37}$ index has been widely used at middle and low latitudes marine environments. However, our knowledge on the application of alkenone paleothermometry in the high latitudes of the Southern Ocean is still largely insufficient. Only a few examples exist, such as that $C_{37:4}$ methyl alkenone was not detected in the 10-12℃ waters, and even in the 1.5℃ waters the abundance was still very minor (Sikes and Volkman 1993), while it was detected in most surface sediment samples at 3.5℃ in spring cruise samples in the Southern Ocean (Sikes et al. 1997). The $U^{k'}_{37}$ index is more proper than U^{k}_{37} when used in sea surface temperature estimations, even in cold conditions (Sikes et al. 1997; Jaeschke et al. 2017). However, Ho et al. (2012) found that there was a significant warming trend between the glacial and inter-glacial periods inferred from $U^{k'}_{37}$ records in the subantarctic, with the discrepancy due to the relative high abundance of the $C_{37:4}$ alkenones during cold intervals. Data on alkenone paleothermometry is still largely lacking and these various results of U^{k}_{37} and $U^{k'}_{37}$-SSTs indicate that more investigations are still needed in the high latitudes of the Southern Ocean.

Considering the importance of the position and strength of westerly winds and the Antarctic Circumpolar Current, reconstructing surface ocean hydroclimatic changes using organic biomarkers (e.g., long-chain *n*-alkanes and alkenones) has been very necessary for better understanding the role of the Southern Ocean in the context of global climate change. Before carrying out such work, it is firstly important to determine the source of organic matter and to estimate whether the U^{k}_{37} index could be useful or not in the Southern Ocean. Here, we analyze the organic geochemical features of long-chain *n*-alkanes, alkenones and the compound-specific carbon isotope (long-chain *n*-alkanes C_{23}-C_{31}) in the ocean sediments from one core in the South Pacific sector of the Southern Ocean (66°13′47.16″S, 168°11′8.34″E). Our main objectives are: (a) to evaluate the source of long-chain *n*-alkanes based on their chain length distributions and individual carbon isotopes, (b) to report the distributional features of di-, tri- and tetra-unsaturated alkenones, and (c) to assess the applicability of the alkenones indices in the high latitudes of the Southern Ocean for the reconstruction of paleoclimate change and the possible prediction of climate in the future.

2. Materials and methods

2.1 Materials

The gravity core R23 was drilled at 168°11′8.34″E, 66°13′47.16″S at a water depth of 2967 m during the "31th Chinese National Antarctic Research Expedition (CHINARE)" cruise in 2014-2015 (Fig. 1). The sediment core is 819 cm long, with a top 10 cm soupy layer that is characterized by high water content. The core was subsampled at an interval of 2 cm. The color of the sediments varies among olive, brown and gray throughout the profile. Based on the wet and dry sieving experiments, the core mainly consists of homogenous clay with minor proportions of sand (63-2000 μm), some ice-rafted debris (IRD; >2 mm) and some foraminifera are randomly found, but sponge spicules present throughout the core with relatively high abundance. No obvious bioturbations were observed in this core. The lack of planktonic foraminiferal $CaCO_3$ in these regional marine sediments makes it difficult to rapidly establish an age model using traditional oxygen isotope method. However, the precise chronological framework of the R23 core can be obtained with the comparison of high-resolution Ba/Ti ratios with LR04 $\delta^{18}O$ curves (Lisiecki and Raymo 2005). The age of R23 core ranges from 3.4 to 330 ka from Wang et al. (unpublished data). In this pilot study, we only focus on the source identification of *n*-alkanes with different chain lengths, and then evaluate the possibility of C_{37} alkenones used as a suitable proxy for calculating the past sea surface temperature in this region. To study the potential of sedimentary organic geochemical features for paleoclimate reconstruction, we choose 12 samples at every ~ 80 cm interval for *n*-alkanes and alkenones analysis in this pilot study. All samples were stored under -20°C in the lab before analysis.

2.2 Lipids biomarker extraction

The lipids analysis procedure followed the methods of Yamamoto et al. (2000). Briefly, all sediment samples were freeze-dried, and then homogenized and powdered. Samples (2-3g) were weighed, and extracted two times with an Accelerated Solvent Extractor (DIONEX ASE 350) using dichloromethane-methanol (6:4 v/v) and then concentrated. The total lipid extract was separated into four fractions using column chromatography (SiO_2 with 5% distilled water; internal diameter, 5.5 mm; length, 45 mm) based on the degree of polarity: F1 (hydrocarbons, 4 ml hexane); F2 (aromatic hydrocarbons, 4 ml hexane-toluene (3:1 v/v)); F3 (ketones, 4 ml toluene); F4 (polar compounds, 4 ml toluene-methanol (3:1 v/v)). N-$C_{24}D_{50}$ and n-$C_{36}H_{74}$ were added as internal standards for the F1 and F3 fraction, respectively. Compounds were quantified using an internal standard (n-$C_{24}D_{50}$ and n-$C_{36}H_{74}$ for *n*-alkanes and alkenones, respectively) and by the proportional relation of the peak areas for each biomarker.

2.3 *n*-alkanes and alkenones analysis

Quantification of compounds was performed on a Hewlett Packard 6890 GC-FID system with a Chrompack DB-1MS column (length, 60 m; i.d., 0.25 mm; thickness, 0.25 lm). The oven temperature was programmed from 70 to 290˚C at 20˚C/min, 290 to 310˚C at 0.5˚C /min, and then held at 310˚C for more than 30 min. Helium was used as the carrier gas, with a flow rate of 30 cm/s. Selected samples were performed using GC-MS for compound identification, the GC column and oven temperature program was the same as GC-FID. The mass spectrometer was run in full scan mode (m/z 50–650). Electron ionization (EI) spectra were obtained at 70 eV. Alkenones were identified using an external standard by GC retention times by analogy with a synthetic standard (provided by M. Yamamoto, Hokkaido University, Japan) and characteristic mass fragments. N-alkanes were identified by comparing mass spectra and retention times with those of the standards and published data.

The carbon preference index (CPI; Bray and Evans 1961) of C_{26}-C_{34} homologues and the average chain length (ACL) of odd C_{27}-C_{35} homologues (Duan and He 2011) used in this study were as follows:

$$CPI = \left(\frac{C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{27}+C_{29}+C_{31}+C_{33}}{C_{28}+C_{30}+C_{32}+C_{34}} \right) / 2 \quad (1)$$

$$ACL = \frac{27\times C_{27}+29\times C_{29}+31\times C_{31}+33\times C_{33}+35\times C_{35}}{C_{27}+C_{29}+C_{31}+C_{33}+C_{35}} \quad (2)$$

The [C_{26}-C_{35}] are concentration of odd and even *n*-alkane. The U^{k}_{37} = ([$C_{37:2}$-$C_{37:4}$] / [$C_{37:2}$ + $C_{37:3}$ + $C_{37:4}$]) index has been proposed to quantify the degree of alkenone unsaturation (Brassell et al. 1986), which is a function of SST. Because $C_{37:4}$ is often absent in open ocean sediments when SSTs are higher than 12˚C (Prahl and Wakeham 1987), the index was simplified to $U^{k'}_{37}$ = ([$C_{37:2}$] / [$C_{37:2}$ + $C_{37:3}$]). We converted the index values to SST using the widely used *E. huxleyi* culture-based calibration proposed by Prahl et al. (1988), U^{k}_{37} = 0.04 T – 0.104 (r^2 = 0.98) and $U^{k'}_{37}$ = 0.034 T + 0.039 (r^2 = 0.99), and the simplified $U^{k'}_{37}$ calibration based on global core top compilations (Conte et al. 2006).

2.5 Carbon isotope analysis

The carbon isotope ratio of *n*-alkane was performed using a gas chromatograph with an DB-5MS column (60 m × 320 μm × 250 μm) interfaced to a Thermofisher MAT-253 isotope-ratio mass

spectrometer via a combustion interface (960℃) consisting of an alumina reactor containing nickel and platinum wires. Helium was used as the carrier gas with a flow rate of 1.2ml/min using splitless injecting. The oven temperature was programmed from 80 to 100 ˚C at 10˚C/min, 100 to 220˚C at 4˚C /min, 220 to 280℃ at 2℃/min, and then held at 280˚C for 15mins. All samples are injected one time for carbon isotope analysis. The analytical error was calculated based on the reproduced analytical results of an external standard, injected once after every sixth sample injection, and had an analytical error of 0.7‰ (1σ). The pre-calibrated isotopic composition of CO_2 was used as a standard. All $\delta^{13}C$ values were expressed versus VPDB.

Based on the isotopic values of *n*-alkanes, we can quantify the percentage source of long chain n-alkanes from C_3/C_4 plants using a binary isotope mass balance model (Thomas et al. 2014):

$$\delta^{13}C_s = f \times \delta^{13}C_{C3} + (1-f) \times \delta^{13}C_{C4} \quad (3)$$

where $\delta^{13}C_s$ are the long-chain *n*-alkanes from sediments, $\delta^{13}C_{C3}$ and $\delta^{13}C_{C4}$ are the carbon isotopic values of long-chain *n*-alkanes from C_3 and C_4 terrestrial higher vascular plants, respectively, and f is the proportion of long-chain *n*-alkanes from C_3 plants. We set the carbon isotopic values of long-chain *n*-alkanes for C_3 and C_4 plants to be -36‰ and -22‰, respectively (Chikaraishi and Naraoka 2007). C_{31} *n*-alkane abundance is relatively higher than C_{29} and C_{33} *n*-alkanes, thus, we use the carbon isotopic values of C_{31} *n*-alkane to calculate the percentage source of long-chain *n*-alkanes from C_3/C_4 plants.

3. Results

3.1 Concentration and distribution of long-chain *n*-alkanes

In the 12 pilot samples from the core R23, we found that there was a significant change in the concentrations of total long-chain *n*-alkanes (C_{23}-C_{35}) in the sediment profile, ranging from 295-787 ng/g (Table 1, Table S1). The distribution pattern of long-chain *n*-alkanes (C_{23}-C_{35}) in each sediment sample was similar, with bimodal distributions peaking at C_{23}-C_{25} and C_{27} or C_{31} (Fig. 2). However, there was no obvious predominant odd-over-even carbon preference, and $CPI_{27\text{-}33}$ varied from 1.1-2.5, with an average of 1.7. The distribution patterns of long-chain *n*-alkanes were divided into two types. One is mid-chain *n*-alkanes (C_{23}-C_{27}), with no predominant odd-over-even carbon preference (CPI ~1), and the other is long-chain *n*-alkanes (C_{29}-C_{35}) with predominant odd-over-even carbon preference. The ACL values of

long-chain *n*-alkanes (C_{27}-C_{35}) were in the range of 29.3-30.7. The ACL values are strongly correlated with CPI (Fig. 3).

3.2 Concentration and distribution of alkenones

$C_{37:4}$, $C_{37:3}$ and $C_{37:2}$ alkenones were all detected in the 12 pilot samples, with total concentrations ranging from 12.6-104.2 ng/g sediment dry wt (Table 2). The distribution pattern of three unsaturated alkenones revealed significant differences among the subsamples, and the relative abundance of $C_{37:4}$, $C_{37:3}$ and $C_{37:2}$ varied from 11-37%, 27-87% and 3-48%, respectively. The tri-unsaturated alkenone ($C_{37:3}$) was the most abundant alkenone in the sediments. Interestingly, a high abundance of tetra-unsaturated alkenone was found in the sediment samples. The SST estimates inferred from the U^{k}_{37} and $U^{k\prime}_{37}$ indexes are between -1.7 to 8.4℃ and -0.4 to 17.9℃, respectively.

3.3 The carbon isotopes of individual *n*-alkanes

Our *n*-alkane-specified carbon isotope analysis of the 12 pilot samples shows a significant change. Therefore, based on the chain length of the *n*-alkanes, we divided *n*-alkanes into two endmembers (Table 1). One is mid-chain *n*-alkanes, which had $\delta^{13}C$ values ranging from -31.5 to -25.4‰ and -32.3 to -26.7‰, with an average of -28.6‰ and -29.4‰ for C_{23} and C_{25}, respectively. The other is long-chain *n*-alkanes (C_{27}, C_{29} and C_{31}), with $\delta^{13}C$ values from -30.1 to -26.3‰ (C_{27}, averaging -28.0‰), -30.4 to -25.0‰ (C_{29}, averaging -27.5‰) and -29.4 to -24.8‰ (C_{31}, averaging -26.9‰). The average $\delta^{13}C$ values of long-chain *n*-alkanes (C_{27}, C_{29} and C_{31}) were higher than mid-chain *n*-alkanes (C_{23} and C_{25}). C_{26} and C_{28} *n*-alkanes had the lowest $\delta^{13}C$ values averaging ~ -34‰. The percentage source of long-chain *n*-alkanes from C_3/C_4 plants using C_{31} $\delta^{13}C$ values varied from 47-80% for C_4 plants (Table 1).

4. Discussion

4.1 Source of mid-chain *n*-alkanes

Our pilot study indicates that the mid-chain *n*-alkanes (C_{23}-C_{25}) are abundant in the sediment profile, and no predominant odd-over-even carbon preference is observed (CPI ~1; Fig. 2). Though contamination of petroleum during coring and sampling may bring *n*-alkanes, our sampling procedures by the crew of the R/V Xuelong in the 31th CHINARE have been devised to prevent any possible contamination by

petroleum, and no any signs of petroleum contamination have been observed while treating sediment samples in the laboratory. All lab-ware was baked at 450℃ in a furnace before using to prevent contamination during analysis of the samples. Blank experiments were also analyzed, and negligible contamination was found. Furthermore, the average $\delta^{13}C$ values of *n*-alkanes with different chain lengths are different (Fig. 4). For example, the average $\delta^{13}C$ values of mid-chain *n*-alkanes (C_{23}-C_{25}) were similar to the *n*-alkanes from marine phytoplankton (Ashley et al. 2020). Therefore, it is very unlikely that these *n*-alkanes were due to petroleum contamination during the coring and sampling.

Several studies have shown that ocean phytoplankton can produce mid-chain *n*-alkanes and *n*-alkanoic acids (e.g., Volkman et al. 1998). N-alkanoic acids are biosynthesized in the acetogenic pathway and then they are converted to *n*-alkanes by enzymatic decarboxylation, thus they have similar distributions (Diefendorf and Freimuth 2017). Mid-chain *n*-alkanoic acids (C_{22}-C_{24}) can be produced by marine plants, such as marine microalgae, diatoms and seaweed (Naraoka and Ishiwatari 2000). Thus, phytoplankton may be a significant source for these mid-chain *n*-alkanes with no predominant odd-over-even carbon preference (CPI ~ 1). Previous study has reported that the average $\delta^{13}C$ values of *n*-alkanoic acids produced by marine phytoplankton were about -28‰ (Ashley et al. 2020). The $\delta^{13}C$ values of C_{23} and C_{25} *n*-alkanes from C_3 plants vary from -40 to -31‰, and those from C_4 plants are in the range of -23 to -18‰ (Chikaraishi et al. 2007). In our pilot analysis of the 12 samples, the average $\delta^{13}C$ values of *n*-alkanes with different chain length vary greatly. The $\delta^{13}C$ values of mid-chain *n*-alkanes (C_{23}-C_{25}; ~ -29‰) are in the range of *n*-alkanes from marine organisms and soil samples (~ -28‰) in the McMurdo Dry Valleys (Hayes et al. 1990; Ishiwatari et al. 1994; Matsumoto et al. 2010), but obviously are lower than lake sediments (~ -15‰) from East Antarctica (Chen et al. 2019). Thus, terrestrial organic matter from Antarctica by ice-rafted debris (IRD) and the contributions through dust transportation from terrestrial ice-free areas via katabatic winds also should be considered (Chewings et al. 2014), but sources from lake sediments at higher latitudes are negligible. The $\delta^{13}C$ values of C_{26} and C_{28} are lower relative to other long-chain *n*-alkanes (Fig. 4), suggesting they may have other sources. Moreover, the $\delta^{13}C$ values of C_{26} and C_{28} in our study samples are also obviously depleted relative to marine organisms and soil samples from Antarctica. It is likely that C_{26} and C_{28} may originate from chemoautotrophic bacteria because they have relatively low $\delta^{13}C$ values and have no odd-over-even predominance (Hayes et al. 1990; Collister et al. 1994). Thus, from the above discussion, we believe that C_{23} to C_{25} should have mixing sources of marine (non-diatom pelagic phytoplankton and marine microalgae) and terrestrial, with the marine source predominant; C_{26} and C_{28} might be originated primarily from chemoautotrophic bacteria.

4.2 Sources of long-chain *n*-alkanes

There are three major sources for long-chain *n*-alkanes (C_{27}-C_{35}) in the South Pacific sector of the Southern Ocean sediments including long range transport of dust from lower latitudes continent, ocean plankton, and soils eroded from Antarctica. Previous studies have shown that short- and mid- chain *n*-alkanes are predominant in Pleistocene age ocean sediments, water columns and suspended particulate matter in the Ross Sea and Antarctic-margin, and long-chain are minor (Harada et al. 1995; Hayakawa et al. 1996; Cincinelli et al. 2008). Moreover, the $\delta^{13}C$ values of *n*-alkanes ranged from -28.5 to -26.2‰, suggesting that their major source was possibly derived from marine organisms (Harada et al. 1995). In the Ross Sea, abundant long-chain *n*-alkanes with low CPI values in ocean sediments have suggested that the organic matter was mainly originated from altered or recycled material mixed with modern marine input (Kvenvolden et al. 1987; Venkatesan 1988; Duncan et al. 2019). Long range transport of terrestrial organic matter and higher plant leaf waxes is also an important source for long-chain *n*-alkanes in the Pacific sector of the Southern Ocean (Bendle et al. 2007; Martinez-Garcia et al. 2009, 2011; Lamy et al. 2014; Jaeschke et al. 2017).

The core R23 is near the Antarctic continent, which is very likely be a potential source of long-chain *n*-alkanes at our site. However, there are no vascular plants in the Antarctic, except for limited terrestrial vegetation (moss and lichen) in relatively low latitudes of the Antarctic Peninsula. Dust contribution of terrestrial material by katabatic winds is negligible due to the lack of exposed, mature soils in the McMurdo Dry Valleys and Victoria Land (Nylen et al. 2004), as well as the long distance of the core site from the coast. Long-chain *n*-alkanes with relatively low $\delta^{13}C$ values (-37 to -30.8‰) in the southernmost Southern Ocean aerosol samples may represent a regional background of well-mixed higher vascular plants through very long range transportation (Bendle et al. 2007). Moreover, Mastumoto et al. (2010) have reported that the chain length of *n*-alkanes ranging from C_{15}-C_{37} was found in McMurdo Dry Valley soil, with the majority as C_{23}, C_{25} and C_{27} *n*-alkanes, but with extremely low abundance of C_{29} and C_{31} *n*-alkanes. Recently, Chen et al. (2019) reported that abundant long-chain *n*-alkanes with highly enriched carbon isotopic ratios (~ -25 to -12‰) in lake sediments from East Antarctic (no vascular plants are present in the surrounding land mass) are predominantly derived from heterotrophic microbes. However, the average $\delta^{13}C$ values of long-chain *n*-alkanes (C_{27}, C_{29} and C_{31}) varying from ~ -28 to -27‰ in the R23 sediments are obviously lower than these in the lake sediments from East Antarctica, as reported by Chen et al. (2019). Therefore, the possibility of long-chain *n*-alkanes (C_{27}-C_{35}) via dust transport from ice-free soils and lake sediments in East Antarctica and ocean phytoplankton to our site is highly unlikely.

The average chain length (ACL) of long-chain *n*-alkanes refers to the average number of carbon atoms/molecule and can be used to indicate their source (Poynter and Eglinton 1990). The ACL values of

long-chain *n*-alkanes (C_{27}-C_{35}) ranged from 29.3-30.7 in the sediment samples, similar to Southern Ocean ACL values with a range of 29.1-30.6 in the surface sediments, both indicating the significant contribution of higher plants (Jaeschke et al. 2017). A significant linear relationship was observed between ACL and CPI (n=12, r^2=0.54; Fig. 3), which can help evaluate the distributional characteristics of long-chain *n*-alkanes distribution. Generally, relatively high CPI values (CPI>3) indicate long-chain *n*-alkanes from higher vascular plants, while low CPI values (CPI ~1) may imply mature organic matter inputs (Eglinton and Eglinton 2008; Duncan et al. 2019). Based on the leaf litter degradation experiments, high odd-over-even predominance declined and long-chain *n*-alkanes ratios (e.g., C_{31}/C_{29}) tended to the value of ~ 1 (Zech et al. 2011). Long-chain *n*-alkanes in dust during long range transportation and deposition could also be decomposed by bacteria, resulting in low CPI values. However, the $\delta^{13}C$ values of long-chain *n*-alkanes have no obvious difference under degradation (Huang et al. 1997; Li et al. 2017), thus it could be useful to trace the sources of organic matter and reconstruct the paleoecological changes. Relatively low CPI values of 1.1 to 2.5 in the R23 sediment core indicate substantial contributions of reworked organic matter, which is most likely related to very low sedimentation rates <2 cm/ka (Jaeschke et al. 2017). Previous studies have shown that the average sedimentation rates were as low as 1.18 cm/ka in Prydz Bay (Wu et al. 2015), and 1.00 cm/ka in ODP 1167 (Theissen et al. 2003). Low CPIs and low sedimentation rates in the DSDP 274 sediment core from the northwest Ross Sea suggest that long-chain *n*-alkanes have been extensively degraded by bacterial activity in the surface layers of the seabed (Duncan et al. 2019). The high abundance of long-chain even *n*-alkanes (C_{26} and C_{28}) with lower $\delta^{13}C$ values in the R23 sediment core also indicates microbial (chemoautotrophic) activity in this region. Altered or recycled organic matter from Antarctica that has been eroded by glaciers and transported by ice rafted debris is important in the study region (Chewings et al. 2014; Duncan et al. 2019). Therefore, we suggest that the long-chain *n*-alkanes (C_{29}-C_{35}) primarily originated from terrestrial higher plant waxes via long range transport of dust from lower latitude continental regions (e.g., Australia and New Zealand), and altered or recycled organic matter from Antarctica may be another secondary source.

Our results are consistent with previous studies in the Southern Ocean, where long-chain *n*-alkanes were reported to originate mainly from long range transport of dust from Australia and New Zealand by prevailing westerlies (Martinez-Garcia et al. 2011; Lamy et al. 2014). For example, relatively enriched carbon isotopic ratios of C_{31} *n*-alkane in the surface sediments from the Australian sector of the Southern Ocean suggest significant contributions of C_4 higher vascular plant waxes (Ohkouchi et al. 2000). More recently, Jaeschke et al. (2017) have reported that the CPI values of long-chain *n*-alkanes ranged from 1.1-10 in the Pacific sector of the Southern Ocean, indicating the contribution of higher plant leaf waxes. Because the location of surface sediments is far from the continent with the potential source regions in

New Zealand and Australia, it is reasonable to believe that the long-chain *n*-alkanes are primarily derive from eolian transport.

4.3 Estimation of C_3/C_4 plant fraction

As discussed above, the long-chain *n*-alkanes (C_{27}, C_{29} and C_{31}) in R23 sediments are primarily derived from higher plant leaf waxes by long range transport of dust. Interestingly, the $\delta^{13}C$ values of long-chain *n*-alkanes were 5-10‰ higher than these in C_3 plants. This difference indicates that considerable amounts of *n*-alkanes are derived from C_4 plant waxes which have significantly higher carbon isotopic values. Many studies have shown that the $\delta^{13}C$ values of long-chain *n*-alkanes of C_3 and C_4 plants range from -40 to -31‰ and -23 to -18‰, respectively (Chikaraishi et al. 2007). Therefore, we can quantify the percentage source of long-chain *n*-alkanes from C_3/C_4 higher plants using a binary isotope mass balance model. We assumed the average $\delta^{13}C$ values of long-chain *n*-alkanes for C_3 and C_4 plants to be -36‰ and -22‰, respectively (Vogts et al. 2009). The relative contributions of long-chain *n*-alkanes (C_{27}, C_{29} and C_{31}) from C_3 and C_4 plants are significantly different in the sediment samples. For the carbon isotopic values of C_{31} *n*-alkanes, 80% originated from C_4 plants in the 398cm section; however, only 47% originated from C_4 plants in the 762cm section (Table 1). Ohkouchi et al. (2000) reported that the relative contributions of C_{31} *n*-alkanes from C_3 and C_4 plants are about 60% and 40% in the surface sediments from the Australian sector of the Southern Ocean, respectively (Ohkouchi et al. 2000). The different contribution of C_3/C_4 plants may be related to the climate change (e.g. temperature and precipitation) in the source regions (Huang et al. 2001). Based on the above discussion, it is reasonable to infer that the source of the long-chain *n*-alkanes was mainly derived from long range transport of dust from New Zealand and Australia. Therefore, this result paves the way for a future study that will allow us to analyze the $\delta^{13}C$ values of long-chain *n*-alkanes to reconstruct the past changes of C_3/C_4 plants in the source area.

4.4 Assessing U^{k}_{37} and $U^{k\prime}_{37}$-derived SST records

In our 12 sediment samples, $C_{37:4}$, $C_{37:3}$ and $C_{37:2}$ alkenones were all well-detected. The major alkenone was $C_{37:3}$, with a relative abundance ranging from 27-87%. Interestingly, we also found abundant $C_{37:4}$ in the R23 sediments, ranging from 11-37%. This is similar to a previous study in higher latitude of the Pacific sector of the Southern Ocean (Sikes et al. 1997), but significantly higher than the sedimentary abundance from the relatively low latitude of the Southern Ocean (Jaeschke et al. 2017). Previous studies have shown that $C_{37:4}$ is often absent in open ocean sediments where SSTs are higher than 12°C (Prahl et al. 1987). The

modern annual SST in our study site is about 0℃, thus high abundance of $C_{37:4}$ alkenone may be related to the extremely low temperature. Numerous studies have demonstrated that a high abundance of $C_{37:4}$ in surface sediments is related to low-temperature and low-salinity surface water masses in the Arctic (Sicre et al. 2002; Bendle et al. 2005, 2005; Harada et al. 2006). Analysis of 106 surface water and sediment samples from the Atlantic, Pacific and Southern Ocean, indicated that the relative abundance of $C_{37:4}$ methyl alkenone had no obvious relationship with SST and salinity, but it might respond to some other environmental factors including growth rate, light, or nutrients (Sikes and Sicre 2002). However, most samples were from the Atlantic and Pacific Oceans and there were few studies on the distributional characteristics of alkenones in the high latitudes of the Southern Ocean. Moreover, the relationship of temperature and salinity is strongly linear in the Atlantic and Southern Oceans, suggesting that any relationship to salinity is an artifact of the covariance with temperature (Sikes and Sicre 2002).

To determine whether SST affects the relative abundance of $C_{37:4}$ methyl alkenone, we calculated the sea surface temperature based on the U^{k}_{37} and $U^{k'}_{37}$ index using the formula reported by Prahl et al. (1988) and Conte et al. (2006), respectively (Table 2). Our results show that SST data between U^{k}_{37}- and $U^{k'}_{37}$-SST were, as we expected, obviously different (Fig. 5). When the relative abundance of tetra-unsaturated alkenone was higher, we found $U^{k'}_{37}$-SST was obviously warmer than U^{k}_{37}-SST in 166, 243, 323, 550, 626, 762 and 818 cm sediment sections, and the difference between $U^{k'}_{37}$ and U^{k}_{37}-SST is in the range of 4.8-10.9℃. Based on the average summer SST from the World Ocean Atla (WOA09) data set (Locarnini et al. 2010), the modern sea surface temperature in our study site was about 0-1℃. The $U^{k'}_{37}$ and U^{k}_{37}-SST in the top two samples (16 and 88 cm) are similar to modern averaged summer SST. For the historical period, Ho et al. (2012) reported the difference of SSTs inferred from the U^{k}_{37} index between glacial and interglacial periods in the Pacific sector of the Southern Ocean (54°22′S, 80°05′W) was about 7-8℃. According to modern observation and the top samples, we suggest that the highest SST in our study site should be lower than 7-8℃ in the warmer periods, which was much lower than $U^{k'}_{37}$-SST. Therefore, the $U^{k'}_{37}$ index in the higher latitudes of the Southern Ocean may cause a largely warmer SST.

Ho et al. (2012) also found the $U^{k'}_{37}$-SST records were significantly warmer in glacial periods, and that the U^{k}_{37} index is a more suitable SST proxy in the sub-Antarctic and higher latitude Pacific (Ho et al. 2012; Haddam et al. 2018). Other studies have shown a significant relationship between the relative abundance of $C_{37:4}$ and temperature (Prahl et al. 1988). Moreover, several other studies indicate %$C_{37:4}$ is closely related to cold water mass expansion (Bard et al. 2000; Martínez-Garcia et al. 2010). Although the factors influencing $C_{37:4}$ alkenone abundance in a specific location are complex, a statistically significant relationship between $C_{37:4}$ and temperature has been found if geography and low temperature are considered (Rosell-Melé et al. 1994, 1995). The latitude was relative high at our study site, and the modern annual summer sea surface

temperature was lower than 1°C. The marine algae may synthesize more $C_{37:4}$ alkenones to adapt to the extremely cold conditions. Importantly, there are few U^k_{37}-SST records in the Southern Ocean at latitudes higher than 60°S. Therefore, our study indicates that the usage of U^k_{37} index is feasible for the reconstruction of past SST in the Southern Ocean. Moreover, we point out here that more studies on surface water and sediment samples in high latitudes are required to confirm the relationship between $C_{37:4}$ alkenones and sea surface temperature. In summary, based on our study results, long-chain *n*-alkanes are primarily derived from terrestrial higher plant waxes via long range transport of dust from lower latitude continental regions (e.g., Australia and New Zealand), and the U^k_{37} index can be used as a reliable index for calculating sea surface temperatures in this region.

5. Conclusions

We have presented pilot results of the relative distribution and individual $\delta^{13}C$ values of long-chain *n*-alkanes and the organic geochemical characterization of alkenones in 12 samples selected from a sediment core collected from the Pacific sector of the Southern Ocean. Our results suggest that the abundant long-chain *n*-alkanes (C_{27}-C_{35}) with a significant odd-over-even carbon preference might have originated from terrestrial higher plant waxes, possibly via long range transport of dusts from Australia and New Zealand. The mid-chain *n*-alkanes (C_{23}-C_{25}) preserved in the sediments have small odd-over-even carbon preference, possibly indicating mixing of marine (non-diatom pelagic phytoplankton and marine microalgae) and terrestrial sources. The C_{26} and C_{28} *n*-alkanes with relatively lower $\delta^{13}C$ values indicate an origin from marine chemoautotrophic bacteria. The $\delta^{13}C$ values of long-chain *n*-alkanes (C_{27}-C_{31}) range between -30.8 to -24.8‰ in the sediments, approximately 5-10‰ higher than in terrestrial C_3 higher plants. The carbon isotopic values of long-chain *n*-alkanes to be analyzed from the core will provide insights into the history of C_3/C_4 plants in response to Pleistocene climate change. Furthermore, we found that the abundances of tetra-unsaturated alkenones in the sediments are approximately 11-37%, relatively higher than all those previously reported from lower latitudes adjacent to the Pacific sector of the Southern Ocean. We conclude that tetra-unsaturated alkenones are sensitive markers of low SSTs, and therefore suggest the feasibility of using U^k_{37} in further SST reconstructions in the Pacific sector of the Southern Ocean.

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Author's contributions

Min-Te Chen, Xiaodong Liu and Xin Chen proposed the topic, conceived and designed the study, and they wrote the draft of this paper. Xin Chen and Da-Cheng Lin conducted the experiments. All the co-authors contributed to the discussion, and edited and commented on the paper. Linmiao Wang and Zhifang Xiong provided the chronology framework of R23 core. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets in the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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Table 1 Concentrations, $\delta^{13}C$ values and typical indices based on *n*-alkanes in the subsamples with different sediment depth. The relative contribution of long chain *n*-alkanes from C_3 and C_4 plants are calculated by carbon isotopes of the C_{31} *n*-alkane.

Depth (cm)	$\delta^{13}C_{23}$ (‰)	$\delta^{13}C_{24}$ (‰)	$\delta^{13}C_{25}$ (‰)	$\delta^{13}C_{26}$ (‰)	$\delta^{13}C_{27}$ (‰)	$\delta^{13}C_{28}$ (‰)	$\delta^{13}C_{29}$ (‰)	$\delta^{13}C_{31}$ (‰)	*n*-alkanes[a] (ng/g)	C_4 (%)	C_3 (%)	ACL[b]	CPI[c]
16	-29.6	-28.8	-29.9	-33.2	-28.5	-32.2	-27.4	-28.3	445	55	45	30.1	1.6
88	-29.5	-31.8	-27.3	-30.0	-26.3	-33.1	-25.1	-25.5	328	75	25	30.3	2.0
166	-25.4	-26.4	-26.7	-32.5	-28.3	-38.0	-27.1	-27.8	295	59	41	30.1	2.1
243	-27.1	-26.8	-26.8	-30.4	-26.7	-33.3	-29.8	-28.3	362	55	45	30.3	2.5
323	-29.8	-31.2	-30.6	-35.0	-28.3	-32.1	-29.4	-27.9	324	58	42	29.3	1.3
398	-31.5	-35.9	-30.0	-36.7	-28.6	-34.6	-25.0	-24.8	787	80	20	29.6	1.3
482	-26.8	-28.4	-29.3	-30.3	-26.8	-30.1	-27.4	-26.6	411	67	33	30.7	1.9
550	-27.1	-30.7	-29.3	-35.1	-27.8	-31.2	-27.8	-25.4	420	76	24	30.1	1.6
626	-30.4	-32.2	-31.7	-34.6	-29.6	-30.9	-26.4	-25.8	344	73	27	29.6	1.6
698	-28.6	-30.6	-29.0	-32.7	-27.8	-31.8	-27.0	-25.8	490	73	27	29.3	1.1
762	-28.8	-29.3	-30.0	-35.3	-26.7	-32.1	-30.4	-29.4	455	47	53	29.8	1.6
818	-28.8	-28.7	-32.3	-37.4	-30.1	-35.8	-27.7	-27.2	503	63	37	30.1	1.7

a: Total concentrations of C_{23}-C_{35} *n*-alkanes

b: $ACL_{27\text{-}35} = \sum(i \times X_i)/\sum X_i$, where X is abundance and i ranges from C_{27}-C_{35} odd *n*-alkanes

c: $CPI_{27\text{-}33} = 0.5 \times \sum(C_{27}\text{-}C_{33})/(C_{26}\text{-}C_{32}) + 0.5 \times \sum(C_{27}\text{-}C_{33})/(C_{28}\text{-}C_{34})$

Table 2 The relative abundance and concentrations of $C_{37:4}$, $C_{37:3}$ and $C_{37:2}$ alkenones and based on U^{k}_{37}- and $U^{k'}_{37}$-SST in the subsamples with different sediment depth.

Depth (cm)	$C_{37:4}$ (%)	$C_{37:3}$ (%)	$C_{37:2}$ (%)	Alkenones (ng/g)	U^{k}_{37}-SST[a] (℃)	$U^{k'}_{37}$-SST[b] (℃)
16	12	85	4	90.7	0.6	−0.1
88	11	87	3	104.2	0.7	−0.4
166	30	40	30	13.2	2.8	11.5
243	21	51	28	15.3	4.4	9.2
323	35	48	17	14.7	−1.7	6.6
398	16	64	19	50.1	3.5	5.6
482	15	80	6	65.1	0.5	0.7
550	37	38	24	12.6	−0.6	10.3
626	30	44	26	14.0	1.8	9.9
698	23	59	18	19.1	1.2	5.7
762	25	27	48	30.2	8.4	17.9
818	30	36	34	19.0	3.6	13.2

a: $U^{k'}_{37} = C_{37:2}/(C_{37:2}+ C_{37:3})$

b: $U^{k}_{37} = (C_{37:2}-C_{37:4})/(C_{37:2}+ C_{37:3}+ C_{37:4})$

FIGURE CAPTIONS：

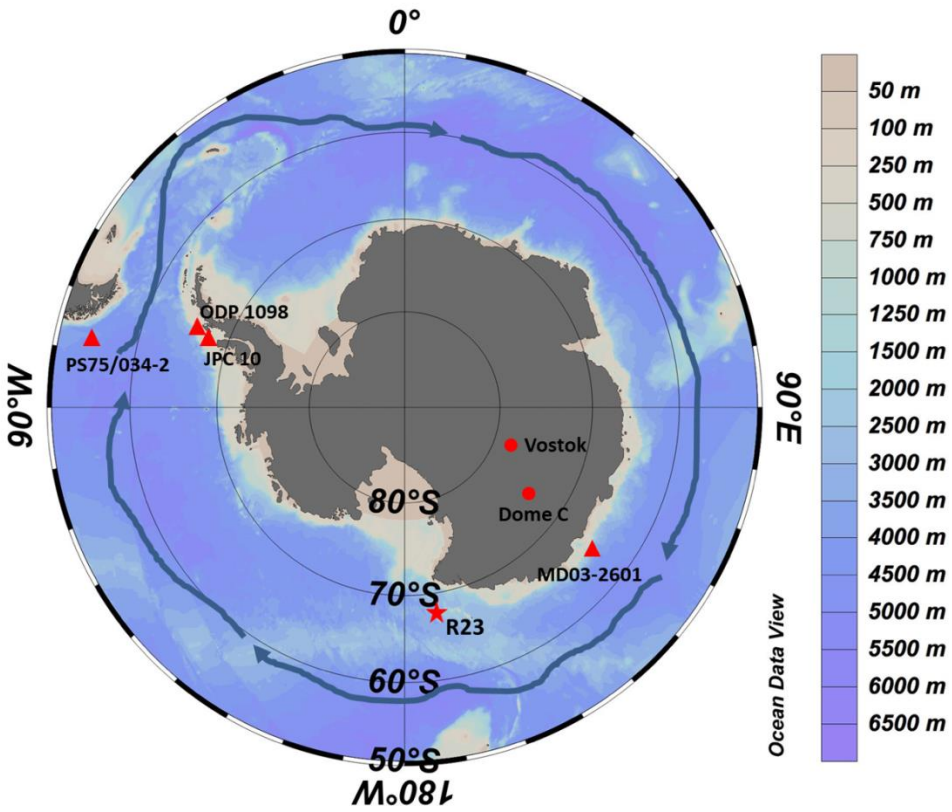
Fig. 1. Map of the Southern Ocean and the continent of Antarctica. Red pentagram denotes the site of the sediment core in our study. Red triangles indicate sites of sea surface temperature or sea subsurface temperature records reported in previous studies. The SST record in the PS75/034-2 sediment core was used for the U^{k}_{37} index (Ho et al., 2012), whereas other sediment cores (ODP 1098, JPC 10 and MD03-2601) were used for TEX_{86} (Shevenell et al., 2011; Kim et al., 2012; Etourneau et al., 2013). The thick blue line indicates the Antarctic Circumpolar Current (ACC). The solid dots denote ice core locations in the Antarctic, including Dome C and Vostok.

Fig. 2. The relative abundance of long chain *n*-alkanes (C_{23}-C_{35}) at different depths of the sedimentary section.

Fig. 3. Relationship between $ACL_{27\text{-}35}$ and $CPI_{27\text{-}33}$ of long chain *n*-alkanes.

Fig. 4. The average $\delta^{13}C$ values of *n*-alkanes. Error bars represent 1 standard deviation of 12 samples.

Fig. 5. The relative abundance of $C_{37:4}$, $C_{37:3}$ and $C_{37:2}$ alkenones and the calculated sea surface temperature based on U^{k}_{37} and $U^{k'}_{37}$ index at different depths of the sedimentary section. The light grey and light blue bands represent modern average summer SST and highest SST during the Holocene at the same latitude of the Southern Ocean, respectively. The age of R23 core is cited from Wang et al. (unpublished data).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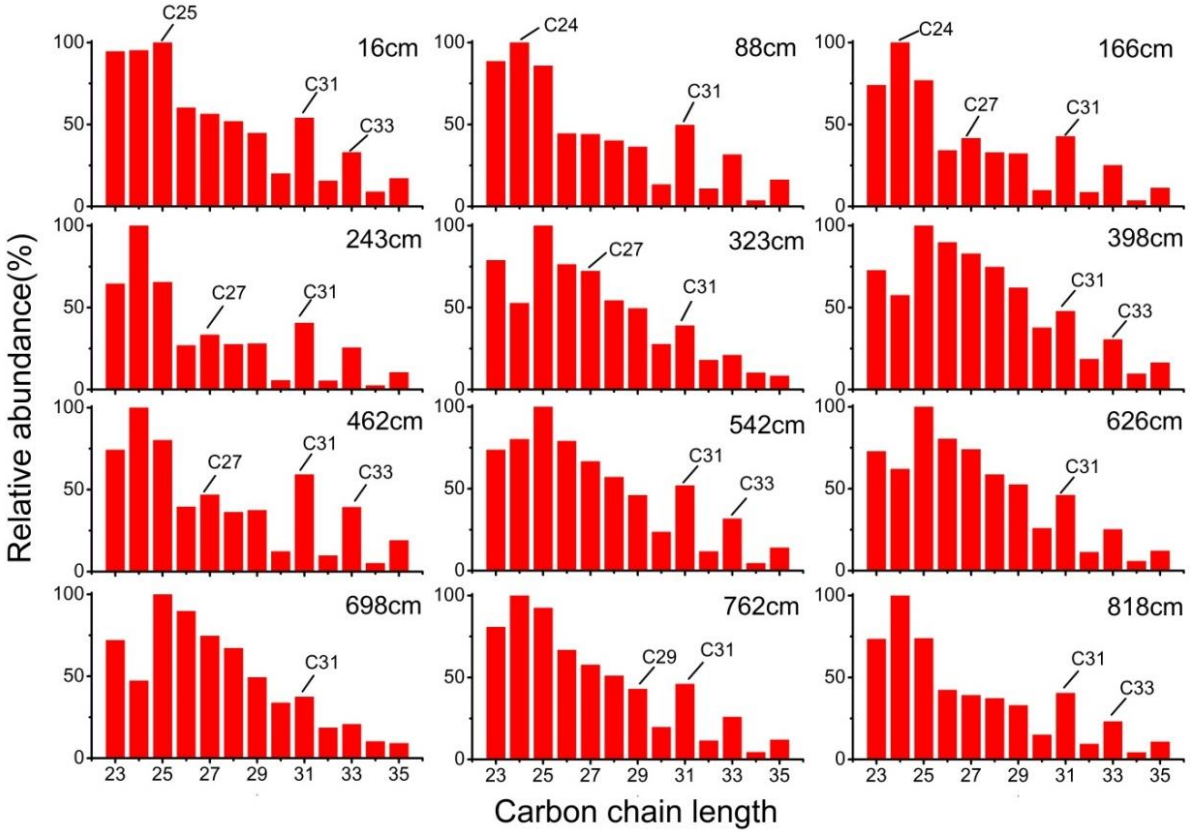
90°E
180°W
90°W
80°S
70°S
60°S
50°S
ODP 1098
JPC 10
PS75/034-2
Vostok
Dome C
MD03-2601
R23
50 m
100 m
250 m
500 m
750 m
1000 m
1250 m
1500 m
2000 m
2500 m
3000 m
3500 m
4000 m
4500 m
5000 m
5500 m
6000 m
6500 m
Ocean Data View

Figure 1



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682 **Figure 2**

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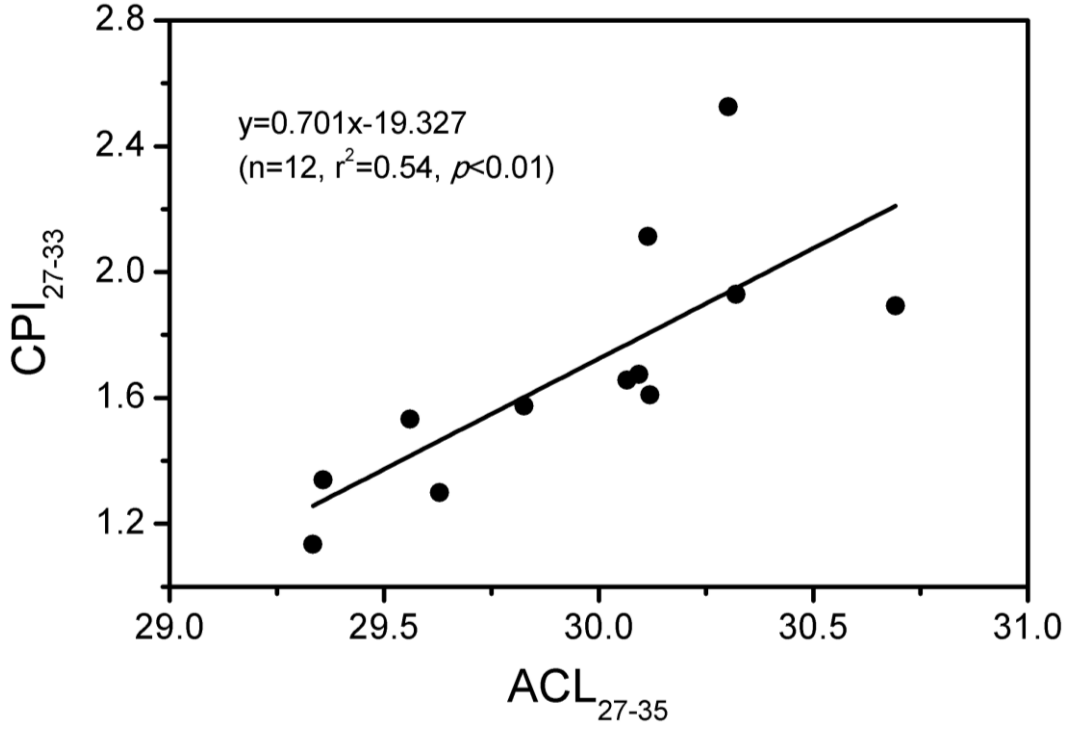

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686 **Figure 3**

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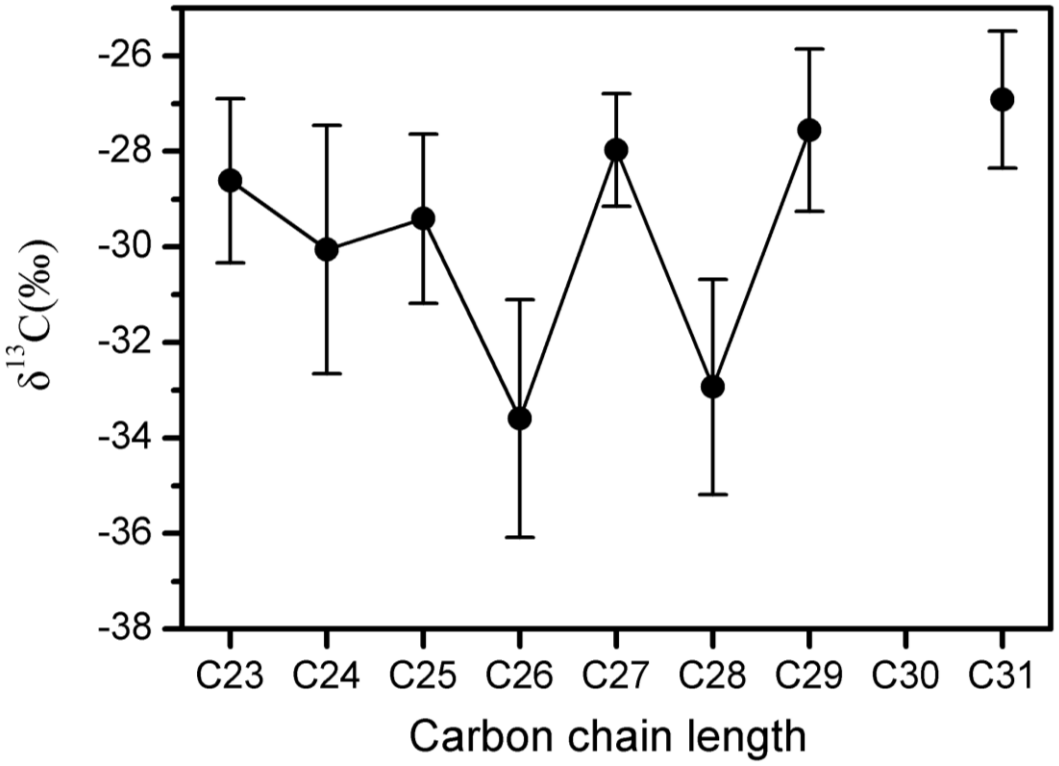

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690 **Figure 4**

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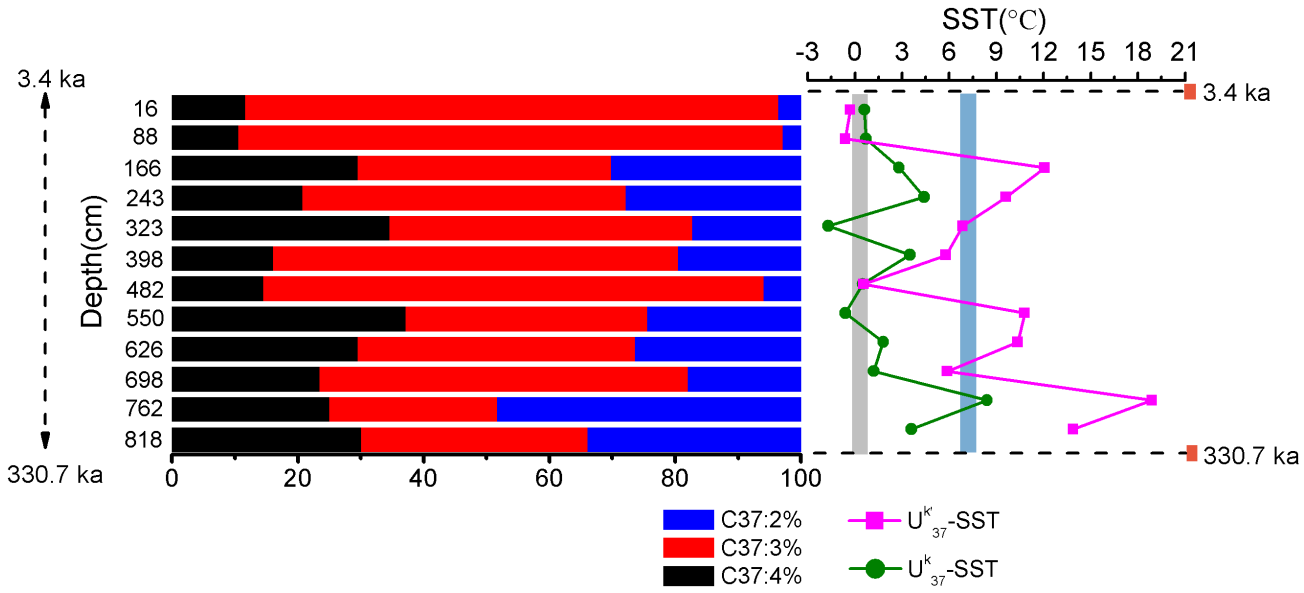

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694 **Figure 5**

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