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Organic geochemical characterization on a seal excrement sediment core from Fildes Peninsula, Western Antarctica

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Abstract Organic geochemical analysis was performed on a sediment core HN1 from Fildes Peninsula on King George Island, Western Antarctica. Short-chain *n*-alkanes were the main components of the aliphatic hydrocarbons present, and they were likely to be from algae and bacteria; *n*-C_{23} was likely derived from moss. Fecal sterols and phytol dominated the alcohol composition, and may have come from seal feces and vegetation, respectively. The fluctuations in their concentrations generally have responded to historical changes in the ecosystems near the region. The even-carbon fatty acids, such as *n*-C_{16}, *n*-C_{18} and *n*-C_{24}, dominated the alkenoic acid composition, which mainly originated from bacteria, moss and zooplankton. The low concentrations of unsaturated fatty acids showed a predominance of $C_{16:1}$ and $C_{18:1}$ unsaturated acids, and demonstrated that the sediment was well preserved and had a simple and stable source of organic materials.

Keywords **Seal, biomarker, fecal sterol, carboxylic acid, Western Antarctica**

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0 Introduction

Due to its remoteness and weak biological activity, the Antarctic region is an ideal place for studying global changes caused by anthropogenic activities and one of kernel regions for international global change studies. As the top predator in the food chain of Western Antarctica, there is a large population of seals which are sensitive to changes in the Antarctic ocean environment and ecosystems; thus they can be a good indicator of environmental changes in the marine system[1-4]. Current paleoecological research into Antarctic seals mainly focuses on isotope studies and inorganic geochemical analysis of seal hairs, seal dropping affected lake sediments, evolution of the paleoclimate and paleoenvironment, and the effect of contamination[1-14] but reports on the paleoecology of seals using organic geochemical methods are very limited[15-16].

Fildes Peninsula is the largest ice-free area in the King George Island region, Western Antarctica. Because of the large biomass, the eighth Antarctic Treaty Consultative Meeting designated Fildes Peninsula as the site of special scientific interest and an hotspot and ideal area for Antarctic environment and global change research[15-16]. There are several Antarctic Specially Protected Areas (ASPA) and Antarctic Specially Managed Areas(ASMA, known as Sites of Special Scientific Interest[SSSI] before 2002). In this study, we performed organic geochemical analysis on a sediment core from Fildes Peninsula on King George Island, Western Antarctica, in order to explore the source of organic material input and depositional environment in this region.

1 Study area and sample collection

Fildes Peninsula is the largest oasis in the King George Island, Western Antarctica with a total area of 38 km^2 (8 km × 2.5–4.5 km) (Figure 1)[17]. In this study, some sediments were collected from a drilling core HN1 (355 mm long) in a terrestrial catchment (62°11′57″S, 59° 58′48″W, at an altitude of 2 m), which is in a depositional

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basin in the first marine terrace on the Fildes Peninsula (Figure 1). During the field investigation, a PVC pipe with a diameter of 120 mm was pushed vertically into the catchment center to excavate the sediment core. After the PVC pipe was retrieved, both ends were hermetically sealed.

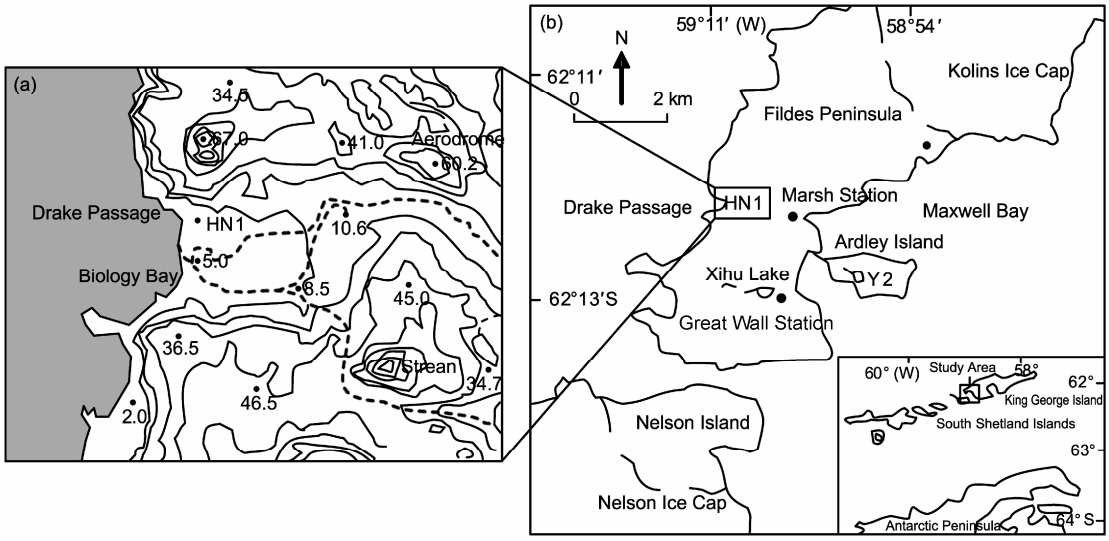

Figure 1 Map of Fildes Peninsula showing the HN1 sampling site.

2 Sample analysis

The top section sediments (255 mm) of the core HN1were identified as seal excrement deposition (Table 1)[18] and sliced at 5 mm intervals. Several subsamples of key sections were selected for a bioelement profile for the sediment core HN1[18]. The subsamples were freeze-dried prior to analysis. The detailed analytical procedures have been described previously[15]. Briefly, sediment samples were Soxhlet extracted with 2:1 (v/v) dichloromethane/methanol for 72 h. The extracts were concentrated by rotary evaporation and then saponified using 0.5 M KOH/MeOH. Neutral lipids were partitioned out of the basic solution with hexane. The pH value of the saponified extract was then adjusted to a value of 2.0 with 6 N HCl and the acidic lipids were extracted with 20% dichloromethane in hexane. The acidic lipids were allowed to sit in the presence of anhydrous Na_2SO_4 overnight in order to remove trace water. The neutral lipids were further separated using a 5% deactivated silica gel for column chromatography using solvents of increasing polarity from hexane through methylene chloride. The fractions containing hydrocarbons (eluted with hexane) and *n*-alkanols/sterols (eluted with methylene chloride) were collected separately. The alcohol and acid fractions were treated with BSTFA (*N*, *O*-bis-trimethylsilyltri Xuoroacetamide) to form trimethylsilyl (TMS)-ether derivatives, and then analyzed using a HP 5972 gas chromatography-mass selective detector (GC-MSD) in SCAN mode. The GC column used was a 50 m × 0.32 mm i. d. × 0.17 μm film thickness DB-5 capillary column. All analyses were performed in the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science (CAS).

Table 1 Sample numbers and the depths of the sediment core HN1

Sample number	HN1-23	HN1-26	HN1-32	HN1-37	HN1-42	HN1-46	HN1-47
Depth /mm	245	230	200	175	150	130	125
Sample number	HN1-48	HN1-49	HN1-52	HN1-57	HN1-62	HN1-67	HN1-71
Depth /mm	120	115	100	75	50	25	5

3 Result and discussion

3.1 Aliphatic hydrocarbons

The composition and concentrations of aliphatic hydrocarbons at the three depths (100 mm, 150 mm and 245 mm) of sediment core HN1 are plotted in Figure 2. The composition of the different aliphatic hydrocarbons, mainly C_{14}-C_{25}, at different depths were similar. The concentrations of long even-chains were low, and those of C_{14}, C_{16} and C_{23} were high (Figure 2). The short even-chain hydrocarbons in the sediment core HN1 were mainly derived from algae and

bacteria[19]. The even-dominance of hydrocarbons might be related to the salt water or saline depositional environment[20]. The sediment core HN1 was collected from a terrestrial catchment of a depositional basin in the first marine terrace. The basin may have experienced the process of transgression and natural reclamation, and thus the HN1 core was the sediment product of seawater.

Moss is the primary vegetation around the sampling site on the Fildes Peninsula and the dominating plants in the sediment core HN1. Zhang et al. (2000) proposed that the hydrocarbons of sediments from frozen lakes on the Fildes Peninsula were dominated by *n*-C_{23} and mainly originated from moss[21]. Therefore the *n*-C_{23} in the sediment core HN1 likely originated from mosses.

In the sediment core HN1, the aliphatic hydrocarbons contained relatively high levels of mono-olefins dominated by $C_{14:1}$, $C_{16:1}$ and $C_{18:1}$, and the concentrations of alkenes were lower than those of corresponding alkanes. The $C_{27:1}$-$C_{29:1}$-dominated alkenes have been reported in the sediment of Richardson Lake on Enderby Island, East Antarctica[22]. Volkman et al. (1999) found $C_{29:1}$, $C_{34:1}$, $C_{34:2}$, $C_{34:3}$ and $C_{34:4}$ alkenes in the sediment of Ace Lake on Vestfold Oasis, East Antarctica[23]. Matsumoto et al. (1997) showed that the alkenes in the sediment of Vanda Lake, McMurdo, were derived from epibenthic algae[24]. Also, Zhang et al. (2000) found that alkenes in lake sediments in the Fildes Peninsula, Western Antarctica, were dominated by $C_{23:1}$ and $C_{25:1}$[21]. Wang et al. (2007) made similar observations for penguin ornithogenic sediments on Ardley Island, Western Antarctica[25]. Abundant alkenes detected in sediments indicated that organic matter was well preserved and natural hydrogenation was insignificant.

Unsaturated hopenes usually originate from C_{30} hopanoids or the precursor of C_{35} bacteriohopane tetrols, which are regarded as biomarkers of bacteria and epiphyte activities[26]. Hop-22(29)-en and hop-17(21)-en were detected in the HN1 sediments. Their concentrations increased with depth, suggesting more activity from bacteria and epiphytes at the bottom than on the surface.

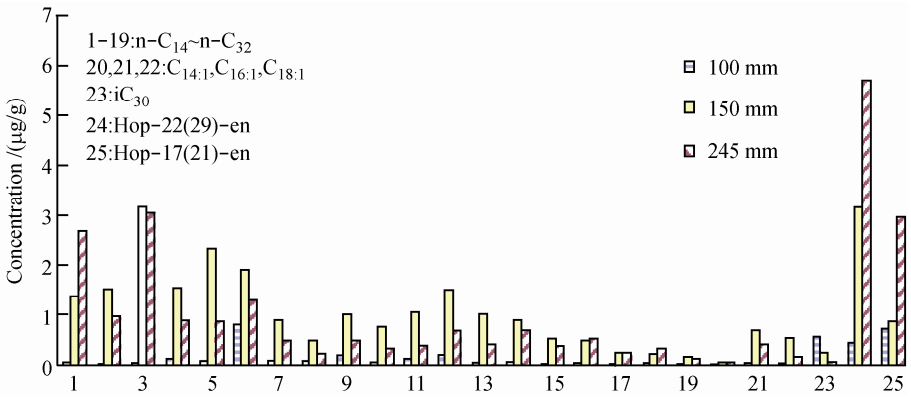

Figure 2 Concentrations and distribution of alkanes in the sediment core HN1 at the three depths of 100, 150 and 245 mm.

3.2 Alkanol and sterol compositions

The composition and concentrations of the alcohols at three depths (100 mm, 150 mm and 245 mm) of the sediment core HN1 are plotted in Figure 3. High concentrations of phytol and sterols exist in the HN1 sediments. The plant sterols were dominated by sitosterol, and feces sterols dominated by coprostanol, epicoprosterol, cholesterol and cholestanol. The low concentration of *n*-alkanols had a carbon number range of C_{12}-C_{26}, and peaked at C_{18} and C_{26}. In general, aquatic algae and bacteria have *n*-alkanol distributions were dominated by C_{12} to C_{22} components[27-28]. The presence of *n*-$C_{12\text{-}22}$ alkanols indicates the presence of low level lake plants, C_{24} submerged macrophytes[29-31], and $C_{26\text{-}30}$ land based plants[32-33]. On the Antarctic continent, Wang et al. (2007) reported that algae exhibited *n*-alkanol distributions dominated by C_{16}-C_{20}, and mosses and lichens present were indicated by *n*-alkanols C_{22}-C_{26} and C_{28}-C_{30}, respectively[15]. Wang (2007) and Huang (2010) used phytols to reconstruct the historical changes of vegetation abundance in penguin colonies[15-16]. Crawling seals could bring land plants into the lake catchment[34-35], and as a result the organic matter in the sediment core HN1 could come from both aquatic algae and land-plants. Considering the sampling site and the habitat of the seals, we inferred that the *n*-alkanols originated from algae and mosses and the high concentration of phytols present indicated abundant plant input[36].

Considering the sampling site and abundant seal hairs (which were found the sediment core HN1), we assumed that the sterols came from seal excrement. Venkatesan and Santiago (1989) reported that seals and sea lion excrement contained a very low level of coprostanol and no epicoprostanol and epicoprostanol, but in fresh fecal samples cholesterol accounted for 82% of the total sterols[37]. Martins et al. (2002) concluded that cholesterol typically accounted for more than 90 % of the sterols in the

fresh feces of *Leptonychotes weddellii*, *Mirounga leonine*, *Hudrurga leptonyx*, and *Arctocephalus gazella*[38]. Our study area and sampling site was close to theirs, but the proportion of cholesterol in sterols of the sediment core HN1 was only 50 % and the proportion of epicoprostanol was 38 %. This difference was likely due to the abundant bacteria and epiphyte input. Some anaerobic bacteria can convert coprostanol to epicoprostanol in nature[39]. Bull et al. (2002) proposed that cholestanol found in sediments was likely due to natural hydrogenation of cholesterol[40]. Martins et al. (2002) noted that in Antarctic sediments, epicoprostanol dominated over coprostanol[38]. The distribution profiles of these sterols in the sediment core HN1 can provide useful information for future reconstruction of historical seal population changes and the responses of ecosystems to environmental changes.

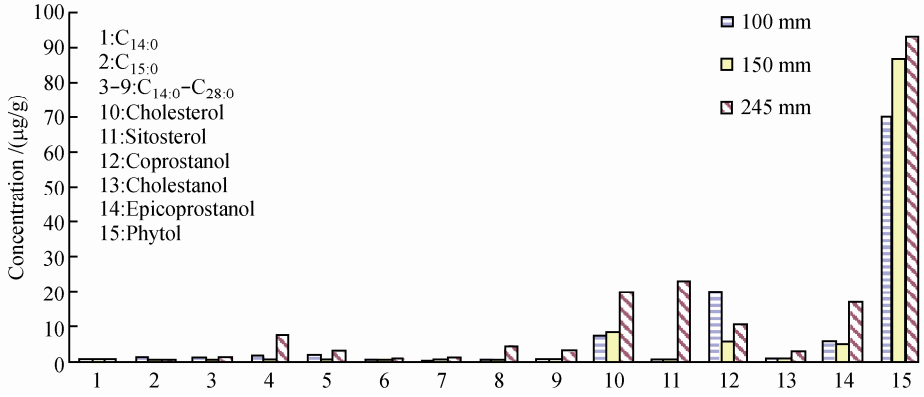

Figure 3 Composition and concentrations of alcohols in the sediment core HN1 at the three depths of 100, 150 and 245 mm.

3.3 Carboxylic acid compositions

The composition and concentrations of carboxylic acids of the sediment core HN1 at the three depths (100 mm, 150 mm and 245 mm) are shown in Figure 4. The composition of carboxylic acids ranged from C_{12} to C_{26} with maximum peaks at C_{16} and C_{24}. The levels of unsaturated acids, mainly peaked at $C_{16:1}$ and $C_{18:1,}$ were low cencentrations. These results are similar to those from penguin ornithogenic sediments on Ardley Island, Western Antarctica[25]. The short even-chain C_{12}-C_{20} *n*-alkanoic acids were thought to mainly originate from algae, zooplankon and bacteria[31, 41-44].

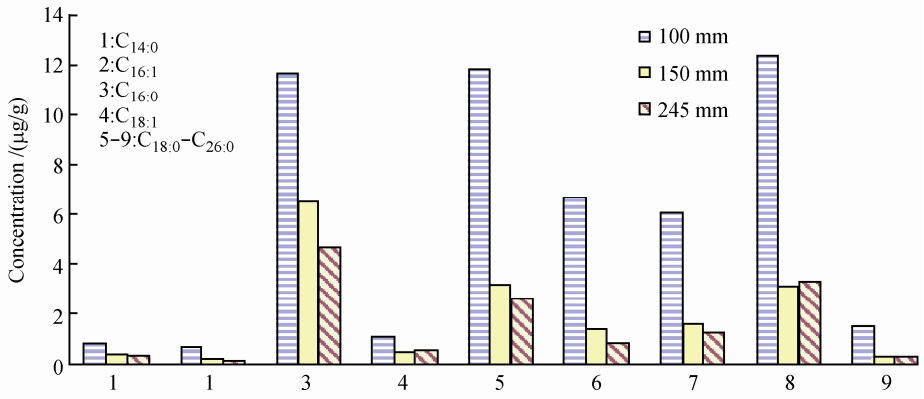

Figure 4 Composition and concentrations of carboxylic acids in the sediment core HN1 at three depths of 100, 150 and 245 mm.

Because of its sensitivity to change, the $C_{18:1}$ acid is often used as indicator of bio-origin[45]. The unsaturated acids in the sediment core HN1, mainly peaked at $C_{16:1}$ and $C_{18:1,}$ but they were at low levels as noted above and their distributions were stable in the whole sediment core. Therefore, the source of organic matter in the sediment core HN1 from Antarctica was stable and simple than other regions. Unsaturated fatty acids, especially at the ratio of $C_{18:2}$ over $C_{18:0}$, are used as indicators of air temperature variability[46]. Larger ratios correspond to lower temperatures, and larger ratios are characteristic of organic matter in Antarctic lake sediments[46]. Zhang et al. (2000) reported that the ratio of $C_{18:2}$ over $C_{18:0}$ on the Fildes Peninsula of King George Island, Western Antarctica was higher than that on the Gucheng Lake, Nanjing[21], and that the changes in the ratio were used in paleoclimate reconstruction[21]. In the

HN1 sediments, $C_{18:2}$ acid was not detected which was similar to some observations from penguin ornithogenic sediment on Ardley Island, Western Antarctica[25]. The reason for these results remains unclear and further research is needed.

4 Conclusions

（1） The *n*-alkanes in the sediment core HN1 were mainly derived from bacteria, algae and mosses. The bacteria and epiphytes at the bottom were more active than at surface. Abundant mono-olefines indicated that organic matter in the sediment core HN1 was well preserved.

（2） Fecal sterols and phytol in the sediment core HN1 might originate from seal feces and plants. High concentrations of fecal sterols indicate that seal fecal sediment occurred in the sediment core HN1. The fecal sterols and phytols can be used as a tool to reconstruct ecosystem evolution of the seal colony on Fildes Peninsula.

（3） The alkenoic acids in the sediment core HN1 originated from algae, plankton and bacteria. The distributions of $C_{16:1}$ and $C_{18:1}$ unsaturated acids suggested that the source of organic matter in the sediment core HN1 from Antarctica was stable and simple than other regions.

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