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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

Investigating organic compounds in marine sediments can potentially unlock a wealth of new information in these 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, located in the far reaches of the Pacific sector of the Southern Ocean. We analyzed a suite of organic compounds in the core. The results show abundant long-chain *n*-alkanes (C_{29}-C_{35}) with predominant odd-over-even carbon preference, suggesting 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 plant waxes. In the analysis, we found that the mid-chain *n*-alkanes (C_{23}-C_{25}) have a small odd-over-even carbon preference, indicating 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 the 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 the 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 essential 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 westerly winds and ACC's location and intensity 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 are the major components of *n*-alkanes in the surface ocean sediments around Antarctica. These compounds mainly derived from phytoplankton and bacteria based on carbon preference index (CPI) and specific-compound carbon isotopic values (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 latitudes of the Southern Ocean are usually considered to be little influenced by river and continent soils, based on the above results, the sources of *n*-alkanes in the ocean sediments are thought to be complicated; thus their eco-environmental implications are still being explored.

Subtropical to polar sea surface temperature (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 $C_{37:4}$ 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 in middle and low latitude marine environments. However, our knowledge on the application of alkenone paleothermometry in the high latitudes of the Southern Ocean is still largely insufficient. A few examples exist, such as that $C_{37:4}$ methyl alkenone was not detected in the 10-12℃ waters. 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 relative abundance of $C_{37:4}$ alkenone in the surface sediments showed no significant relationship with modern SST, suggesting that the $U^{k'}_{37}$ index may be 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 the U^{k}_{37} records display better agreement with planktic foraminifera $\delta^{18}O$ and other SST records at the same sites, suggesting the U^{k}_{37} is more suitable for SST reconstructions in the subantarctic Pacific. 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) is necessary to better understand the role of the Southern Ocean in the context of global climate change. Before carrying out such work, it is crucial 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 of long-chain *n*-alkanes (C_{23}-C_{31}) in the ocean sediments from one core in the South Pacific sector of the Southern Ocean (R23, 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 alkenone, and (c) to assess the applicability of the alkenones indices in the high latitudes of the Southern Ocean for reconstructing past climate changes.

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 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 are present throughout the core with relatively high abundance. No obvious bioturbations were observed in this core. 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 (2-3 g) 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.

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 μm). 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 *Emiliania 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*-alkanes was performed using a gas chromatograph with a DB-5MS column (60 m × 320 μm × 250 μm) interfaced to a Thermofisher MAT-253 isotope-ratio mass spectrometer via a combustion interface (960°C) 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°C at 2°C/min, and then held at 280˚C for 15 mins. 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; Vogts et al. 2009). 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 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, Fig. 2). 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. 3). However, there was no apparent predominant odd-over-even carbon preference, and $CPI_{27\text{-}33}$ varied from 1.1-2.5, with an average of 1.7 (Fig. 2). 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 daminant 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. 4).

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 in the sediments. Interestingly, a high abundance of tetra-unsaturated alkenone was found in the sediment samples. The SST estimates we 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 with no predominant odd-over-even carbon preference in the sediment profile (CPI ~1; Fig. 3), and the contamination of petroleum may cause this during coring and sampling. However, our sampling procedures by the crew of the R/V Xuelong in the 31st CHINARE have been devised to prevent any possible contamination by petroleum, and no 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 the 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

(Table 1, Fig. 5). 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 coring and sampling. The abundant mid-chain *n*-alkanes (C_{23}-C_{25}) with no predominant odd-over-even carbon preference were natural characteristics in the sediment samples of core R23.

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). A 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). In our pilot analysis of the 12 samples, the average $\delta^{13}C$ values of *n*-alkanes with different chain lengths 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 are lower than lake sediments (~ -15‰) with shallow water depth from East Antarctica (Chen et al. 2019). Thus, the terrestrial organic matter from ice-free areas of Antarctica transported by ice-rafted debris (IRD) and aeolian may also contribute to mid-chain *n*-alkanes (Chewings et al. 2014). Still, the source from shallow lake sediments at higher latitudes was considered negligible. The $\delta^{13}C$ values of C_{26} and C_{28} are lower than other long-chain *n*-alkanes (Fig. 5), 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. The C_{26} and C_{28} may likely 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 mid-chain *n*-alkanes (C_{23} to C_{25}) have mixing sources, including marine (non-diatom pelagic phytoplankton and marine microalgae) and terrestrial organic matter, but C_{26} and C_{28} *n*-alkanes might be originated mainly 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, ocean plankton,

and sediments eroded from Antarctica. Previous studies have shown that short- and mid-chain *n*-alkanes are predominant in Pleistocene age ocean sediments, modern water column suspended particulate matter in the Ross Sea and Antarctic margin, while long-chain *n*-alkanes have a minor contribution (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). For example, Bendle et al. (2007) studied organic geochemical characteristics in Southern Ocean aerosol samples. The results showed that the abundant long-chain *n*-alkanes with relatively low $\delta^{13}C$ values (-37 to -30.8‰) represented a regional background of well-mixed higher vascular plants through long-range transportation.

The core R23 is near the Antarctic continent, and so the organic matter from Antarctica may 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 from terrestrial material through aeolian transportation is negligible due to the lack of exposed, mature soils in the McMurdo Dry Valleys and Victoria Land (Nylen et al. 2004; Lewis et al. 2008, 2016), as well as the long-distance of the core site from the coast. 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 shallow lake sediments from East Antarctic (no vascular plants are present in the surrounding landmass) were 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 lower than these in the lacustrine sediments from East Antarctica. Therefore, the sources of long-chain *n*-alkanes (C_{27}-C_{35}) from ice-free soils and shallow lacustrine sediments in East Antarctica via dust transport and ocean phytoplankton is negligible.

The ACL of long-chain *n*-alkanes refers to the average number of carbon atoms/molecule and can 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, p < 0.01; Fig. 4). Generally, relatively high CPI values (CPI > 3) indicate long-chain *n*-alkanes from higher vascular plants, while low CPI values (CPI ~1) may imply post-depositional degradation and mature organic matter inputs (Eglinton and Eglinton 2008; Duncan et al. 2019). According to leaf litter degradation experiments, the odd-over-even predominance of *n*-alkanes was observed to decline. The long-chain *n*-alkanes ratios (e.g., C_{31}/C_{29}) were tended to ~ 1 (Zech et al. 2011). Based on this result, it is reasonable to infer that *n*-alkanes in the dust might have experienced a certain degree of degradation during long-range transportation and post-deposition, which could result in low CPI values. Furthermore, relatively low CPI values of 1.1 to 2.5 present in the R23 sediment core may also be considered to microbial degradation under very low sedimentation rates < 2 cm/ka (Tiedemann 2012; Jaeschke et al. 2017; Duncan et al. 2019). 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 seabed surface layers (Duncan et al. 2019). Under the condition of degradation, the $\delta^{13}C$ values of long-chain *n*-alkanes have no obvious difference (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. 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 indicates microbial (chemoautotrophic) activity in this region. Altered or recycled organic matter from Antarctica that has been eroded by glaciers and transported by IRD 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. 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 in our study site is far from the potential source regions of land continents (New Zealand and Australia), it is reasonable to believe that the long-chain *n*-alkanes in the R23

sediment core are primarily derived from terrestrial higher plant leaf wax through long-range eolian transportation.

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 those 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. 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 762 cm 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). Previous studies have demonstrated that the primary drivers for the distributions of C_3/C_4 plants are climatic and atmospheric pCO_2 etc. (Huang et al. 2001; Edwards et al. 2010). Compared with C_3 plants, C_4 grasses usually favor relatively lower pCO_2 and arid conditions due to their greater water use efficiency and carbon concentrating mechanism (Edwards et al. 2010). Therefore, the different contributions of C_3/C_4 plants may be related to 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 (Neff and Bertler 2015). Therefore, these results indicate that the $\delta^{13}C$ values of long-chain *n*-alkanes could be used to reconstruct the past changes of C_3/C_4 plants in the source area and then investigate climatic variations.

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

$C_{37:4}$ alkenone was found in the R23 sediments with relative abundance ranging from 11-37%. This is similar to a previous study in the higher latitude of the Pacific sector of the Southern Ocean (Sikes et al. 1997) but significantly higher than the sedimentary abundance from the lower latitudes 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°C; thus, the 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; Harada et al. 2006, 2012). Analysis of 106 surface water and sediment samples from the Atlantic, Pacific, and the Southern Ocean indicated that the relative abundance of $C_{37:4}$ methyl alkenone had no apparent relationship with SST and salinity. Still, it might respond to some other environmental factors, including growth rate, light, or nutrients (Sikes and Sicre 2002). For example, $\%C_{37:4}$ showed a negative linear correlation with sea surface salinity (SSS), nutrients and late summer SST in the suspended particles and sediment profiles from the Bering Sea (Harada et al., 2012). However, SST and SSS showed a strong negative linear relationship in the north Atlantic and the Bering Sea because of sea ice melting during the summer season, suggesting that the relationship of $\%C_{37:4}$ and salinity may be the artifact the covariance with temperature (Sikes and Sicre 2002). Moreover, up until now, 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.

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 was, as we expected, obviously different (Fig. 6). When the relative abundance of tetra-unsaturated alkenone was higher, we found $U^{k'}_{37}$-SST was 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℃. However, the SST difference calculated by these two indexes is relatively small in the sediment sections of the lower abundance of $C_{37:4}$ alkenone. Based on the average summer SST from the World Ocean Atlas (WOA09) data set (Locarnini et al. 2010), the modern sea surface temperature in our study site was about 0-1℃. For the historical period, the highest subsurface temperature is about 4-5℃ during the Holocene at similar latitudes, including the eastern Antarctic continental margin (Kim et al. 2012) and western Antarctic Peninsula (Etourneau et al. 2013). According to modern observation and SST reconstruction during the late Pleistocene, we suggest that the highest SST in our study site should be lower than 5℃ in the warmer periods, which was much lower than $U^{k'}_{37}$-SST. Therefore, all these results indicate higher $\%C_{37:4}$ is most likely controlled by extremely low SST in the R23 sediments and the U^{k}_{37} index is more feasible than $U^{k'}_{37}$ in the relatively higher latitudes of the Southern Ocean.

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 influencing factors

on the relative abundance of $C_{37:4}$ alkenone are complex, a statistically significant relationship between U^{k}_{37} index and SST has been found in the surface sediments from high latitudes of the North Atlantic Ocean (Rosell-Melé et al. 1995). This result further validates the general applicability of the U^{k}_{37} as a reliable climatic proxy for SST reconstructions in the relatively cold climate regions (Rosell-Melé et al. 1994, 1995). The latitude was relatively high at our study site, and the modern annual summer SST was lower than 1°C. The marine algae may synthesize more $C_{37:4}$ alkenones to adapt to the extremely cold conditions. Notably, 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 the U^{k}_{37} index is feasible for reconstructing past SST in the Southern Ocean, but 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.

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 dust from Australia and New Zealand. The mid-chain *n*-alkanes (C_{23}-C_{25}) preserved in the sediments have low odd-over-even carbon preference, perhaps 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. Furthermore, the relative abundance of tetra-unsaturated alkenone in the sediments varies from 11 to 37%, higher than those previously reported in the lower latitudes of the South Pacific Ocean. We conclude that tetra-unsaturated alkenones are sensitive markers of low SSTs, suggesting 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. 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. The 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 concentrations (C_{23}-C_{35}), ACL ($C_{27\text{-}35}$-C_{35}) and CPI (C_{27}-C_{33}) values of *n*-alkanes at different depths of the sedimentary section.

Fig. 3. The relative abundance of long chain *n*-alkanes (C_{23}-C_{35}) at different depths of the sedimentary section.

Fig. 4. Relationship between $ACL_{27\text{-}35}$ and $CPI_{27\text{-}33}$ of long chain *n*-alkanes.

Fig. 5. The average $\delta^{13}C$ values of *n*-alkanes. Error bars represent 1 standard deviation of 12 samples.

Fig. 6. 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.

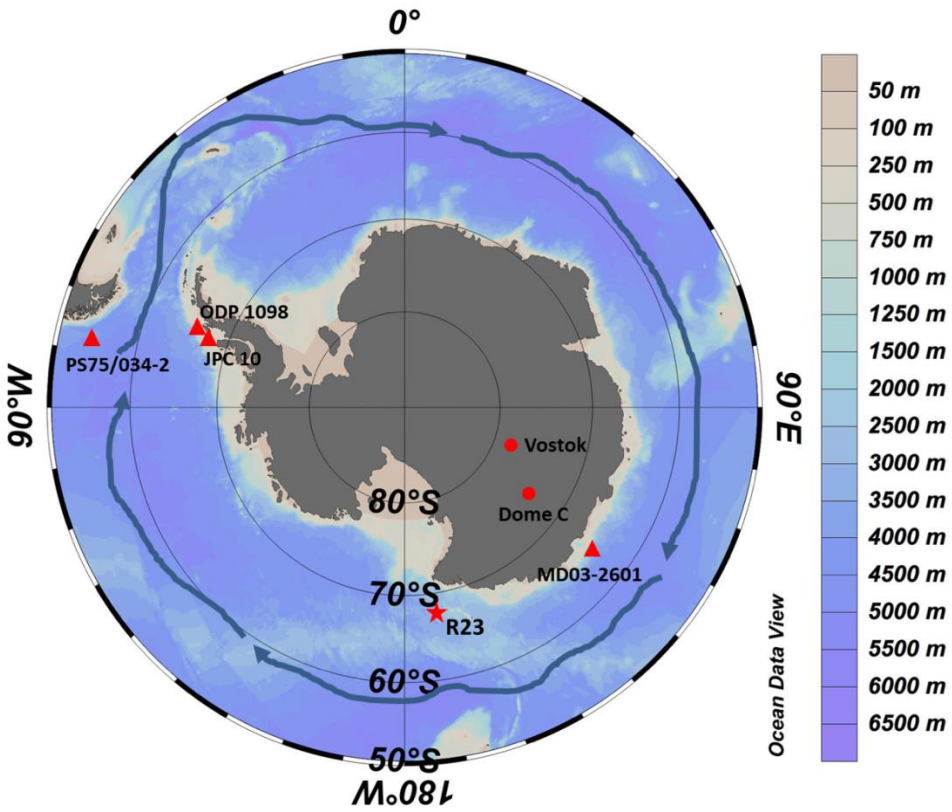
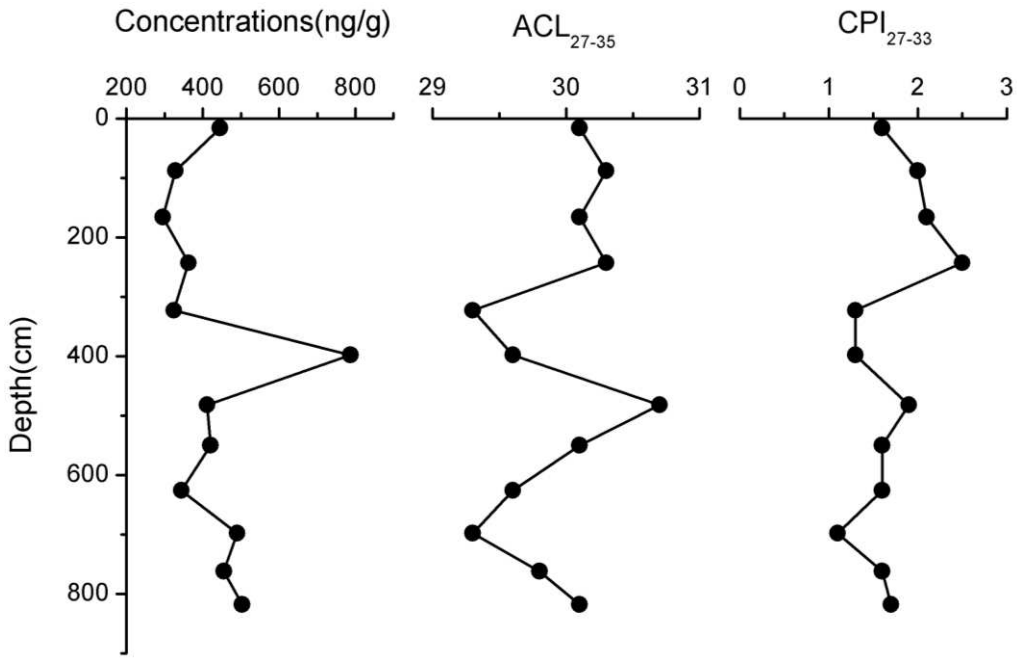

0°
90°W
90°E
180°W
80°S
70°S
60°S
50°S
ODP 1098
JPC 10
PS75/034-2
Vostok
Dome C
MD03-2601
R23
50 m
100 m
250 m
500 m
750 m
1000 m
1250 m
1500 m
2000 m
2500 m
3000 m
3500 m
4000 m
4500 m
5000 m
5500 m
6000 m
6500 m
Ocean Data View

Figure 1



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653 **Figure 2**

654

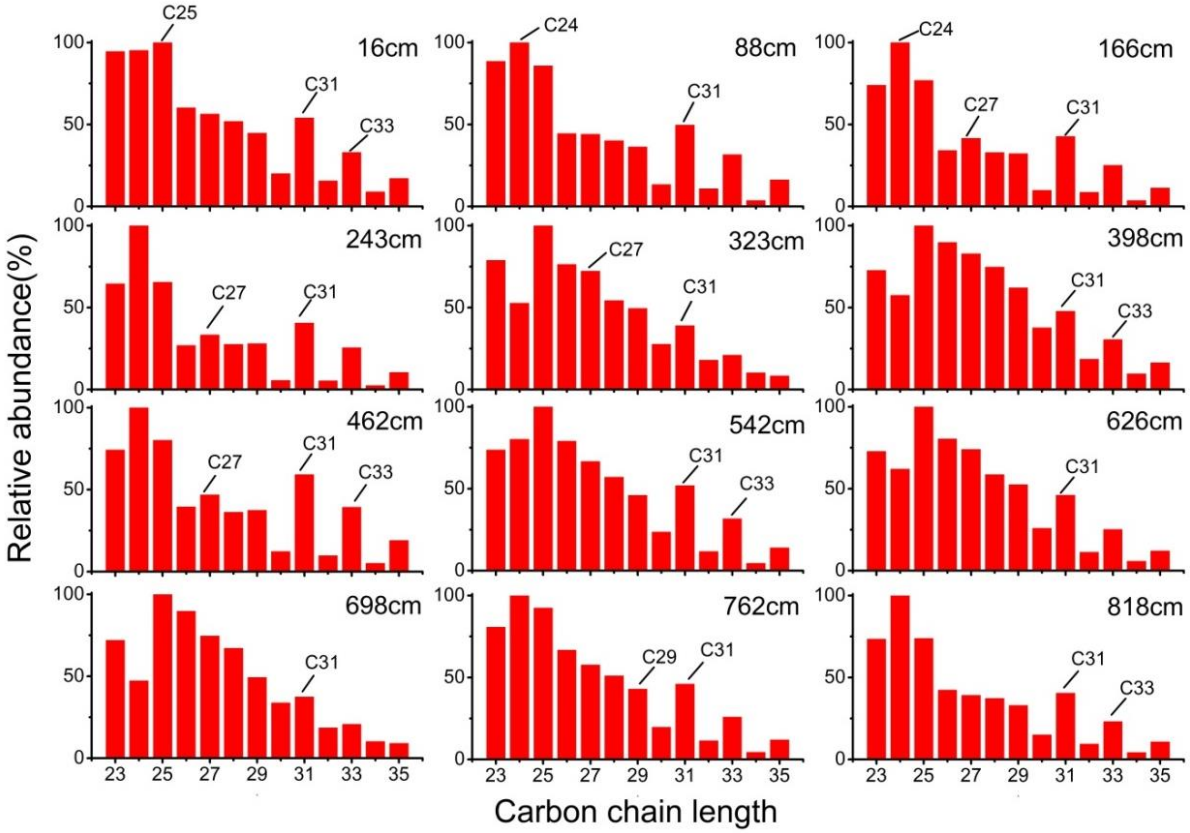

Relative abundance(%)
Carbon chain length
16cm
C25
C31
C33
88cm
C24
C31
166cm
C24
C27
C31
243cm
C27
C31
323cm
C27
C31
398cm
C31
C33
462cm
C27
C31
C33
542cm
C31
C33
626cm
C31
698cm
C31
762cm
C29
C31
818cm
C31
C33
0
50
100
23
25
27
29
31
33
35

Figure 3

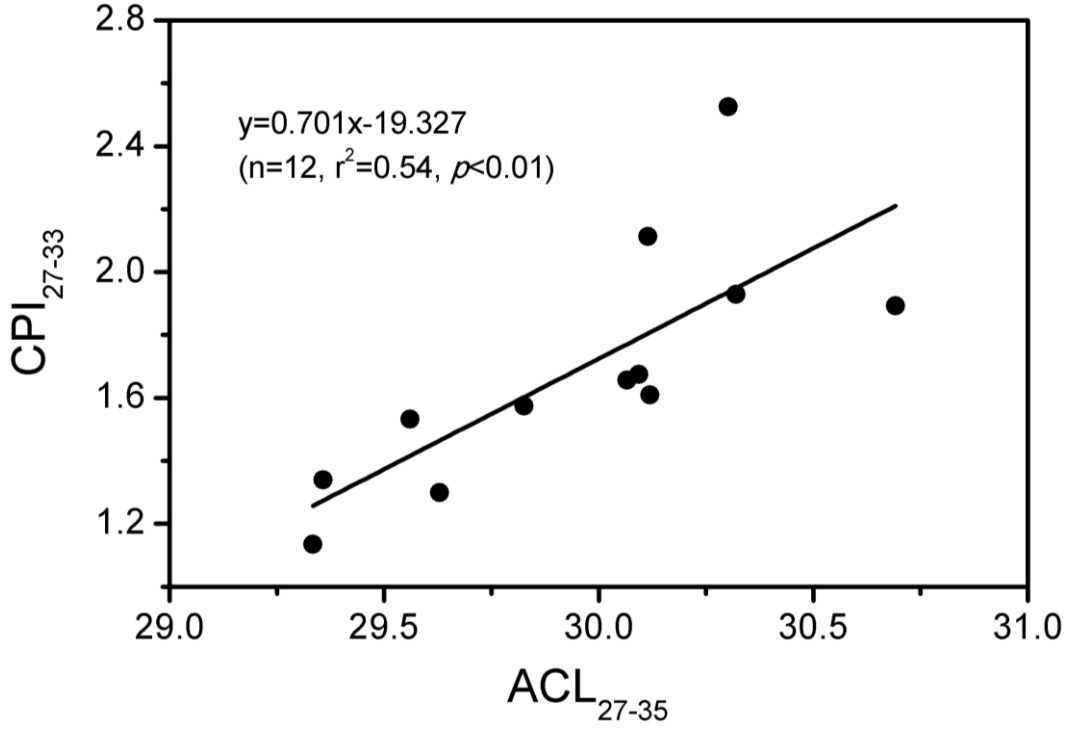
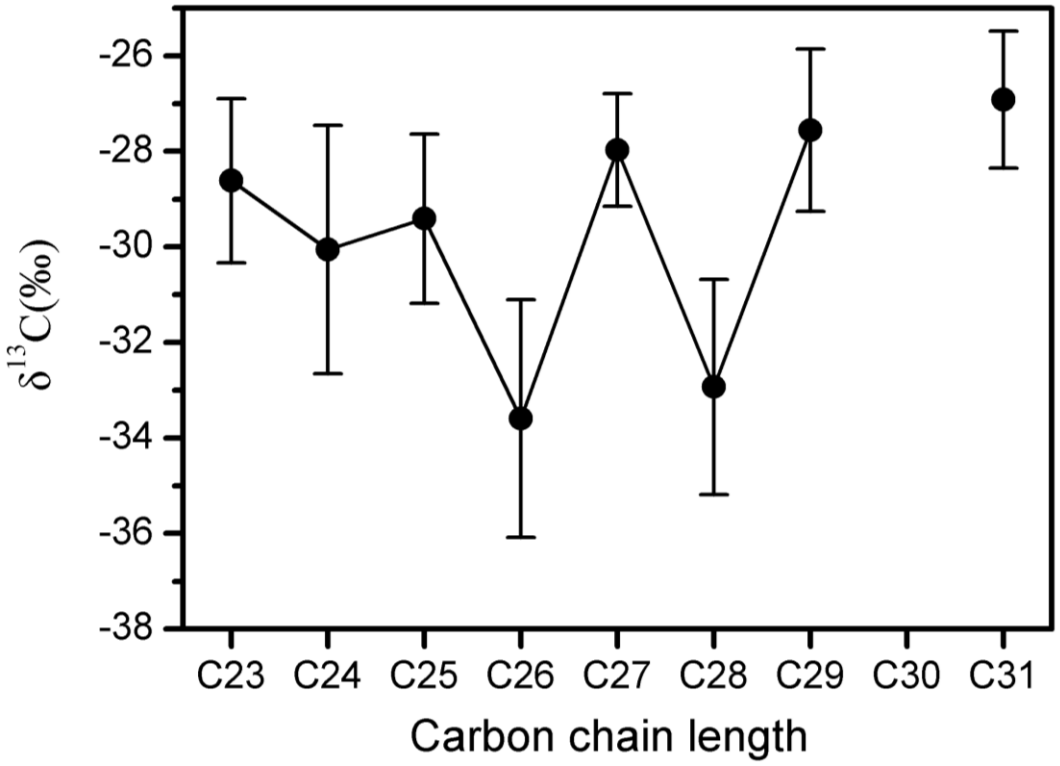

y=0.701x-19.327
(n=12, r2=0.54, p<0.01)
CPI27-33
ACL27-35
2.8
2.4
2.0
1.6
1.2
29.0
29.5
30.0
30.5
31.0

Figure 4



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665 **Figure 5**

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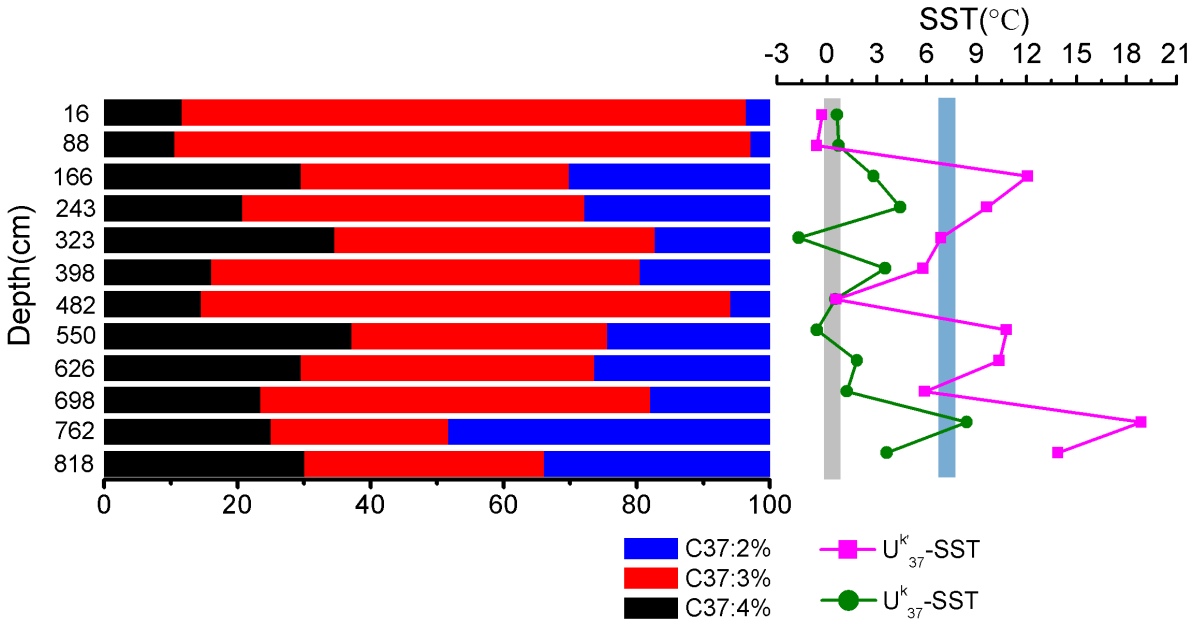
SST(°C)
-3 0 3 6 9 12 15 18 21
Depth(cm)
16
88
166
243
323
398
482
550
626
698
762
818
0 20 40 60 80 100
C37:2%
C37:3%
C37:4%
U^k'37-SST
U^k37-SST

Figure 6

Figures

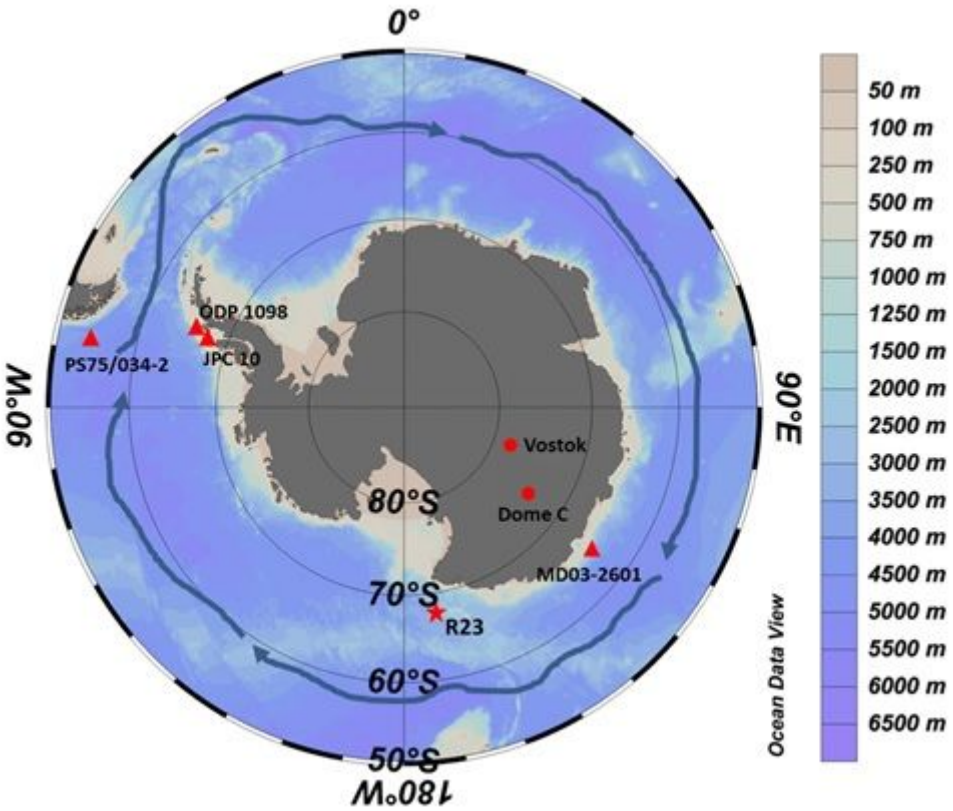

Figure 1

Map of the Southern Ocean and the continent of Antarctica. The 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_37^k index (Ho et al., 2012), whereas other sediment cores (ODP 1098, JPC 10 and MD03-2601) were used for TEX86 (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.

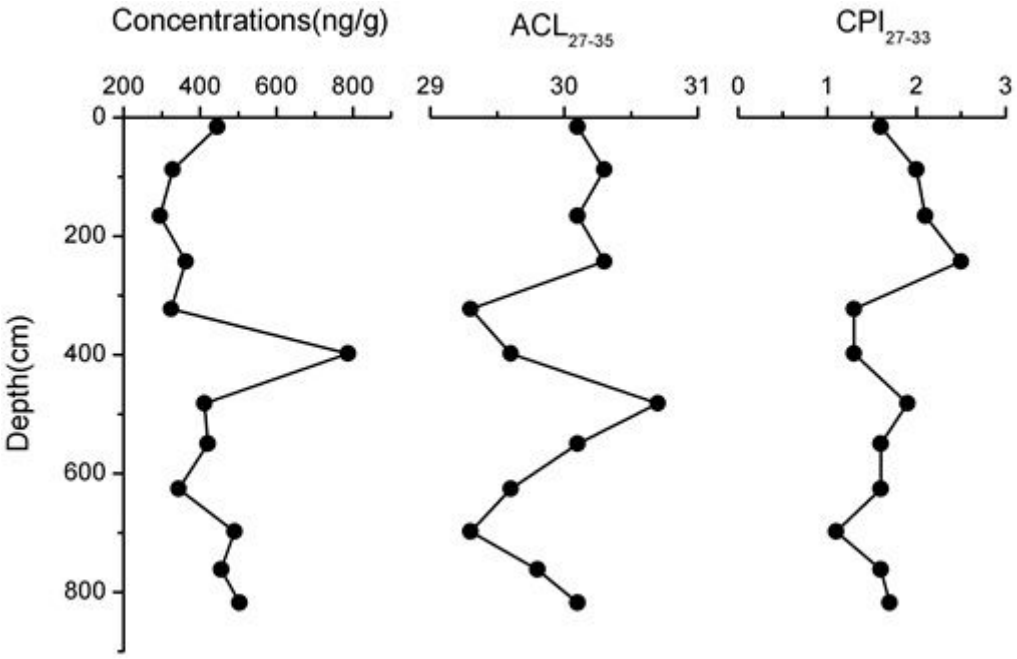

Figure 2

The concentrations (C23-C35), ACL (C27-35-C35) and CPI (C27-C33) values of n-alkanes at different depths of the sedimentary section.

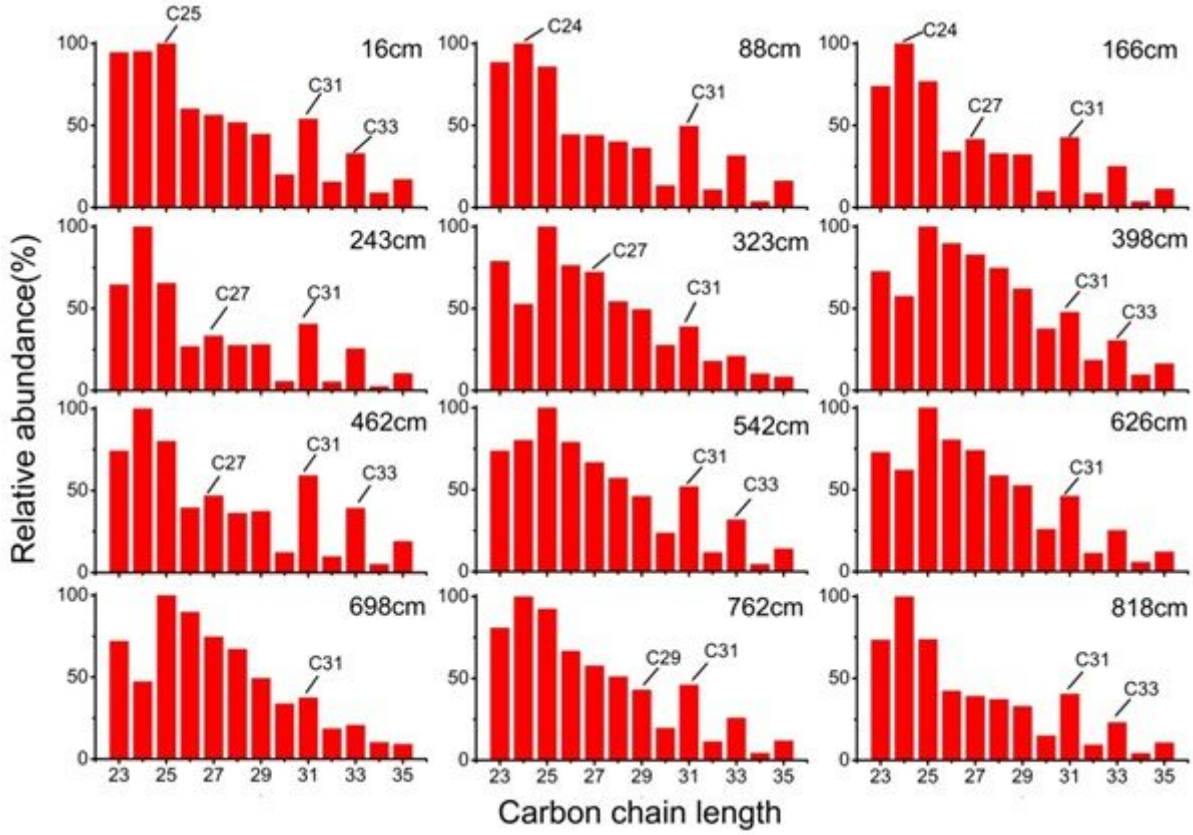

Figure 3

The relative abundance of long chain n-alkanes (C23-C35) at different depths of the sedimentary section.

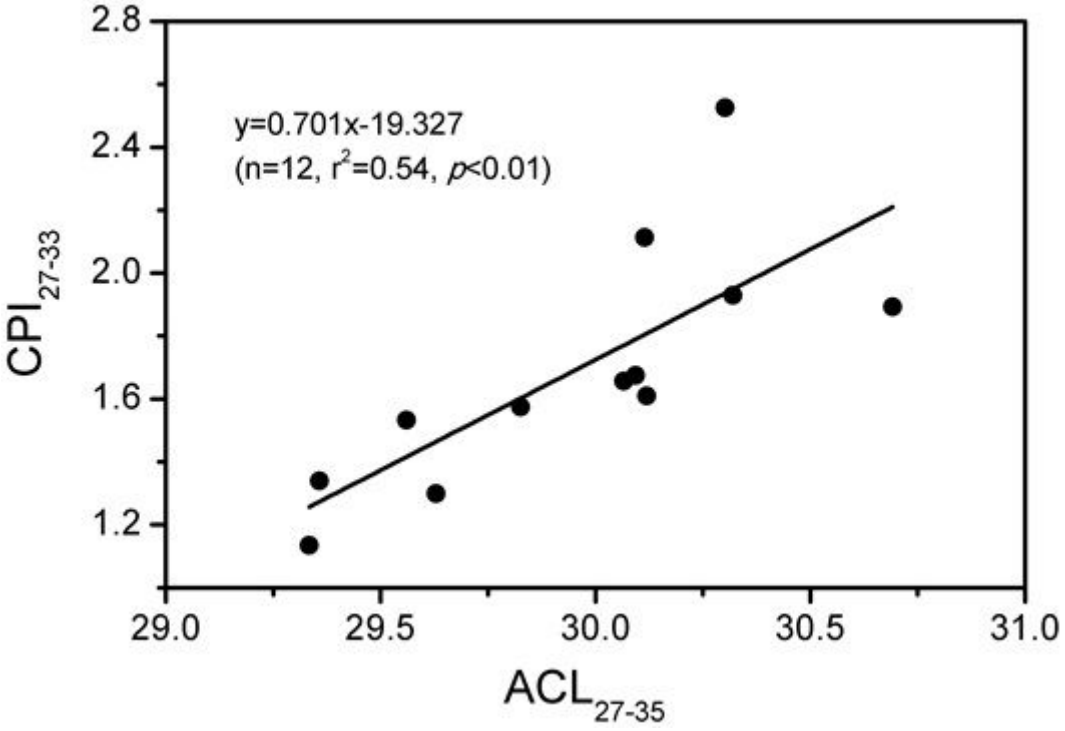

Figure 4

Relationship between ACL27-35 and CPI27-33 of long chain n-alkanes.

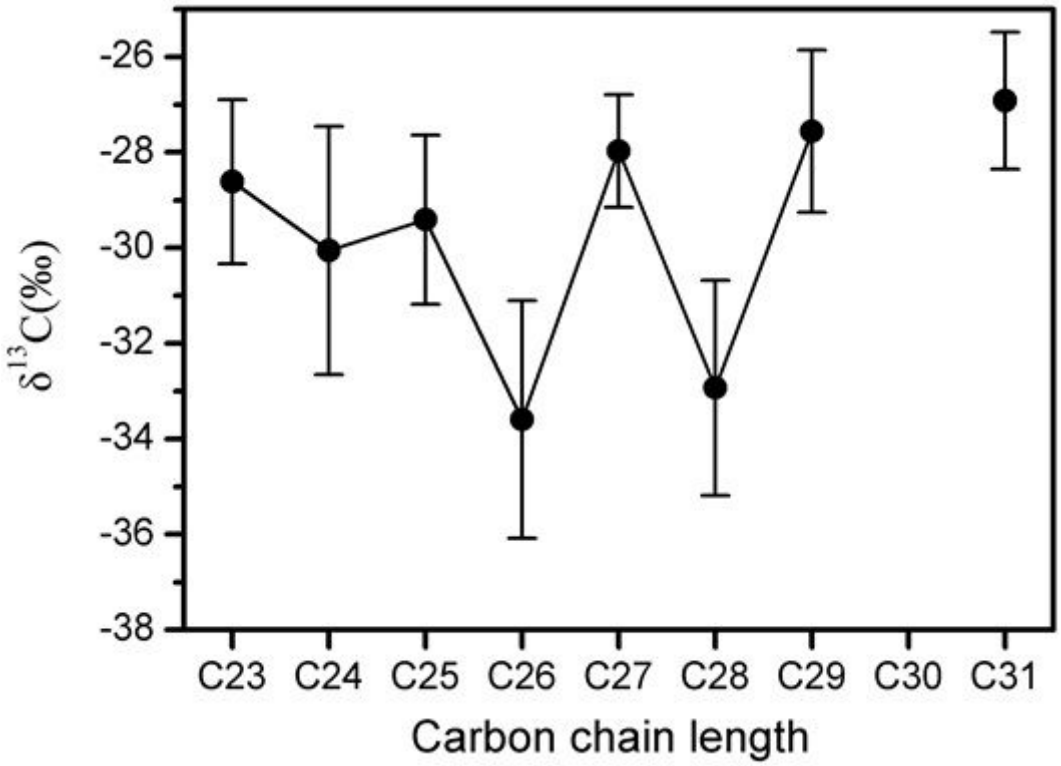

Figure 5

The average δ13C values of n-alkanes. Error bars represent 1 standard deviation of 12 samples.

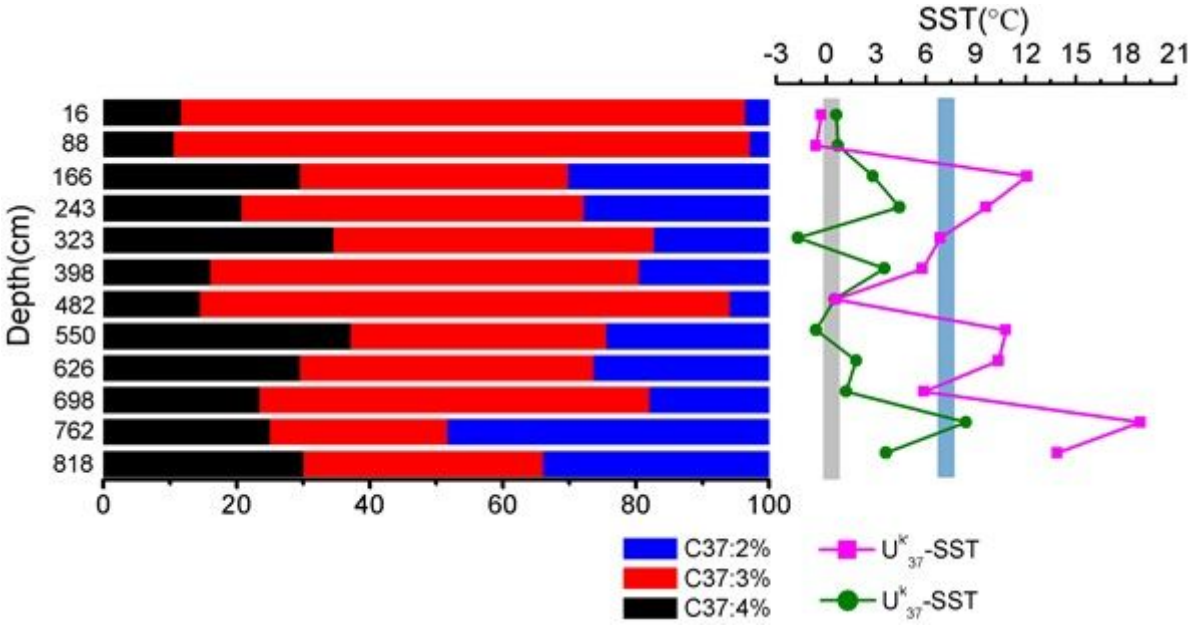

Figure 6

The relative abundance of C37:4, C37:3 and C37:2 alkenones and the calculated sea surface temperature based on U_37^k and U_37^k' 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.

Supplementary Files

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