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$\delta^{13}C$ and $\delta^{15}N$ in the ornithogenic sediments from the Antarctic maritime as palaeoecological proxies during the past 2000 yr

Xiao-Dong Liu [a], Hong-Chun Li [b,c], Li-Guang Sun [a,*], Xue-Bin Yin [a], San-Ping Zhao [a], Yu-Hong Wang [a]

[a] *Institute of Polar Environment, University of Science and Technology of China, Hefei, Anhui 230026, PR China*
[b] *Department of Earth Sciences, University of Southern California Los Angeles, CA 90089, USA*
[c] *College of Resource and Environment Science, Southwest University, Chongqing 400715, PR China*

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Abstract

In this paper, we have examined carbon and nitrogen isotopic compositions in two ornithogenic sediment profiles from the Ardley Island and Barton Peninsula of Antarctica for palaeoecological changes during the past 2000 yr. The $\delta^{13}C$ values of the two sediment profiles range from −22.26‰ to −19.15‰ (PDB) in Core G and from −24.01‰ to −19.87‰ in profile A, showing that the predominant carbon source in the sediments plausibly comes from terrestrial and aquatic plants in Antarctic such as mosses, lichens, and algae in lakes. As these $\delta^{13}C$ values are also close to those in the fresh lake sediments that are not influenced by penguin guano, one may not use the $\delta^{13}C$ values as evidence for the influence of guano on the sediments. The $\delta^{15}N$ values of the two profiles range from 4.75‰ to 18.34‰ (air) and from 5.17‰ to 10.38‰ for Core G and Core A, respectively. The $\delta^{15}N$ variations have positive correlations with the trends of the bio-element contents in the sediments. As the levels of these bio-elements in ornithogenic sediments had been used to reconstruct the changes of historical penguin population and tundra vegetation abundance and diversity, we then suggest that the $\delta^{15}N$ records can be utilized to study palaeoecological processes of penguin. Our results show that penguin population and activity has generally decreased over the past 2000 yr. From 1300 to 900 yr BP and from 1790 to 1860 AD, penguin population and activity experienced two strong decreases. It will be interesting to understand the cause of these decreases.

Keywords: ornithogenic sediments; carbon and nitrogen isotope; palaeoecology; penguin; Antarctica

1. Introduction

Nitrogen and carbon isotopes have become increasingly important for studying ecosystem function and animal ecology as they may provide distinct information about the origin, formation and pathways of different biological materials [1]. Since these isotopes follow the path of assimilated carbon and nitrogen in organisms [2,3], they have been applied to trace the origins and migration of wildlife and human populations [4–6], and to examine the exchange of energy and nutrients between ecosystems especially at the ocean–land interface [7–11]. These isotopes have also been used for determining an organism's trophic level and the importance of different prey items in the diet [12–15].

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* Corresponding author. Fax: +86 551 3601415.
E-mail address: slg@ustc.edu.cn (L.-G. Sun).

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With these isotopic signals in Antarctic lake sediments, we attempt to detect palaeoecological processes of Antarctic animals in the past.

Penguins have been known of traveling hundreds of kilometers, walking and tobogganing on the sea ice to reach their rookeries. However, there seems to be a negative relation between the distance of the colonies from the edge of the sea ice in October when nesting activity starts and the size of the colony. Availability of food, sea-ice, and climatic conditions are the main influence factors [16]. The populations of Antarctic penguin as a reliable bio-indicator of ecosystem and environmental changes have been studied over the last decade ([17] and references therein). The results of the studies have showed that the changes in the population can reflect directly and indirectly ecological responses to regional climate and sea-level changes [17].

The penguin relics in their abandoned colonies, marked by the presence of nest stones, ornithogenic soils, food, bones, feathers, fragments of eggs, may provide considerable information about the past population, diet and migration of penguin species and the factors responsible for their drastic changes. On one hand, these older relics are generally not well preserved and difficult to be obtained. For example, the surface of old ornithologenic soils containing penguin remains can be entirely eroded and scoured by glacial advances, or dissolved in the wetter climatic zone of maritime Antarctica [18,19]. On the other hand, the remnants of ancient penguin droppings in the lake sediments near penguin colonies may be identified by their geochemical characteristics. Therefore, these geochemical characteristics may provide continuous information about historical penguin population changes [20–22]. Nine elements including sulfur (S), phosphorus (as P_2O_5), calcium (as CaO), copper (Cu), zinc (Zn), selenium (Se), strontium (Sr), barium (Ba) and fluorine (F) have been found to be enriched and significantly correlated with each other in the sediments amended by penguin guanos [20–22]. These so-called “bio-elements” of penguin guanos are significantly higher in the sediments impacted by penguin guanos than the unaffected ones [18,20–24]. Because these elements from penguin guanos are almost not mobile in the sediments of Antarctic lakes and depressions, their assemblage may be an important geochemical signal for indication of impact from penguin droppings or guano soils in Antarctica [21,22]. Although the levels of these bio-elements have been used to identify the input of guano and to reconstruct the changes of historical penguin colony including penguin population, abundance and diversity of vegetation in the areas abandoned by penguins [25], the origin of organic matter and these “bio-elements” in lake sediments await to be explored. The use of C and N isotopes in lake sediments may uncover the mystery about the source of organic matter. Combining the isotope records with the bio-element contents in the sediments, we may examine penguins' ecological responses to climate changes and human activity.

During the Fifteenth Chinese Antarctic Research Expedition (CHINARE-15) in 1999, we collected a 54-cm-long sediment core named as Core G from Lake G on the Ardley Island, and a 20-cm depth sediment profile named as Core A from an inter-zone depression between Gentoo penguin (*Pygoscelis papua*) nesting places and tundra vegetation on the adjacent Barton Peninsula. Our previous geochemical analysis of typical bio-elements, visual description, and X-ray photo suggested that both sediment profiles were influenced by penguin droppings [25,26]. In this paper, we analyze carbon and nitrogen isotopic compositions in both sediment sequences and examine the correlations between bio-element concentrations and nitrogen isotopic ratios. The results provide us possible application of stable isotopes as complementary geochemical proxies for studying the palaeoecological processes of Antarctic penguins on a large time scale.

2. Study area

The Ardley Island (62°13′S, 58°56′W), a 2-km-long and 1.5-km-wide island, is about 500 m east of Fildes Peninsula, Maxwell Bay, King George Island and connected to the Fildes Peninsula through a sandy dam (Fig. 1). The Great Wall Station of China is located about 0.5 km to the west. The study area has a cold oceanic climate, characteristic of maritime Antarctica. According to the meteorological records from the Great Wall Station, the mean annual precipitation is about 630 mm, the annual average relative humidity is about 90%, and the mean annual air temperature is around −2.6 °C with a winter low at −26.6 °C, summer high at 11.7 °C. It is free of snow and ice during the summer. Geologically, the island mainly consists of tertiary andesitic and basaltic lavas and tuffs together with raised beach terraces. The topography of the island is relatively flat with the highest elevation of 70 m. Seventy-eighty percent of the island is covered by vegetation, predominantly consisting of mosses and lichens.

The Ardley Island is one of the most important penguin colonies in the maritime Antarctic region.

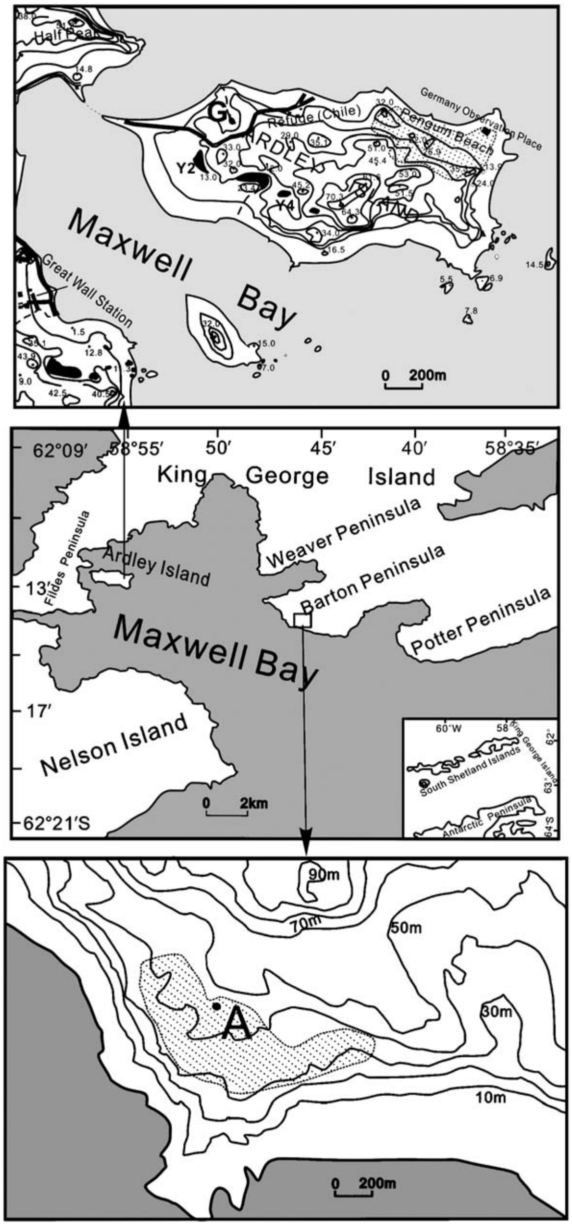

Fig. 1. The studied area showing the location of sampling sites (marked as G and A in the top and bottom figures, respectively). The top and bottom figures are the enlargement of Ardley Island and Barton Peninsula, respectively. The black solid areas shown in the top figure are lakes. The dotted area in the top and bottom figures indicates modern penguin colonies.

During the breeding period, the number of penguins on this island is about 10,200. The major species are Gentoo (*P. papua*, 74%), Adélie (*Pygoscelis adelie*, 21%) and Chinstrap (*Pygoscelis antarctica*, 5%) [25]. It is estimated that the penguins on the Ardley Island discharge about 139 tons of droppings based on the hypothesis that each penguin excretes ~85 g droppings (dry weight)/day during the breeding period. Droppings are either directly deposited in lakes or transferred by ice or snowmelt water into lakes, and accumulated with lake sediments. Due to very cold temperatures and snow coverage, decomposition of organic matter in the sediments is slow, so that the sediments have good preservation conditions. Lake G, located on the northwest of the island, is a shallow pond with a water depth ~0.5 m at an altitude of 28 m (Fig. 1). According to field observations, the surrounding area of Lake G has numerous abandoned penguin rookeries. These abandoned nesting places are covered by dense dark-green carpets of vegetation. A 54-cm-long sediment core (Core G) was collected from Lake G in 1999.

The Barton Peninsula, located in the southeast of the King George Island, is also one of the main penguin colonies. During the summer breeding period, the number of penguins on this peninsula is up to 15,000, mainly Gentoo penguins (*P. papua*, about 9%) and Chinstrap penguins (*P. antarctica*, about 91%) [26]. Penguin nesting places are located on the upland about 30–40 m above the sea level. The tundra in the north of the nesting sites is dominated by mosses and lichens, covering half of the peninsula. One 20-m interzone depression with no vegetation is located between the nesting places and tundra vegetation, in where a 20-cm depth sediment profile is taken and named as Core A (Fig. 1).

3. Materials and methods

3.1. Sediment profiles

The sediment core G was collected by driving a PVC pipe with 12-cm diameter into the soft substrate of Lake G (Fig. 1). The core was transported directly to domestic laboratory and preserved in cold storage prior to geochemical analyses. In laboratory, X-ray photo of Core G was taken on a SHIMAVISON EX II X-ray photometer in the hospital of University of Science and Technology of China (USTC). The sediment core was then sectioned at 1 cm interval for elemental and stable isotopic analyses. The concentrations of “bio-elements” including Zn, F, Sr, P, Cu, Se, and Ca in the sliced samples were analyzed and reported by [23].

For Core A, we used bamboo shovel to excavate a 20-cm-deep sediment profile on the Barton Peninsula (Fig. 1). In this profile, we collected one sample from the upper 0.8 cm that was in situ fresh penguin guano and 12 subsamples in the rest 19.2 cm sediments at 1.6 cm intervals. The middle part (from 0.8 cm to 18 cm) of the profile mainly consists of black or brown–black clay with large amounts of mosses. The bottom part with moss contains "unpleasant smell", likely indicating the influence of ancient penguin guano. The contents of bio-elements in the subsamples were determined and reported in [26]. In this study, the carbon and nitrogen isotopic compositions were determined for the 12 subsamples below 0.8 cm. For the purpose of comparison, we also determined the stable carbon and nitrogen isotope compositions in six marine animal species excrement samples (AP, ES, WS, FS, GP and SP) and three plant species samples (Y3L, XL and XM) from the study area. As the field view, these plant samples were not influenced by the animal excreta (see definition of these abbreviations in Table 2).

According to Tatur et al. [18], penguin colonies usually start under abiotic conditions, then colonized and finally abandoned for the maritime Antarctic; the initial nesting places are characterized by a large number of pebbles or gravels; the abandoned rookeries are colonized by the nitro-coprophilic alga (*Prasiola crispa*) and then mosses or lichens growing on the ornithogenic soils. In our previous studies, based on sedimentary lithological characteristics and elemental geochemical study the sediments in Cores G and A had been well identified as being amended by penguin droppings instead of seal excrements or other seabird faeces [25]. Here, we give other three reasons to further support this conclusion. First, a large number of abandoned penguin rookeries in the Lake G catchment have been observed in the field. The existence of these penguin rookeries on the Ardley Island suggests that historically large size of penguin colonies could be present around Lake G at least 3000 yr ago [21,22]. Therefore, the penguin droppings were likely deposited in Lake G by catchment snowmelt or directly in the water, similar to the adjacent Y2 and Y4 lakes influenced by penguin [21,27], Second, if sediments were influenced by seal excrements, they should contain numerous seal hairs [28,29]. However, in the present study we could not find any seal hairs in both Cores G and A, thus seal excrements are unlikely incorporated in the cores. Third, in Core A we find some penguin feather fractions which are identified with reference to modern penguin feather. Also, several adjacent sediment cores retrieved from the Barton Peninsula have been proven to contain abundant penguin droppings [26]. Combined with the young chronology for Core A and large size of penguins currently inhabited around the sample site, we suggested that the droppings incorporated into the sediments of Core A should be predominantly derived from penguins.

3.2. Stable isotope analyses

Carbon and nitrogen isotopic analyses were performed in the Department of Earth Sciences at the University of Southern California, USA. For nitrogen isotopes, three modern samples of each animal and plant species were determined. All the samples were dried and ground into powder. About 7–25 mg powder was combusted at ~900 °C to produce CO_2 and N_2 gases. The carbon and nitrogen isotopic compositions of resultant CO_2 and N_2 gases were determined by using IsoPrime Continuous Gas Flow Mass Spectrometer made by Micromass. Stable isotope abundances were expressed in δ notation as the deviation from standards in parts per thousand (‰) according to $\delta X = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where X is ^{13}C or ^{15}N and R is the corresponding ratio $^{13}C/^{12}C$ or $^{15}N/^{14}N$. The R_{standard} values were based on the PeeDee Belemnite (PDB) for ^{13}C and atmospheric N_2 (AIR) for ^{15}N. Replicated measurements of internal laboratory standards indicate that the analytical precision of the isotopic measurements was within ±0.05‰ for carbon and ±0.2‰ for nitrogen.

3.3. LOI, TOC and TN determination

According to local soil geochemical study [30], most of the King George Island soils are formed by physical disintegration of bedrock due to extremely cold climatic condition and relatively weak biological activity. The soil mineralogical compositions are dominated by non-clay silicate minerals, very similar to the bedrock. This is consistent with the result of Zhao and Li [31], who suggested that carbonate minerals could not be found in most of the soil profiles especially in the soils covered with mosses and lichens. Zhao and Li [31] pointed out that based on chemical equilibrium and solubility isotherm of $CaCO_3$ and CO_2 in water the deposition of autogenetic calcite could not occur in soil solution, surface water and lake water in the studied area. Furthermore, for most of lakes in the area, appearance of biogenetic carbonate may be impossible due to relatively shallow water depth and extremely low temperature. Considering that the bedrocks of Ardley Island are mainly basaltic lavas and tuffs with non-carbonate minerals and the island is covered by vegetation, the content of carbonate in the lake sediments seems to be negligible. The data results of loss on ignition at 550 °C (LOI$_{550\ °C}$) and 950 °C (LOI$_{950\ °C}$) in the lake sediments from the Ardley Island and Barton Peninsula confirm such a phenomena. A total of 60 and 49 sediment samples from the Ardley Island and Barton Peninsula, respectively, have been analyzed for LOI$_{550\ °C}$ and LOI$_{950\ °C}$ percentage. The wet sediments were first analyzed for water content by weighing differences between wet and dry sediment which was dried at 105 °C. Then, the dried samples were combusted for 3–4 h at 550 °C to determine the percent loss on ignition (LOI$_{550\ °C}$). After that, the temperature was increased gradually up to 950 °C within 0.5 h, and the samples were combusted for another 2 h at 950 °C to determine the percent loss on ignition (LOI$_{950\ °C}$). Total organic carbon (TOC) and total nitrogen (TN) concentrations were also analyzed for some samples. TN was determined with the Kjeldahl digestion method with an error less than 0.5%. The chemical volumetric method was used to measure TOC with a duplication error of 0.5%. In the present study, we used the calculated TOC/TN ratios as C/N values.

3.4. Radiometric and radiocarbon dating

The chronology of Core G was determined by conventional radiocarbon dating and cosmogenic radioisotope dating methods in Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences (CAS). Conventional radiocarbon dating was performed on handpicked moss remains (*Amblystegiaceae*, *Drepanocladus aduncus*) at four different depths (Table 1). Using tweezers and a needle, the moss materials were separated and mechanically cleaned from the sediments under a binocular microscope. After treatment with diluted HCl to remove possible carbonate content, ^{14}C measurement was conducted on organic carbon components by using a Quantalas-1220 liquid scintillometer. The radiocarbon ages were reported as yr BP (years before 1950). The quoted errors in the dates are based on the reproducibility of measurement.

For Core G, the top 10 cm sediments were sectioned into 10 samples at 1 cm interval. About 3 g of each sample was dried and then ground to the fine powder in the laboratory. The analysis of radionuclides (^{210}Pb, ^{226}Ra and ^{137}Cs) in these samples was performed by an Ortec HPGe GWL gamma spectrometry with low background and intrinsic germanium detectors. Supported ^{210}Pb in each sample was assumed to be in equilibrium with measured ^{226}Ra. Unsupported ^{210}Pb activity at each depth was calculated by subtracting ^{226}Ra activity from total ^{210}Pb activity. The results of total ^{210}Pb, ^{226}Ra and ^{137}Cs activity in the top 10 cm sediment layer of Core G are shown in Fig. 2.

3.5. Data analysis

In this study, Pearson correlation analysis and linear regression were used to examine the relationships between nitrogen isotope and bio-elements, carbon isotope. All the statistical calculations were performed with the aid of ORIGIN 6.1 package. We accepted *p*-values of <0.01 as statistically significant.

4. Results and discussions

4.1. Chronology

As shown in Fig. 2, ^{137}Cs profile shows higher activities than background in the upper 3 cm of Core G. A peak ^{137}Cs activity at the depth of 1.5 cm indicates that the 1965 fallout maximum from the atmospheric testing of nuclear weapons pertains to this depth. Significant levels of unsupported ^{210}Pb were detected in the top 5 cm and the total ^{210}Pb activities were in equilibrium with the ^{226}Ra activity below 6 cm. The oldest ^{210}Pb-datable sediments in the core are located at 4.5 cm and correspond to an age of 130 yr BP based on a constant rate of supply (CRS) dating model [32]. The presence of ^{137}Cs peak together with the sharp decline in ^{210}Pb activity at 5 cm also suggests that the sediments in the core have not been disturbed.

All the radiocarbon dates in Table 1 were calibrated into calendar years before present (cal. BP) using the INTCAL98 calibration data set [33] method A in the

Table 1

^{14}C conventional and calibrated ages of the samples from G lake sediment core

Laboratory number	Dated material	Depth (cm)	^{14}C conventional age (yr BP)	Calibrated age (cal. yr BP)	
				Intercept	2 sigma
G-08	Aquatic moss remains	7–8	720±55	666	559–733
G-18	Aquatic moss remains	34–35	1120±55	1051	1173–930
G-27	Aquatic moss remains	47–48	1765±55	1695	1822–1537
G-31	Aquatic moss remains	52–53	2120±55	2116	2183–1985

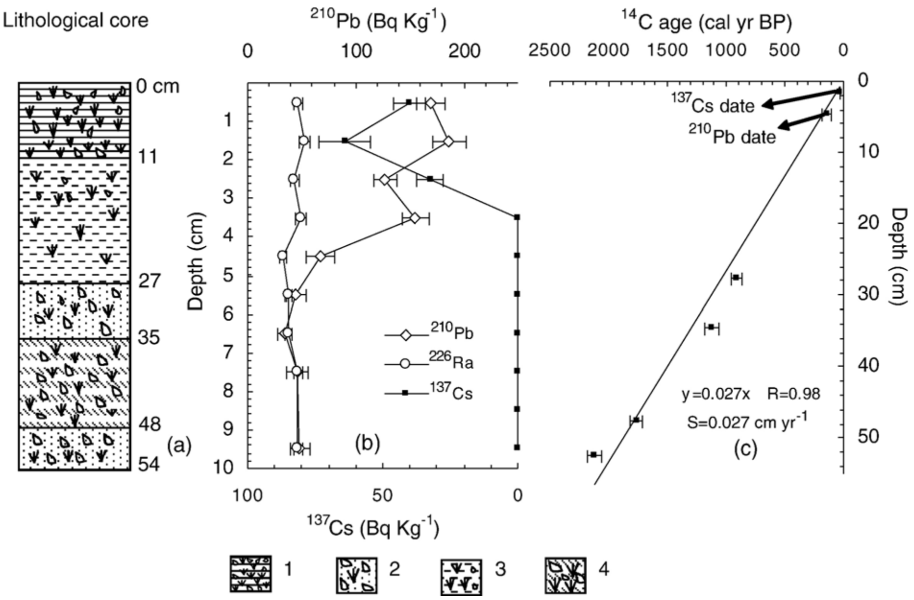

Fig. 2. (a) Sediment lithostratigraphy of the sediment core G. Legend for lithology: (1) the moss humus; (2) the dark clay and gravel debris with little moss relict; (3) hardy sedimentary layer from penguin droppings with some moss relict; (4) the gravel debris from the nesting sites with the clay and moss relict. (b) ^{210}Pb, ^{137}Cs versus depth in Core G. The peak of ^{137}Cs corresponds to the 1965 fallout maximum from the atmospheric testing of nuclear weapons, in good agreement with the result of ^{210}Pb measurements. (c) Ages of ^{14}C and cosmogenic radioisotopes versus depth in Core G. S is sedimentation rate.

CALIB 4.1.2 program [34]. The radiocarbon ages are stratigraphically consistent, perhaps indicating good preservation of sediments after deposition. According to [35], mosses give the most reliable ^{14}C ages in the Antarctic Peninsula. An age–depth model based on the results of ^{14}C, ^{137}Cs and ^{210}Pb dating methods is illustrated in Fig. 2. The linear correlation shown in Fig. 2 yields a linear sedimentation rate of 0.027 cm/yr, in agreement with that of the upper 55 cm sediments from the adjacent Lake Y2 (~0.029 cm/yr) [21]. Based on this linear sedimentation rate, we have calculated the ages of the sediments at each depth in Core G.

The chronology of Core A has been established in [26]. According to ^{210}Pb and ^{137}Cs dating, the time span for surface 4–5 cm depth is about 60 yr, and the mean sedimentation rate of the sediment profile is estimated as about 0.08 mm/yr. Thus, the whole sedimentary sequence approximately covers 250 yr.

4.2. Carbon isotope

The results of $\mathrm{LOI}_{550\ ^{\circ}\mathrm{C}}$ and $\mathrm{LOI}_{950\ ^{\circ}\mathrm{C}}$ percentage show that $\mathrm{LOI}_{550\ ^{\circ}\mathrm{C}}$ values vary from 6.7% to 68.3% (averaging 33.6%, $n=60$) on samples from the Ardley Island and from 2.3% to 82.8% (averaging 36.1%, $n=49$) on the Barton Peninsula samples. The $\mathrm{LOI}_{950\ ^{\circ}\mathrm{C}}$ values have a range of 1.1%–3.1% and a mean value of 1.8% on the Ardley Island samples, and a range of 0.6%–2.7% and a mean of 1.3% on the samples of Barton Peninsula. Based on the high $\mathrm{LOI}_{550\ ^{\circ}\mathrm{C}}$ values and low $\mathrm{LOI}_{950\ ^{\circ}\mathrm{C}}$ values, we conclude that the carbonate content in the sediments on both Ardley Island and Barton Peninsula is negligible relative to the organic matter abundance. Therefore, the influence of inorganic carbon on the determined δ^{13}C values should be minor. Similarly, as reported by Liu et al. [36], the nitrogen is mainly associated with organic matter in the sediments and soils influenced, and the inorganic nitrogen fraction is minor. Consequently, the influence of inorganic nitrogen on the δ^{15}N values in the ornithogenic lake sediments is also insignificant.

As shown in Table 2, the δ^{13}C values range from −22.26‰ to −19.15‰ in Core G and from −24.01‰ to −19.87‰ in Core A. The average δ^{13}C value of fresh marine animal excrements is -27.27 ± 1.21‰ ($n=6$), similar to those reported by Cocks et al. [10] for the soils from Nunataks with breeding snow petrel (−24.6‰ to −26.9‰, $n=6$) and those by Mizutani and Wada [37] for the soils of penguin rookeries at Cape Bird (−27.1‰ to −28.9‰, $n=7$). In order to discuss the origin of sedimentary carbon, we list the δ^{13}C values of the G and A profiles with other δ^{13}C values of materials from different origins in Antarctic region reported in previous studies in Fig. 3.

Table 2

Determined $\delta^{13}C$ and $\delta^{15}N$ values in the sediment profiles G and A, fresh animal excrements (AP, ES, WS, FE, GP and SP), and plants (Y3L, XL and XM)

Core G			Core A			Modern		
Depth (cm)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Depth (cm)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	No.	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
1.5	−19.19	4.79	2.4	−19.87	10.00	AP	−27.11	7.03 ± 0.41
2.5	−19.15	4.75	4	−24.01	6.12	BG	n.d.	7.37 ± 0.18
3.5	−19.19	4.89	5.6	−23.01	7.69	ES	−28.02	10.52 ± 1.02
4.5	−19.31	5.32	7.2	−23.05	6.70	WS	−28.19	15.35 ± 0.09
5	−19.85	6.43	8.8	−22.79	5.63	FS	−25.72	10.28 ± 0.20
5.5	−20.34	7.83	10.4	−22.54	5.17	GP1	−28.63	n.d.
6.5	−20.8	9.03	12	−21.82	6.32	SP	−25.97	17.68 ± 0.48
7.5	−21.2	11.33	13.6	−22.37	7.40	GP2	−28.37	12.54 ± 0.85
12.5	−21.51	10.74	15.2	−22.67	8.99	Y3L	n.d.	−3.55 ± 0.49
14.5	−21.19	12.60	16.8	−23.01	10.38	XL	n.d.	3.21 ± 0.20
16.5	−21.39	9.90	18.4	−23.27	10.34	XM	n.d.	6.59 ± 0.29
18.5	−21.14	10.49	20	−22.89	10.16			
20.5	−21.31	10.34						
23.5	−21.32	9.07						
26.5	−21.23	10.97						
27.5	−22.26	12.29						
28.5	−22.05	13.74						
30	−21.74	14.55						
32	−21.34	15.91						
34	−21.28	16.63						
36	−21.47	16.94						
37.5	−21.72	16.71						
39.5	−21.44	16.94						
41	−20.97	17.99						
43	−20.93	18.2						
44.5	−20.59	17.74						
45.5	−20.44	18.34						
47	−20.55	17.9						
49	−20.73	18.03						
51	−21.1	17.32						
53	−21.93	16.1						

AP, BG, ES, WS, FS, GP1 and SP are fresh marine animal excreta from the study area; GP2 is Gentoo penguin guano scooped from penguin rookery. AP: Adélie penguin (*Pygoscelis adelie*); BG: Black-backed gull (*Larus dominicanus dominicanus*); ES: Elephant seal (*Mirounga leonina*); WS: Weddell seal (*Leptonychotes wedellii*); FS: Fur seal (*Arctocephalus gazella*); GP1: Gentoo penguin (*Pygoscelis gentoo*) from the Barton Island; SP: Southern giant petrel (*Macronectes giganteus*); GP2: Gentoo penguin (*P. gentoo*) from the Ardley Island; Y3L is lichen around fresh lake and not influenced by animal activity; XL is lake algae from Xihu lake on the Fildes Peninsula; XM is tundra moss around the Xihu lake, which is not influenced by guano; n.d.: not determined. With regard to the nitrogen isotope listed in the table, three samples for each species are analyzed.

In Fig. 3, the $\delta^{13}C$ values of the sediment G and A profiles overlap with these of fresh lake sediments, tree-type C3 plants, and Antarctic C3 plants such as lichens, lake algae and mosses. Our sampling sites are predominantly vegetated by lichens, mosses and lake algae. Tree-type C3 plants and C4 plants are not found. Therefore, the $\delta^{13}C$ values of the sediment G and A profiles indicate that the organic matter in the sediments comes mainly from Antarctic C3 plants, possibly with or without mixture of fresh Antarctic animal excrements.

The $\delta^{13}C$ values of Cores G and A are also in the ranges of the carbon isotopic composition of sediments from the adjacent Fildes Peninsula. These fresh lake sediments are not influenced by marine animal activity, and the deposited organic matters are predominantly composed of lake algae and the remains of terrestrial vegetation such as mosses, lichens, etc. [39,40]. Hence, using the $\delta^{13}C$ values alone we cannot make a conclusive evidence for guano's influences in the sediment profiles G and A. This finding is consistent with the observation in the study of the origin of soil carbon by Cocks et al. [10] who also pointed out that $\delta^{13}C$ values may not be useful indicators of seabird effects on the Antarctic ecosystems. It is necessary to use nitrogen isotope to trace the origin of the organic matter in the sediments.

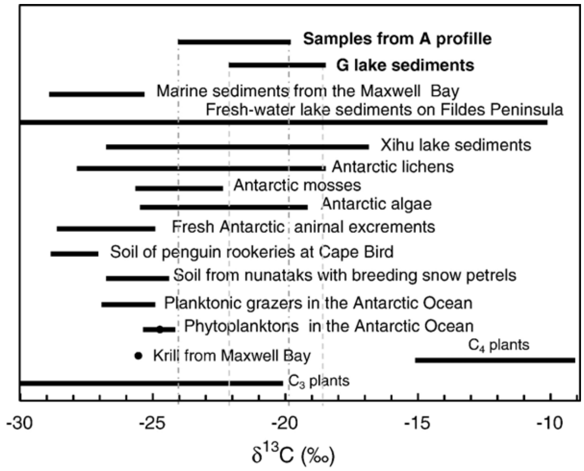

Fig. 3. δ^{13}C value ranges of the organic matters of different origins in the Antarctic region. From top to bottom: the marine sediments from Maxwell Bay [38]; the fresh water lake sediments on Fildes Peninsula [39]; the Xihu lake sediments in the area of Great Wall Station [40]; the lichens, mosses, alga [41]; the fresh Antarctic animal excrements (this paper); the soil of penguin rookeries at Cape Bird [37]; the soil from Nunataks with breeding snow petrels [11]; the planktonic grazers and phytoplanktons in the Antarctic Ocean [42]; the krill from Maxwell Bay [43] and the C3 and C4 plants [44].

4.3. Nitrogen isotope

In Table 2, seven independent marine animal excrement samples have an average δ^{15}N of 11.54±3.95‰. The δ^{15}N values of plant samples not significantly influenced by marine animal activity are in the range of −3.55‰ to 6.59‰. Compared to a small change in δ^{13}C values in the lacustrine sediments, the nitrogen isotopic compositions of Core G exhibit a wide variation range, being 4.75–18.34‰ (Table 2 and Fig. 4). This may be due to the notable differences in the relative sizes of carbon and nitrogen pools in the samples. According to the C/N data for marine animal excrement, vegetation and sediment samples, the C/N value of the fresh faeces in the Antarctic region is 5.65±1.86 (n=12), and some plants such as mosses and lichens, etc. and vegetation-covered soils have C/N values mostly >10 [36]. Three samples from the G lake sediments showed C/N ratio in the range of 6.14–9.35. Although there are only three samples from the G lake sediments, their C/N ratios show a range similar to those of marine animal excrement's sediment samples collected from the adjacent Fildes Peninsula (5.4–8.96, n=30) [36] and ornithogenic soils in the maritime Antarctic (4.0–7.3, n=9) [18].

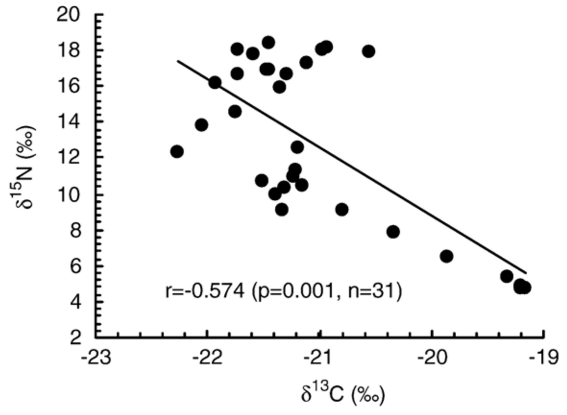

Fig. 4. A negative relationship between the δ^{15}N and δ^{13}C values in the G lake sediments is shown by a linear fitting.

The C/N ratios of Core G indicate that the nitrogen abundance is typically much lower than that of carbon in the sediments influenced by marine animal excrements. Hence, the nitrogen pool is expected to be more sensitive to isotope changes than carbon, resulting in relatively large changes of nitrogen isotopic values. The C/N ratios of the sediments are close to the fresh animal excrements, but significantly lower than those of plants. This is consistent with the result of chemical compositions of the soils collected from the sites currently inhabited by penguins. The soils affected by penguin droppings have much higher nitrogen concentration, but lower carbon content than black humus of plant origin. With the vegetation entering abandoned rookeries, a rapid increase in C/N value in the ornithogenic organic matter of relic soils would occur. Furthermore, during the succession of vegetation in an age sequence of abandoned nesting sites, the C/N ratios in the relic soils would increase continuously [18]. Therefore, the guano is likely to be a high nitrogen source in the lake sediments, agreeing with our previous results that the Lake G sediments are significantly impacted by penguin guanos [25].

The δ^{15}N values in Fig. 5 exhibit the change of δ^{15}N values in five periods: (1) the highest but relatively constant δ^{15}N values (17–19‰) appear in the sediments below 34 cm depth (before ~1300 yr BP); (2) the δ^{15}N strongly decreases from 34 cm to 24 cm depths, with a drop of ~8‰. This period spanned from 1300 to 900 yr BP; (3) relatively constant values around 10–11‰ between 24 cm and 7 cm depths, corresponding to the period of 900–250 yr BP; (4) again another sharp decrease in the δ^{15}N from depth of 7 cm to 4 cm (250–150 yr BP); and (5) the lowest values (~5‰) occurred in the upper 4 cm during the past 150 yr.

In Period (1), the δ^{15}N values in Core G are higher than those of fresh animal excrements (13.33±3.13‰), close to the δ^{15}N of the ornithogenic soil of Antarctica [10,45]. As high δ^{15}N values are commonly used for indication of animal-derived nitrogen influence in soils or plants [9–11,45], the high δ^{15}N values during Period (1) may reflect the input of isotopically heavy guano soil around Lake G.

Two explanations may be for the high δ^{15}N values: trophic enrichment and further kinetic fractionation *in site* [8,10,46]. Trophic enrichment refers to the ^{15}N enrichment in organic matters as they pass up the food chain to the consumer that excretes the nitrogen [8]. In the Antarctic food chain, δ^{15}N generally displays a stepwise increment of about 3‰ at each successive trophic level. The δ^{15}N value of an animal's excrement is proportional to its position in the food chain [9]. Antarctic penguins have δ^{15}N values higher than other marine animals due to their high position in the food web of the Southern Ocean ecosystem [1]. Isotopic fractionation resulting from NH_3 volatilization is another important factor. Up to 80% of the nitrogen compositions in the marine animal excrements are uric acid or urea, with minor amounts of NH_4 and protein [46]. Urea or uric acid can be rapidly transformed into ammonia through aerobic decomposition [8–11,37,46]. Ammonia is depleted in ^{15}N and easily lost to the atmosphere by volatilization, leading to enrichment of heavy isotopes in the remaining nitrogen [47,48]. Thus, high δ^{15}N values during Period (1) in Core G reflect strong influence of penguin activity.

During Period (2), a 8‰ decrease in the δ^{15}N probably indicates strong weakening of guano soil input. After that, the amount of guano soil input kept relatively stable during Period (3), resulting in relatively constant nitrogen isotopic values. Subsequently, the sharp decrease in the δ^{15}N values during 250–150 yr BP (Period 4) probably indicates another strong decrease in the input of guano soils. For the upper 4 cm sediments (Period 5), their nitrogen isotopic compositions are close to those of the plants not influenced by guano (Table 2), suggesting that the input of guano soils into G lake sediments was minor during the past 150 yr.

The large variation of δ^{15}N values in Core G is unlikely caused by the changes of diversity of penguin species and their diet in the study area. According to the nitrogen isotope analyses for fresh excreta of sea animal species in Table 2, the Adélie penguin (*P. adelie*) and black-backed gull (*Larus dominicanus dominicanus*) have approximate nitrogen isotope ratios due to their similar diet compositions and identical trophic level in the Southern Ocean ecosystem though they are completely different seabird species. These δ^{15}N values are also close to those of fresh Adélie penguin droppings sampled from Cape Bird of Antarctic Ross Island (8.0±0.4‰, $n=4$) [37]. Furthermore, as listed in Table 2, the Gentoo penguin (*Pygoscelis gentoo*) guano, the remnant of fresh dropping subjected to microbial degradation, has a δ^{15}N value of 12.54±0.85‰ ($n=3$), similar to average δ^{15}N of 13.4‰ ($n=6$) in Adélie penguin guano from Cape Bird [37]. These data seem to suggest that the δ^{15}N value in the excreta could not change significantly with the penguin species. Nevertheless, compared to the fresh excreta of seal species (Table 2), the fresh penguin droppings have remarkably low δ^{15}N values. This may be due to the fact that the trophic level of seal is relatively high. The Southern giant petrel (*Macronectes giganteus*) faeces has the highest δ^{15}N value (17.68±0.48, $n=3$) because of its scavenging of other birds/mammals and opportunistic/generalist feeder [49].

In the Antarctic region, the prey compositions of different penguin species may vary geographically and temporally [50,51]. The main diet of penguins in the south Antarctic is the Antarctic krill (*Euphausia superba*) plus insignificant amount of fish, but their main diet is fish in the north. There are remarkable differences in the diets of different penguin species at northern localities, but such differences are less pronounced at southern and western sites. Our study area is located in Ardley Island, southwestern Antarctic, belonging to so-called maritime Antarctic (Fig. 1). In such a study area, Gentoo, Adélie and Chinstrap penguins feed predominantly on Antarctic krill, with fish contributing only marginally to the diet according to some palaeoecological and modern literatures [25,51–53]. The change of penguin diet over the past 3000 yr may be insignificant, and the effect of diets of different penguin species on the bio-elements in penguin droppings and ornithogenic sediments was testified to be negligible [21,22]. Therefore, we suggested that the effect of the diet on the sedimentary δ^{15}N values should be insignificant in Core G.

Furthermore, the dietary compositions of penguin during the last four decades may change with the decrease in baleen whale stocks due to commercial whaling, since a presumed increase in food availability for penguin may take place. However, Fraser et al. [54] suggested that overlap in the foraging niches of penguins and whales was actually less significant than that suggested by the whale reduction hypothesis, because they found no changes in penguin breeding phenology during the past 40 yr. The comparison of δ^{15}N values in modern seal hairs with the historical ones in the sediments containing excrements from the adjacent Fildes Peninsula showed that the seals had stable trophic levels and insignificant changes of their diet over the past 150 yr [55]. This might imply that the change of krill abundance resulted from intensive commercial fishery and climatic changes in recent decades of years could not cause serious influence on the dietary compositions of sea animals in the study area. Thompson and Sagar [56] studied long-term trend in diet of rockhopper penguins (*Eudyptes chrysocome*) colonized in the sub-Antarctic zone using nitrogen isotope signatures from proteins in feathers. Their results showed that the δ^{15}N signature over the past 120 yr had no changes, reflecting the penguins maintained their preferred diet krill over the relatively long timescale.

Although other factors such as nitrate utilization, denitrification and N fixation may influence sedimentary δ^{15}N, nitrogen source seems to be the major factor to control the δ^{15}N in the sediment profile G. Based on the concentration changes of bio-elements P (P_2O_5), Ca (CaO), Sr, F, Cu, and Zn versus depths (Fig. 5), visual description, and X-ray photo of sediment Core G, Sun et al. [25] suggested that there existed a seesaw-like relationship between the historical penguin colony and tundra vegetation abundance. A rise in penguin population leads to the enlargement of penguin colonies, whereas the vegetation near the active penguin colony is wizened and even destroyed due to toxic overmanuring and trampling by penguins. A drop in penguin population leads to the contraction of active area and even abandonment of penguin colony. At the same time, tundra area expands and abandoned colonies are covered by vegetation due to the nutritious ornithogenic soil and the end of penguin trampling. Therefore, the opposite relationship for the change patterns of penguin guano and moss relict abundances may appear in Core G. As illustrated in the lithostratigraphy of Fig. 2, the moss relicts seemed to display significant change throughout the Core G, and the upper sediment unit is much rich (Fig. 2). Unfortunately, in the present study we could not accurately count the abundance of plant relicts within each sample. But, the bio-element concentration changes in the sediments amended by penguin droppings can be used as an indirect measure of changes in historical penguin guano [21–23].

The rise in penguin population leads to the enlargement of penguin active area and the lack of vegetation, which results in the enrichment of the bio-elements in the sediments. In order to examine possible association between the δ^{15}N values and the bio-element concentrations (P, Ca, Sr, F, Cu and Zn), an analysis of Pearson correlation was performed for these six bio-elements and the δ^{15}N. The results were given in Table 3, showing that the δ^{15}N values were significantly and positively correlated with all the bio-elements. The two independent proxies show the same patterns in Core G, suggesting that they are impacted by the same external factors—penguin guano. The higher levels of bio-elements in the sediments reflect elevated penguin populations and expanded penguin colony and active area. Thus, more guanos or ornithogenic soils with heavy nitrogen isotope were transported and incorporated into the lake sediments, giving higher δ^{15}N values. Reduced penguin populations and contracting penguin colony would decrease bio-element concentrations in the lake sediments due to decreasing guano input. In this case, nitrogen source in the lake sediments should be mainly contributed by Antarctic plants with low δ^{15}N. The positive correlation illustrates that nitrogen isotope compositions in the Lake G sediments can be a good

Table 3
The correlation coefficients between δ^{15}N and δ^{13}C, six bio-elements in the G lake sediments

	δ^{13}C	P_2O_5	CaO	Cu	Zn	F	Sr
Coefficient	−0.574	0.866	0.724	0.518	0.814	0.772	0.636
P value	0.001	<0.001	<0.001	0.008	<0.001	<0.001	0.003
Sample no.	31	25	25	25	25	25	19

All the correlations listed in the table are significant at the level of 0.01.

indicator of guano input and be applied in studies of Antarctic penguin palaeoecological processes.

The above conclusion is further supported by a negative correlation between δ^{13}C and δ^{15}N values ($r = -0.574$, $n = 31$) (Fig. 4). This kind of relationship has been interpreted as the result of mixing isotopically distinctive carbon and nitrogen source [57,58]. As shown in Table 2 and Fig. 3, Antarctic plants such as mosses, lichens and lake algae generally have lighter δ^{15}N, but heavier δ^{13}C than these of fresh animal excrements. Thus, the high δ^{15}N values and low δ^{13}C values in the bottom sediments of Core G indicate influence of penguin dropping. In contrast, the low δ^{15}N values and high δ^{13}C values of the top part suggest weak influence of penguin dropping. In the field investigations around Lake G, we did not find evidence of modern colonies of penguins, and the surface of the area was covered by dense dark-green carpets of vegetation.

The lithological character and elemental geochemistry in Core G has revealed a process of oscillation–contraction for the historical penguin colony around the Lake G [25]. As mentioned earlier, the assemblage of nine "bio-elements" including S, P, Ca, Cu, Zn, Se, Sr, Ba and F is considered to be an important geochemical biomarker for the sediments influenced by penguin droppings. However, because background concentration of these elements in the weathered sediments may vary, these elements could display different geochemical behaviors. In Fig. 5, the concentrations of P_2O_5, CaO, F, Sr, Cu and Zn in Core G show significant correlations through the depth, thus these elements are identified as bio-elements for penguin guano [25]. For Core A in the Barton Peninsula, the assemblage of bio-elements includes S, P, Ca, Cu, Zn, Se, Sr and Ba (Fig. 6), showing the same source form penguin guano [26]. Comparing the concentrations of these bio-elements in Core G with these in Core A, lower concentrations in Core A were probably attributed to the different lithology of the sediments that contain large amounts of plant remnants, whereas the sediment of Core G is mainly composed of debris, penguin droppings and ornithogenic soils.

In both Core G and Core A, similar trends of nitrogen isotope and bio-element concentrations can be observed though there are some obvious deviations (Figs. 5 and 6). The possible reasons of the deviations may include: (1) the concentrations of these bio-elements are not only affected by the material source, but also by other factors such as the dilution, grain-size effects, and preserving conditions. The influencing degree of these factors on each bio-element may be different since their chemical properties are very different. (2) All the bio-element concentrations measured in this study are total, they are not only derived from penguin guano, but also from the local bedrock and weathered soil around the catchment, thus the background concentrations in the weathered soil and local bedrock may cause fluctuations of the bio-element concentrations. Consequently, the concentration data of chemical elements in bulk sediments may not reflect the true variation of their geochemical behaviors as bio-indicators of penguin guano. (3) Although the nitrogen source is considered to be the

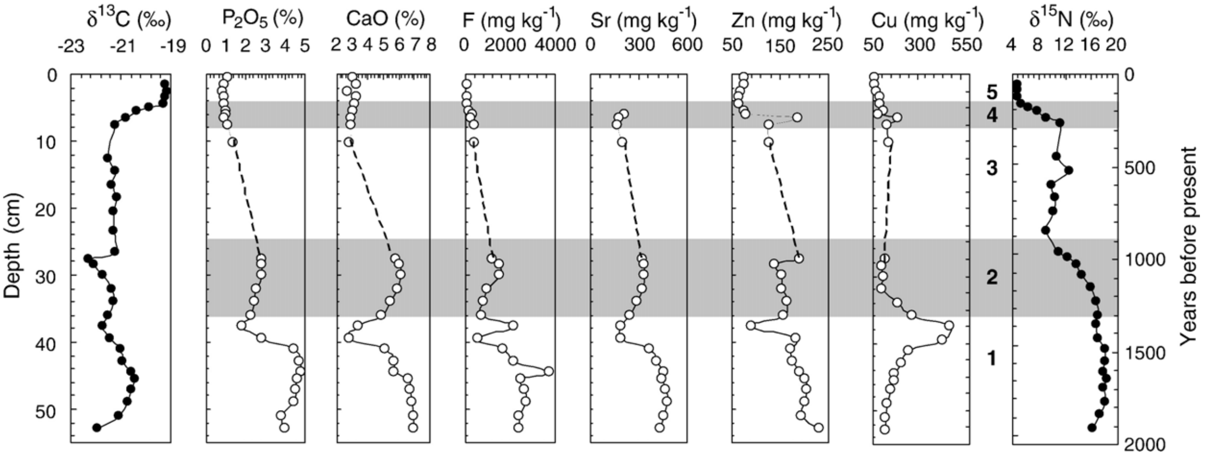

Fig. 5. The δ^{13}C, δ^{15}N and bio-elemental concentrations in the G lake sediments. The concentrations of bio-elements in the hard sediment layer between 11 cm and 27 cm depth were not determined. Five periods of varied penguin population and activity have been determined based on the δ^{15}N record. The periods 1, 2, 3, 4 and 5 correspond to the distinct intervals of penguin population discussed in the text.

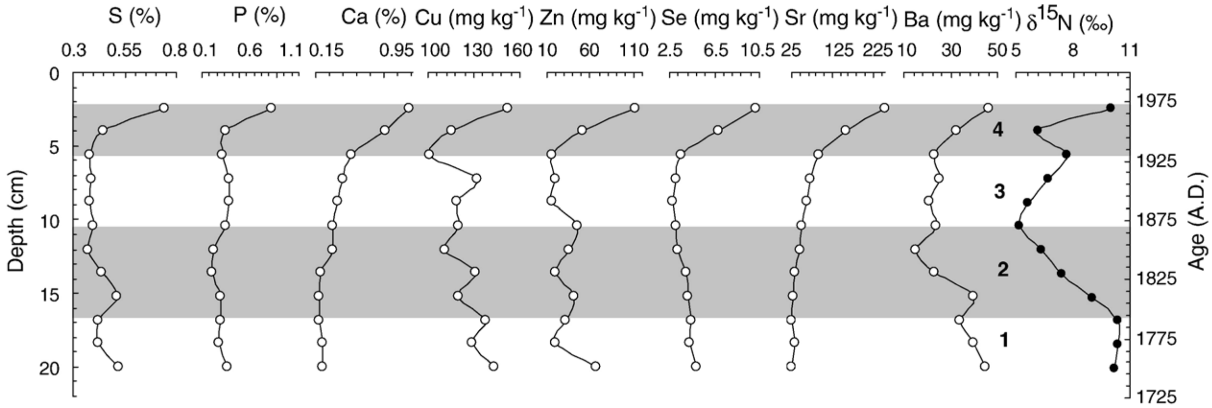

Fig. 6. The δ^{15}N and bio-element concentrations in the sediment profile A. The periods 1, 2, 3, and 4 are identical with the distinct intervals of penguin population (activity) discussed in the text.

major factor controlling the δ^{15}N values in the sediments, other processes such as NH_3 volatilization, nitrate utilization, denitrification and N fixation may also have minor effect on the sedimentary nitrogen isotope. These minor factors may cause somewhat deviation for the true change pattern of δ^{15}N. The above-integrated reasons may cause the divergence of bio-element and nitrogen isotope proxies at times.

Although the record of Core A is much shorter than the record of Core G, it reveals higher resolution of geochemical signals during the past 250 yr. Based on the δ^{15}N record of profile A (Fig. 6), we are able to interpret Antarctic penguin activity around the Barton Peninsula spanning the last 250 yr. Before 1790 AD (Period 1), the δ^{15}N values were high around 10.3‰, showing moderate penguin size and activity. From 1790 AD to 1870 AD (Period 2), the δ^{15}N had a ~5‰ decrease to a minimal value of 5.17‰, reflecting a strong weakening of penguin activity and a notable decrease in penguin population. Then, the δ^{15}N increased to 7.8‰ between 1870 AD and 1930 AD (Period 3), indicating slightly return of penguin activity. Since 1930 AD (Period 4), the δ^{15}N value shows first a decrease and then an increase to a level that is close to 200 yr ago. The increase in the δ^{15}N during the recent several decades is corresponding to the elevated contents of bio-elements. This increase probably reflects the increase in the penguin population on the Barton Peninsula [26]. It is worth to mention that the general trends and values of δ^{15}N records in both sediment profiles G and A during the past 250 yr are consistent, though the youngest samples in both profiles show discrepancy. This similarity may imply that the δ^{15}N records reflect a regional variation of Antarctic penguin history. Furthermore, most of the bio-element concentrations in the profile A do not exhibit the decrease trend from 1790 AD to 1860 AD as indicated by the δ^{15}N trend (Fig. 6). As mentioned earlier, dilution effect, grain-size, inorganic source and preservation of the bio-elements may influence their palaeoecological implication. The nitrogen isotopic compositions in the sediments may be a better and more sensitive proxy of palaeoecological processes.

In summary, the variations in the δ^{15}N values of the sediment profiles G and A reflect penguins' impact on the sediments, with heavier δ^{15}N indicating stronger penguins' impact. Our data results show that penguin population and activity in the study area has decreased during the past 2000 yr. Whether this decrease is influenced by climate changes or human activity is unclear. The first strong decrease in penguin population and activity was corresponding to the Medieval Warm Period when climates in Europe were warm and wet. The second strong decrease occurred between 1790 and 1860 AD, corresponding to the late half of the Little Ice Age when the climates in Europe were cold and dry. Holocene climatic signals from the Antarctic continental shelf and Antarctic lakes have been proven to be almost correlated to expansion and retreat of glaciers in Europe [59]. For example, the late Holocene climatic records by the marine sediments from the eastern Bransfield Basin of Antarctic Peninsula clearly identify two climatic events of Medieval Warm Period (MWP) and the Little Ice Age (LIA), which are the strongest of the late Holocene warm and cold periods, respectively [60]. Given our present data, we suggested that the changes in the historical penguin populations seemed to be associated with the palaeoclimatic fluctuations, and extremely warm and cold climate conditions could result in their reduction. However, further investigation of palaeoclimate and penguin history in entire

Antarctica may shed the light on the cause of variations in penguin population and activity.

5. Conclusions

Using the carbon and nitrogen isotopic compositions of the sediments from the Ardley Island and Barton Peninsula in Antarctica, we have interpreted the source of organic matter in the sediments. The δ^{13}C values show that organic matter in the sediments are mainly from the Antarctic C3 plants such as lichens, lake algae and mosses, with or without mixture of fresh Antarctic animal excrements. It is difficult to use the δ^{13}C values alone for interpretation of guano's influences.

The variations of δ^{15}N in the sediments appear to reflect the impact of penguin droppings on the origin of organic nitrogen, with heavier δ^{15}N indicating stronger penguins' impact. Therefore, we are able to use the δ^{15}N record as an effective proxy for changes in penguin populations and penguin colony in the Antarctic.

According to the δ^{15}N, δ^{13}C and bio-element concentration records of profiles G and A, we have reconstructed variations in the size of penguin population and colony of penguin living the study area during the past 2000 yr. The records show that penguin population and activity has generally decreased over the past 2000 yr. From 1300 to 900 yr BP and from 1790 to 1860 AD, penguin population and activity experienced two strong decreases. The cause of these decreases needs to be further investigated.

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