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# Molecular organic geochemistry of ornithogenic sediment from Svalbard, Arctic

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**Abstract** The molecular biomarker compositions of the ornithogenic sediments (YN), from Svalbard, Arctic were investigated. The results showed that n-alkanes had a bimodal pattern and their odd-even preference was not obvious. The alkanes contained unresolved complex mixtures (UCM) and relatively high levels of pristine and retene, indicating pollution from the nearby coal mines. The *n*-alkanols in the sediments had even-to-odd preference, and they might originate mainly from modern biota. Sistosterol, the main sterol in herbivores feces, was the dominant sterol, indicating that sitosterol might be a good biomarker of input from the birds feces in the sediments. The fatty acids of the sediments showed even-to-odd preference, and the main unsaturated fatty acid is $C_{18:1}$ acid. The α-hydroxyl acids and ω-hydroxyl fatty acids were also detected in the sediments. In summary, the organic matters in the YN sediments were from the adjacent coal mines, bird feces, and plants.

**Key words** Arctic, Ornithogenic Sediment, biomarkers, sitosterol, alkanols, fatty acids.

## 1 Introduction

Bird is an important component of the global ecosystem. The fluctuation of birds' population can reflect the influence of the global climate changes on the ecosystem[1]. One of the records of historic activities of seabird is ornithogenic sediments. For example, studies of the ornithogenic sediments in Antarctica, South China Sea[3] and the Arctic showed that the bioelements in those ornithogenic sediments can be applied as proxies for historical seabird populations. The comparison between changes of bird population and climate changes indicated that the climate changes were one of the major and direct factors influencing seabird populations[1-3].

Svalbard (78°55.6'N, 11°56.4'E), Arctic, is an important international scientific base for Arctic research and a sensitive area for studying the climate changes of Holocene in the Arctic[4-6]. We collected a 118 cm-long sediment core (named YN) in a palaeo-notch from the first strandflat in the area. The sampling site is located at the Bird Sanctuary with many breeding seabirds around. Elemental and isotopic geochemical analyses of the sediment profile showed that it contained significant amount of seabird dropping. Chronological studies of the core indicated that it recorded seabird populations between 12 ka B. P. and 4 Ka B. P. (AMS $^{14}C$) (Liguang Sun, unpublished results). The present study analyzed the molecular organic geochemistry of the ornithogenic sediment core YN and examined the effects of the guano on the surrounding environments.

## 2 Sampling Site and Lithology

Svalbard archipelago, with an area of 62, 700 $km^2$, is 1, 750 km from the North Pole, and it is consisted of three main islands: Spitsbergen, Nordaustlandet (Northeast Land), Edgeøya (Edge Island) and some smaller ones (Fig 1). There are many mountains on the archipelago; Mountain Newton, 1713 m a. s. l., is the highest one. About 60% of the land area of Svalbard is covered by glaciers. Ny-Alesund (78°55′N, 11°56′E) is situated in the Svalbard archipelago at the Norwegian high Arctic, about 15 km from the Greenland Sea. The climate on the island is more gentle and humid than other parts of the Arctic due to the influence of the warm current from the north Atlantic Ocean. The annual mean temperature is - 4 ℃ there. Svalbard is a breeding ground for large numbers of seabirds, including Brunnich's and Black Guillemot, Puffin, Little Auk, Fulmar, and Black-legged Kittiwake. The Svalbard Ptarmigan, found on the larger islands, is the only land bird presenting there for the entire year.

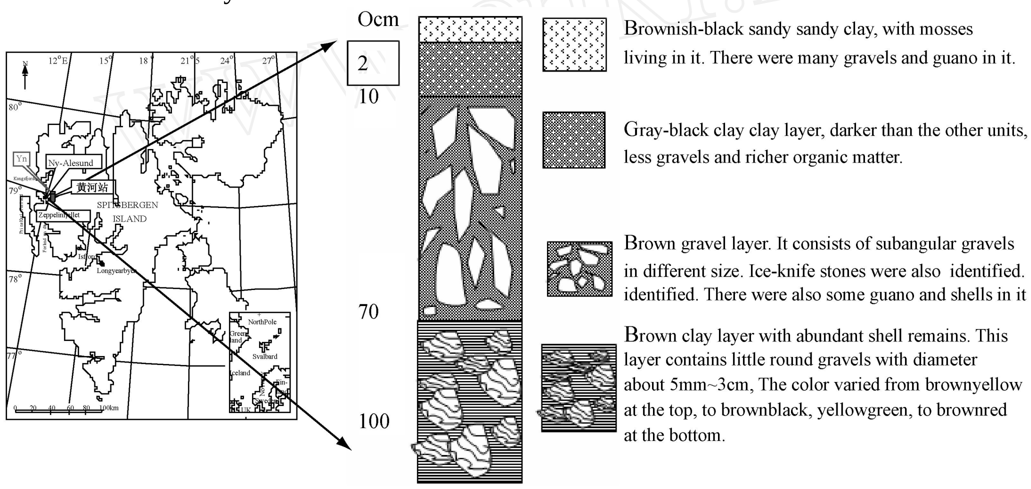


Fig 1 Map for Ny-Alesund, Arctic and lithology of the YN profile.

There is an extensive strandflat system along the west coast of Svalbard, 4 m above the sea level. At the first strandflat of Ny-Alesund, Spitsbergen, we collected a 118 cm long and well-preserved sediment core, named YN, in a palaeo-notch (78°55.6′N, 11°56.4′E).

Based on the results of TOC and elements, we selected 13 samples from the sediment core for molecular organic analysis (Table 1).

## 3 Sample analysis

The freeze-dried samples were Soxhlet extracted for 72 hours with the mixed solution of

Table 1. Samples analyzed in the present study

| Sample | YN-1 | YN-2 | YN-6 | YN-8 | YN-10 | YN-14 | YN-17 |
|---|---|---|---|---|---|---|---|
| Depth (cm) | 0 - 2 | 2 - 4 | 18 - 20 | 38 - 40 | 58 - 60 | 74 - 76 | 80 - 82 |
| Sample | YN-20 | YN-25 | YN-28 | YN-32 | YN-33 | YN-35 | |
| Depth (cm) | 86 - 88 | 96 - 98 | 102 - 104 | 110 - 112 | 112 - 114 | 116 - 118 | |

dichloromethane/methanol (2∶1) and desulfurizing copper. The extracts were concentrated by rotary evaporation and then saponified using 0.5 M KOH/MeOH for two hours. Neutral lipids were partitioned out off the basic solution with hexane. The pH of the saponified extract was then brought to 2 by 6N HCl and acidic lipids were extracted with 20% methylene chloride in hexane (9∶1). Acidic lipids were allowed to sit in the presence of anhydrous $Na_2SO_4$ overnight to remove traces of water. Neutral lipids were further separated on 5% deactivated silica gel column chromatography using solvents of increasing polarity from hexane to methylene chloride. The alcohols and acids fraction was treated with *N, O*-Bistrimethylsilyltrifluoro-acetamide (BSTFA) to form trimethylsilyl (TMS)-ether derivatives.

The alkanes, derivatives of alcohol fraction (including *n*-alkanols and sterols derivates), and the derivatives of acid fraction were analyzed on an HP 5890 gas chromatograph-mass spectrometer with a DB5 (50 m ×0.32 mm ×0.25 μm) capillary column (J&W). Helium was used as the carrier gas. The mass spectrometer was operated in EI mode at 70 eV. Analysis was done in SCAN mode.

The GC oven temperature for treatment of alkanes, alcohols and acid fractions was programmed, respectively, as following:

For alkanes: holding 2 min at 60 ℃, and then increasing to 200 ℃ at 7 ℃/min, after that increasing to 280 ℃ at 3 ℃/min, and hold 30 min at 280 ℃.

For alcohols: holding 2 min at 60 ℃, increasing to 200 ℃ at 10 ℃/min, then increasing to 280 ℃ at 3.5 ℃/min, holding 15 min at 280 ℃, increasing to 300 ℃ at 1.5 ℃/min, and lastly holding 30 min at 300 ℃.

For acids: holding 2 min at 60 ℃, increasing to 150 ℃ at 10 ℃/min, increasing to 300 ℃ at 2.5 ℃/min, and then holding 30 min at 300 ℃.

## 4 Results and Discussion

### 4.1 *Aliphatic hydrocarbon compositions*

The alkane composition of YN showed a bimodal distribution, with the carbon number ranged from C11 to $C_{33}$ (Fig 2). The characteristics of the distributions of normal alkanes (n-alkanes) are very important for the indication of sedimentary environments. In general knowledge, there are four regular types of n-alkanes: back-crest odd-predominant *n*-alkanes (generally occurring in the inland lake-delta plain bog and lacustrine bog), front-crest odd-even-predominant (OEP) *n*-alkanes (generally occurring in marine and deep-lake facies), bimodal OEP *n*-alkanes (generally occurring in paralic facies and inland lake deltas), and even-predominant *n*-alkanes (generally occurring in saline lakes or salt lakes). Therefore the bimodal distribution of the alkanes in YN indicated that the YN sediments have two sources: paralic and inland.

The long carbon chain alkanes in the near surface sediments of YN have obvious odd-to-even carbon number predominance, but the short ones do not. This odd-even-predominance disappeared with the increasing depth (Fig. 2). The hydrocarbons contain unresolved complex matrix (UCM). UCM normally occurs in the soil polluted by petroleum or coal. Gough and Rowland[8] proposed that UCM is possibly composed of a large number of branched hydrocarbons, which are difficult to be separated due to their structural similarities. The larger the area of UCM in the chromatography, the more severe the pollution. The ratio of UCM/T (total area) in YN was about 0.6 - 0.7. Carbon preference index (CPI) of the surface YN sediments was between 2.4 and 2.9, and it decreased to 1.1 - 1.4 with the increasing depth. The OEP ratio of the surface sediments was between 3.4 and 3.9, and it fluctuated around 1.5 - 1.8 at the bottom part of the sediments. All these indexes indicated the influence of the Tertiary coal mine on the YN sediments[9].

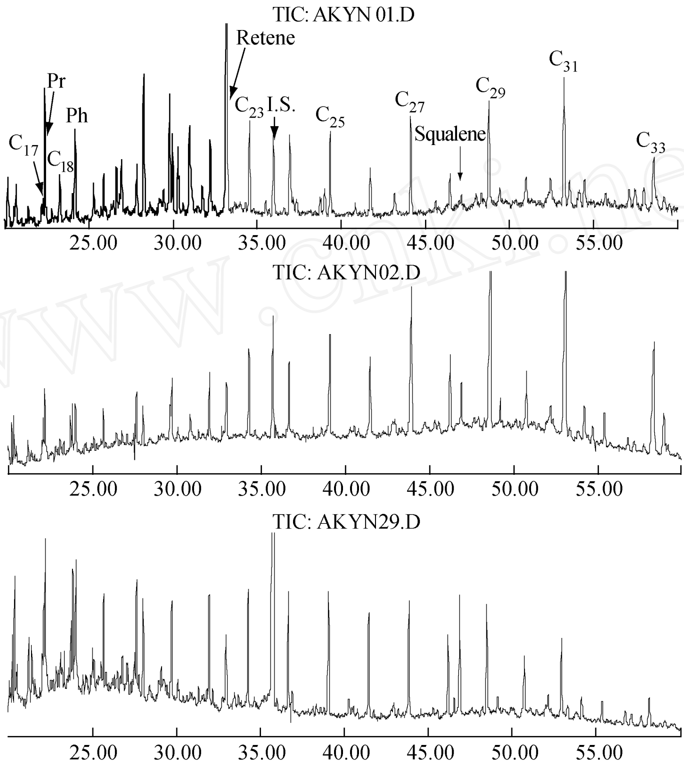


Fig 2 Distribution of alkanes in the YN sediments

Pristane had high concentration in the YN sediments and sometimes appeared as main peak of the alkanes. The sources of pristane and phytane are very complex. Normally, they originate from phytol which are produced by the isoprenoid phytyl side-chain[10]. In weak reductive or oxidative environments, phytol can be degraded to phytenic acids ((Z and E)-3, 7, 11, 15-tetramethylhexadec-2-enoic acids), and then decarboxylated to pristine. In reductive environments, phytol would be dehydrated to isomeric phytadienes and then reduced to phytane via phytene isomers. So the ratio of pristane to phytane (Pr/Ph) is an indicator of the oxicity of depositional environments. High Pr/Ph ratio indicates oxidative environment, and low ratio indicates reductive environments[11]. The formation environment of coal is normally oxidative and pristane-predominant, so Pr/Ph in coal is larger than 1. Retene has a high level in YN, and appears as the main peak in polycyclic aromatic hydrocarbons (PAHs) and hydrocarbons. Retene, also named as methyl isopropyl phenanthrene or 1-methyl-7-isopropyl phenanthrene, is distributed widely in coals, soils, lake sediments, modern marine sediments, fossil resin, etc.,[12] and is a biomarker for the land plant resin. In our study, high concentrations of pristane and retene suggested that the YN sediments are polluted by the coal mine there.

There were many coal mines in the Arctic, and exploitation started in early 20th century[13]. The Ny-Alesund coal mine was officially closed due to a mine tragedy in 1960s. Many researchers showed that coal mining increases the concentrations of heavy metals in the nearby soils and organisms[14-16]. Our results showed that coal layer affects the hydrocarbons compositions of the nearby sediments as well.

### *4.2 Alcohol composition*

The carbon numbers of the alkanols in the YN sediments ranged from 14 to 32 with even-to-odd predominance. Peaks of the $C_{22}$-$C_{28}$ *n*-alkanols dominated the alcohol fraction (Fig. 3). Epicuticular waxes of land plants contain *n*-alkanols that have an even number of carbon atoms from $C_{22}$ to $C_{30}$[7]. The main vegetations on the island are tundra mosses, and among them, *Dicranum angustum*, *Puccinellia phryganodes* and *Salix polaris* are the most abundant ones[17]. Therefore, we suggested that the main peaks of *n*-$C_{22}$ to *n*-$C_{28}$ alkanol in the YN sediments came from the surrounding mosses. The pattern of alcohols changed gradually to bimodal and the concentration of *n*-$C_{18}$ alkanol increased with the increasing depth, indicating an augmented contribution from algae or bacteria at deeper sediments.

The main sterol in YN was sitosterol (24-Ethyl-5α-cholest-22-en-3β-ol), and sitostanol (24-Ethyl-5α-cholestan-3β-ol) was the second abundant sterol. Both are $C_{29}$ sterols. Usually, C29 sterols are biomarkers of land plants, and they were also the major sterols in the feces of herbivores such as hens, ducks, seagulls, magpies, rosella and swans[18]. Since there were many birds living around YN, we suggested that the sterols in the sediments come from guano.

### *4.3 Carboxylic acid compositions*

Fatty acids had bimodal distribution and EOP (even-to-odd preference) in the YN sediments, with carbon number ranged from 14 to 22. The main peak of the front crest is $C_{16}$, and the main peak of the back crest is $C_{22}$ or $C_{24}$ (Fig. 4). The *n*-$C_{16}$ and *n*-$C_{18}$ alkanoic and alkenoic acids are ubiquitous components of biota and their sources are very complex. As suggested by Cranwell[19], the bimodal pattern of alkanoic acids indicates that the short chain acids come from freshwater algae and the long even-chain $C_{24}$-$C_{30}$ n-alkanoic acids from the waxy coatings of land plants. Isotope analysis of the alkanoic acids in the Ruoergai Marsh, Eastern Qinghai-Tibet plateau, China, sediments showed that the

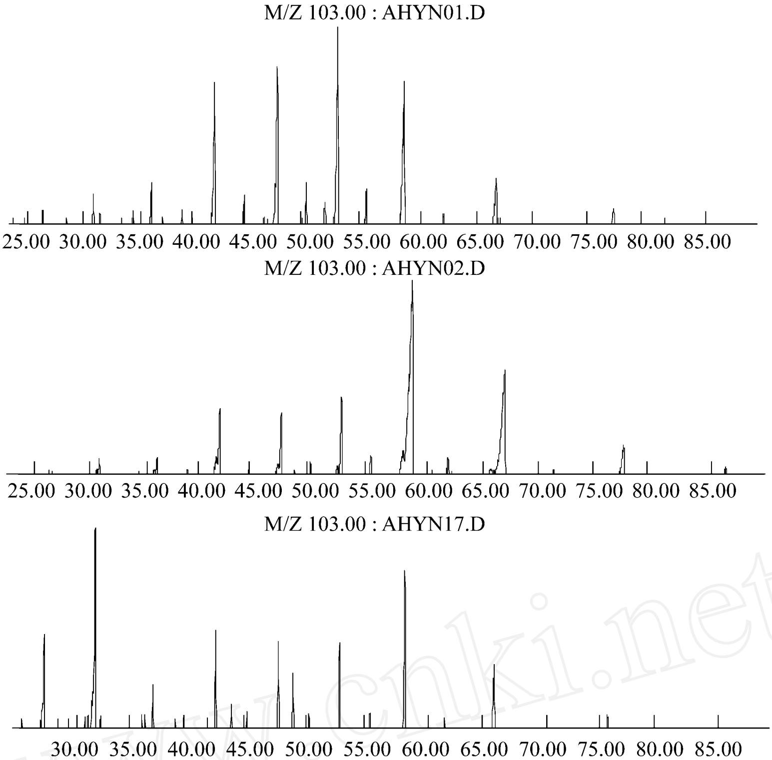


Fig 3 Distributions of *n*-alkanols in the YN sediments

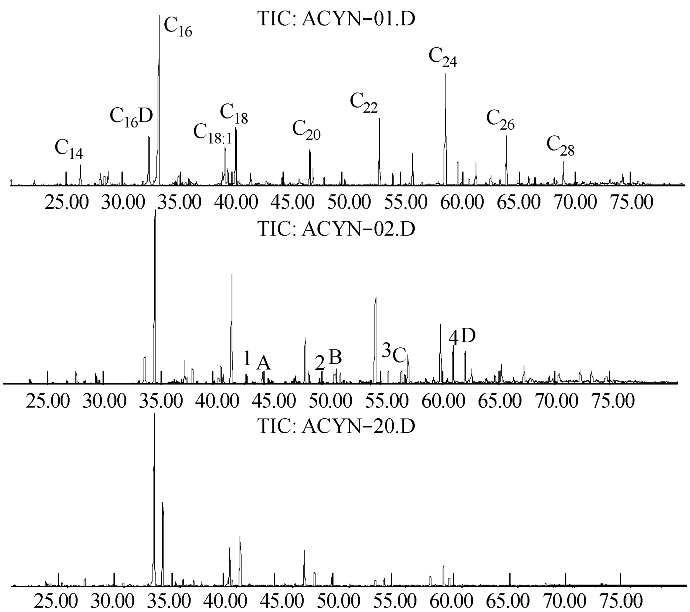


Fig 4 Distributions of carboxylic acids in the YN sediments
(1, 2, 3, 4: ω-hydroxyl acids ($C_{16}$-$C_{22}$); A, B, C, D-β-hydroxyl acids ($C_{16}$-$C_{22}$)).

short chain acids could also originate from land plants[20]. The sources of the short chain fatty acids in YN are not clear, but $n$-$C_{22}$ and $n$-$C_{24}$ acids likely come from the mosses in this area.

The main alkenoic acids in YN were $C_{18:1}$ and $C_{18:2}$ acids. For land plants, algae and bacteria, the existence of alkenoic acids can help them adapt climatic changes and keep cell membranes stable and flexible[21].

Low levels of $\alpha$- and $\omega$-hydroxyl acids were detected in YN. The carbon number ranges from 16 to 22 with even-to-odd predominance. Long chain hydroxyl acids are found in the cutin, suberin and wax of land plants, while short chain ones are found in gymnosperms[22]. The main peak of the hydroxylic acids in YN was $C_{22}$, and these hydroxyl acids probably come from land mosses.

## 5 Conclusions

The large percentage of unresolved complex matrix in the organic matter showed that the sediment core YN was affected by coal layer. The even-to-odd preference of the alkanols, the alkanoic acids, and the predominant hydroxylic acids strongly indicated that the organic matters in the YN sediments also have biogenic sources. Sitosterol was the main sterol, and it could be a good biomarker for the guano sedimentation on Ny-Alesund, Svalbard, Arctic. These results are in consistence with our unpublished findings that the ornithogenic sediments YN have the values of C/N and $\delta^{13}$C close to those of the fresh guano in the Arctic and within the range of marine values and the organic matters in YN very likely come from seabirds' activities such as preying and excreting (unpublished data from Sun *et al*.).

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