Elemental and Isotopic Signatures in the Sediments Influenced by Seal Excrement on Antarctic Fildes Peninsula and Their Potential Paleoecological Applications

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Abstract   The elemental and isotopic signatures in the sediments influenced by seal excrement on Antarctic Fildes Peninsula are examined for their potential palaeoecological applications. The seal hair abundance in sediments exhibits remarkable fluctuation versus depth, indicating similar changes in historical populations of the seals visiting the marine terrace. The combination of $\delta^{13}C$, total organic carbon concentration (TOC), total nitrogen concentration (TN) and atomic C/N ratio shows that the organic matters in sediments with numerous seal hairs have a marine origin and are predominantly derived from seal excrements. The large $\delta^{15}N$ values in sediments are attributed to trophic enrichment and NH_3 volatilization processes. The large variations in the $\delta^{15}N$ values and the negative correlation between the $\delta^{15}N$ values and the seal hair abundances seem to be the results of changes in the paleoclimates and the volatilization rates of the ammonia produced in the seal excrements. The $^{87}Sr/^{86}Sr$ ratios in the acid-soluble fraction of sediments are interpreted as a mixture of the ones from the seal excrements (30%-50%) and the chemically weathered local bedrocks (70%-50%). The calculated proportion of seal-derived Sr based on the $^{87}Sr/^{86}Sr$ ratios has a significant correlation with seal hair abundances in sediments. These results suggest that $\delta^{15}N$ values and the $^{87}Sr/^{86}Sr$ ratios in the acid-soluble fraction of sediments were influenced by seal excrements, similar to seal hair numbers, and thus can potentially be used to estimate the historical seal population in the Antarctic region.

Key words   Antarctica; sediment; seal excrement; isotope ratios; palaeoecology.

1   Introduction

Isotopes of light element, nitrogen (N) and carbon (C), have become increasingly important for modern ecology because they provide distinct information about the origin, formation and pathways of different biological materials (Wada *et al.*

1991). These isotopes have been used to follow the path of assimilated carbon and nitrogen (Tieszen and Fagre 1993; Oelbermann and Scheu 2002), to trace the origins and migration of wildlife and human populations (Chamberlain *et al*. 1997; Harrington *et al*. 1998; Hobson 1999), to examine exchanges of energy and nutrients between ecosystems, especially at the ocean-land interface (Peterson and Fly 1987; Erskine *et al*. 1998; Wainright *et al*. 1998; Cocks *et al*. 1998a, 1998b; Stapp *et al*. 1999), and to determine an organism's tropical level and the importance of different prey items in the diet (Pearson *et al*. 2003; Nyssen *et al*. 2002; Burns *et al*. 1998; Rau *et al*. 1992; Hobson and Welch 1992; Wada *et al*. 1987).

The isotopes of relatively heavy Strontium (Sr) are more suitable for biogeochemical researches. Since ^{87}Sr is the radio decay product of ^{87}Rb and ^{86}Sr is a stable isotope, the ^{87}Sr/^{86}Sr ratio of a sample is unaffected by biological or chemical processes and mass-dependent isotope fractionation and provides information about the sample's provenance and related geologic processes, such as water-rock interaction and mixing of isotopically distinct materials (Gosz *et al*. 1983; Miller *et al*. 1993; Kennedy *et al*. 1997; Capo *et al*. 1998; Vitousek 1999; Blum *et al*. 2001; Barbieri 2002; Lyons *et al*. 2002).

For the Antarctic region, there are extensive literatures concerning the modern ecological researches using these isotopes. However, to our knowledge, these isotopes have not been examined in the sediment profiles influenced by the marine animal excreta, and the combination of these isotopes-a multiple isotopic approach-has rarely been utilized to reconstruct the paleoecological processes of seal, penguin and other marine animals. In recent studies, it has been showed that well-preserved animal relics and remnants such as seal hairs and penguin droppings in the lake sediments near seal or penguin rookeries can be used to estimate the populations of historical seals or penguins (Sun *et al*. 2000, 2001, 2004). In this paper, we report the elemental (C and N) and isotopic signatures of N, C and Sr in sediments with seal hairs and examine their potential palaeoecological applications.

2 Area of investigation

The Fildes Peninsula (longitude 58°40′59″-59°01′50″W, latitude 62°14′02″-62°14′ 02″S) is an ice-free area of the King George Island, the largest of South Shetland Islands (Fig. 1). It is hilly with a total surface area 38 km², an elevation of less than 200 m above sea level, a south-north span of 8km, and a west-east span of 2. 5-4. 5 km. The bedrock is composed of mostly laminar basaltic lava. The studied region has a cold oceanic climate, characteristic of maritime Antarctica, with a mean annual temperature of $-2. 1°C$, a summer high temperature of $11. 7°C$, and a winter low temperature of $-26. 6°C$. The annual precipitation is about 630mm and the annual average relative humidity is about 90%. The vegetation is flourishing in the summer, and the dominant species are mosses, lichens and algaes. A total of 10772 animals live on the Fildes Peninsula according to annual statistical data. On the west coast are some established colonies of marine mammals. Large marine mammals include five pinnipeds of Weddell seal (*Leptonychotes weddellii*), elephant seal (*Mirounga leonine*), leopard seal (*Hudrurga leptonyx*), fur seal (*Arctocephalus gazella*) and crabeater (*lobodon carcinophagus*). These pinnipeds prey mainly on krill, fish and cephalopod. Of those seals, elephant seal is the dominant species with a percentage of

71. 42. The fur seal with a population size of 1592 and a percentage of 14. 78% takes second place (Shen *et al*. 1999). The elephant and fur seals are commonly found on the northern beach along the southwestern coast during moulting and breeding period. Their hairs are deposited in sediments by catchment snow-melt, and this is the basis for reconstructing historical seal populations (Hodgson *et al*. 1997; 1998).
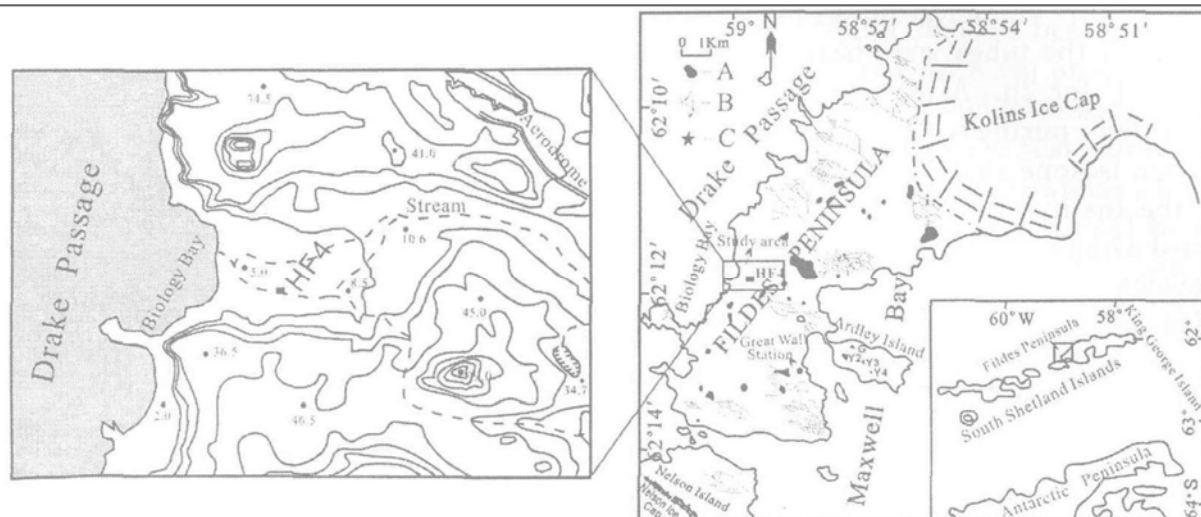

Fig. 1   Map of Fildes Peninsula showing the HF4 sampling site. Right figure: A, B and C indicates lakes, network of meltwater channels and the Great Wall Station, respectively; rectangle shows borders of the left figure. Left figure: detailed geomorphological sketch map of the studied site.

3   Sample collecting and analysis

A sediment core HF4, 42. 5 cm long, was collected from a terrestrial catchment (62°11′57″S, 59°58′48″W), where is a depositional basin located in the second marine terrace with an altitude of 8m on the west coast of Fildes Peninsula (Fig. 1), during the 18th Chinese Antarctic Research Expedition (Nov. 2001 - Mar. 2002). Sampling was performed by vertically drilling a PVC gravity pipe with 12cm diameter down to bedrock and then quickly extracting it, and the sediment core was sectioned at interval of 0. 5 cm for the top 18 cm and 1. 0cm for the remaining sediment, respectively. The lithological sections are illustrated in Figure 2. Within the overall sediment core stratigraphy, seal hairs can be found at some depths, but no plant remains can be observed at any depths. For convenience of discussion, the top 18 cm of HF4, which contains seal hairs, are denoted as HF4-18.

Each section was dried in open air and mixed sufficiently. About 1/8 of each bulk sub-sample was dried for further 24h at 105°C and then used to count seal hairs following the method of Hodgson *et al*. (1998). The seal hair was identified with reference to modern seal hair from the Fildes Peninsula on the King George Island. The counts are expressed relative to 1g of dry sediment and the seal hair number of each section is given in Figure 2.

Total organic carbon concentration (TOC), total nitrogen concentration (TN), carbon, nitrogen and strontium isotope ratios of the sediment sample HF4-18 were analyzed after removal of carbonate and seal hairs. For the purpose of comparison, the element contents and isotopic ratios in the fresh animal excrements from the maritime Antarctica were also analyzed. TN was determined by Kjeldanl digestion method

with errors of less than 0.005%. The chemical volumetric method was used to measure TOC with duplication errors of 0.05%.

Carbon isotope analysis was performed using the sealed tube combustion method (Minagawa and Wada 1984). Briefly, about 1g dried sample was mixed with CuO powder and then placed in the quartz combustion tube together with pre-roasted CuO and Cu wire and a few pieces of thin silver ribbon. After evacuation and sealing under vacuum, the tubes were heated in an induction furnace at 500°C for 30 min and then at 875°C for 2h. After cooling to room temperature, the resulting CO_2 gas was dehydrated, purified, and then separated in a high-vacuum gas transfer system. For nitrogen isotope analysis, Kjeldahl digestion method was used (Minagawa et al. 1984) at the Institute of Soil Science, Chinese Academy of Sciences (CAS). Briefly, 1g dried sample was digested with a mixture of potassium sulfate, copper sulfate and powdered selenium as catalyst and 3ml of conc. H_2SO_4. The digestion test was extended to 5h after the supernatant solution turned clear. The distillate was collected in 5ml 0.1M H_2SO_4 solution. After being concentrated to small volume in a water bath, it was transferred into a pear-type flask and concentrated further till dryness. The nitrogen in the dried specimens was converted into N_2 by Riltenberg method. Resultant CO_2 and N_2 gases were then determined using Finnigun-MAT 251 Mass spectrometer. The measurement precision of the instrument was 0.0005%, and the duplicate precision was 0.03%. Stable isotope abundances were expressed in δ notation as the deviation from standards in parts per thousand (‰) according to $\delta X = [(R_{sample}/R_{standard}) - 1] \times 1000$, 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. Replicate measurements of internal laboratory standards indicate analytical precision of isotopic measurement was within ± 0.05‰ for carbon and ± 0.2‰ for nitrogen.

For strontium isotope analysis, subsamples after air-drying were ground into powder using an agate mortar and pestle, and the >120-mesh fractions were separated from the powder to be analyzed. The dried samples with precise weight were treated with 0.1M HCl in order to ensure that the clay content and silicate fraction were not attacked by the acidic solution (Barbieri 2002). After reaction, acid-soluble and acid-insoluble fractions were separated by filter. The acid-soluble fraction extracted from the analytical sample load represented the soluble carbonate fraction, and the insoluble residual sample approximately stand for siliceous fraction (Barbieri 2002). A standardized method using a cation exchange resin was applied to separate Sr from the other ions. Mass spectrometry analyses of Sr were performed on a Finnign-MAT 262 Multiple Collector Mass spectrometer, and the Sr concentrations in the acid-soluble and acid-insoluble fractions were determined based on the analytical principle of isotopic dilution. The $^{87}Sr/^{86}Sr$ ratios were normalized to an $^{87}Sr/^{86}Sr$ ratio of 0.1194. Reproducibility of the $^{87}Sr/^{86}Sr$ measurement values was tested by replicate analysis of the NBS 987 standard, with a mean value obtained of 0.710257$\pm$21 (expressed as 2σ, $n=22$).

4 Results

4.1 *The variable characteristics of the seal hair numbers versus depth*

The seal hair numbers in each section of HF4, relative to 1g of dry sample are plotted in Figure 2. The top 18 cm sediments (HF4-18) contain some seal hairs, indicating an association with seal activity. The subsequent 5cm of sediment have few seal hairs, and no seal hairs were found below 23cm. In HF4-18, the seal hair numbers show dramatic changes versus depth. The seal hair number starts to increase at 16 cm depth and peaks between 15 cm to 13 cm depth. After that, it begins to decrease and reach a low limit at the depth of 12-8.5 cm. Between 8 cm and 4.5 cm depth, it has a brief increase, and after that it has an increasing trend with some fluctuations. According to Hodgson *et al.* (1997; 1998), the variations of seal hair numbers in the lake sediments indicate the fluctuations of visiting seal populations at the studied site. In the present study, because the sampling site is a depositional basin (Fig. 1), a geomorphological setting that would average out the signal from visiting seals prior to deposition, the seal hairs in the sediments represent an averaged catchment signal rather than the occasional occupation of an *in site* seal wallow. The remarkable variations of the seal hair abundances in HF4-18 thus signify similar changes in the historical populations of the seals visiting the marine terrace on the Fildes peninsula (Sun *et al.* 2004).
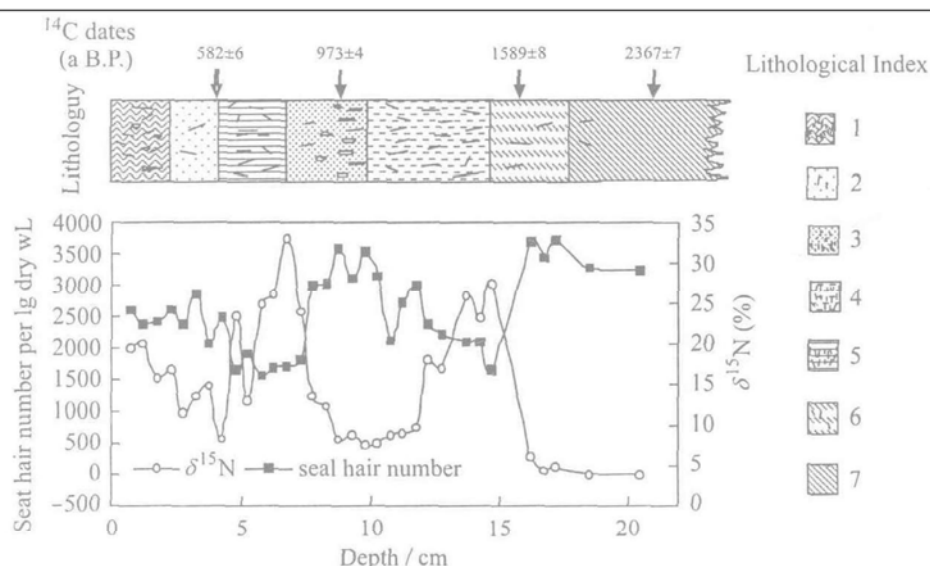

Fig. 2   The determined seal hair number (per 1g dry weight) and nitrogen isotope ratios (δ^{15}N) versus the vertical depth. The lithological section and ^{14}C dates, expressed as year before present (a B. P.), are also shown. Lithologic index: 1. Black mud with seal hairs; 2. Black fine sand with few seal hairs; 3. Deep grey mud with some seal hairs; 4. Black mud with abundant seal hairs; 5. Grey black mud enriched in organic matter with numerous seal hairs; 6. Black silt with few seal hairs and a rounded gravel covering 15 to 16 cm; 7. Black mud with much well-sorted and rounded fine sand, indicating marine sedimentary environment.

4.2   Organic carbon and nitrogen isotope ratios

The determined $\delta^{13}C_{org}$ values and atomic TOC/TN or C/N ratios in HF4-18 are listed in Table 1. The $\delta^{13}C_{org}$ values vary from -25.95 to $-23.87‰$ with an average of $-25.01‰$, and a variation coefficient (VC) of 5%. The atomic C/N ratios are in the range of 5.4-8.96 with an average of 6.99 and a VC of about 10%. The determined $\delta^{13}C_{org}$ and atomic C/N ratios in the fresh marine animal excrements, mosses and mosses-covered soils are given in Table 2. The atomic C/N ratios of HF4-18 is

apparently close to those in the fresh marine animal excrement samples, but significantly lower than those in the mosses and moss-covered soils. The δ^{15}N values of organic matter in the HF4 sediments are illustrated in Figure 2. They vary between 16. 01 and 32.81‰ with an average of 23.96‰ and a VC of 23.1%.

Table 1.   The determined δ13Corg values and atomic TOC/TN or C/N ratios in the HF4 sediments

Depth(cm)	0.5-1.0	1.0-1.5	1.5-2.0	2.0-2.5	2.5-3.0	3.5-4.0	4.0-4.5	4.5-5.0	5.0-5.5	5.5-6.0	6.0-6.5
δ^{13}C(‰)	−24.00	−23.87	−24.42	−24.42	−24.71	−24.95	−24.95	−25.11	−25.37	−25.33	−25.92
C/N	5.94	6.94	6.96	7.18	7.01	7.59	7.33	8.96	6.32	7.10	6.72
Depth(cm)	6.5-7.0	7.0-7.5	7.5-8.0	8.0-8.5	8.5-9.0	9.5-10	10-10.5	10.5-11	11-11.5	11.5-12	12-12.5
δ^{13}C(‰)	−25.3	−25.6	−24.91	−25.2	−24.91	−25.01	−25.1	−24.47	−25.05	−25.77	−25.48
C/N	6.83	6.66	6.47	6.77	6.78	6.67	6.99	7.24	6.72	7.24	6.76
Depth(cm)	12.5-13	13-13.5	13.5-14	14-14.5	14.5-15	15-15.5	16-16.5	17-17.5			
δ^{13}C(‰)	−25.28	−24.98	−25.46	−25.08	−25.19	−25.42	−25.95	−25.92			
C/N	7.09	6.54	8.46	7.44	6.29	6.87	8.33	5.40			

4.3   *Strontium isotope ratios*

The ^{87}Sr/^{86}Sr ratios in the acid-soluble and acid-insoluble fractions of HF4-18 are given in Table 3. The ^{87}Sr/^{86}Sr ratios in the acid-insoluble fractions are between 0.703283 and 0.703947 with an average of 0.703445($n=12$). These values are in good agreement with the Sr isotope composition (0.70314-0.70396) of the bedrock around the studied site (Zhen *et al.* 1988; Li *et al.* 1992; Xing *et al.* 1997). For the samples of acid-soluble fractions, however, the ^{87}Sr/^{86}Sr ratios vary between 0. 705066 and 0.706117 with an average of 0.705507($n=10$), higher than those of the local bedrock, but lower than 0.70918, the ratio in modern-day sea water.

5   Discussion

5.1   *Identification of the carbon and nitrogen source*

The organic carbon isotope compositions of HF4-18 and other previously reported samples of different origins in Antarctica are compared in Figure 3. As is clearly seen from Figure 3, the determined δ^{13}C values of HF4-18 do not fall in the range of the δ^{13}C values of other samples, and thus the δ^{13}C values are insufficient for identifying the origin of the organic carbon in HF4-18. This is consistent with the findings by Cocks *et al.* (1998a) in the study of the origin of soil carbon in Antarctica.

The TOC and TN contents of HF4 indicate that the organic carbon and nitrogen are likely related to seal activity. The average concentrations ($n=30$) of TOC and TN in the top 18cm sections of HF4 with numerous seal hairs, are 1.75% (0.88%-3.10%) and 0.29% (0.14%-0.54%), respectively, but in other sections of HF4 with few or no seal hairs, the mean TOC and TN contents ($n=6$) are 0.37% (0. 26%-0.60%) and 0.07% (0.057%-0.084%), respectively. Additionally, there also exists a significant correlation between TN and TOC, as shown in Figure 4A, suggesting a common origin for carbon and nitrogen. The C/N values of HF4-18 indicate that the organic matters are probably from seal excrements. In general, marine and terrestrial organic substances have typical C/N ratios of <8 and >12, respectively

(Prahl *et al.* 1980; Bordovskiy 1965; Schubert and Calvert 2001). HF4-18 has an average C/N value of 6. 99 (5. 4-8. 96, $n = 30$), close to 5. 65 ± 1. 86 ($n = 12$), the value for fresh seabird droppings and seal faeces in the Antarctic region (Table 2).
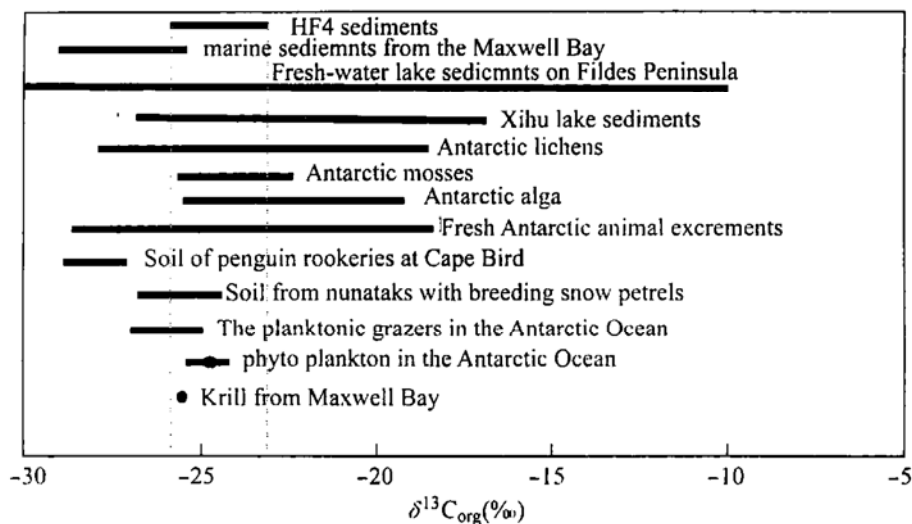

Fig. 3   The variable range of $\delta^{13}C$ values in the organic matters of different origins in the Antarctic region. From top to bottom: the marine sediments from Maxwell Bay (Chen *et al.* 1997), the fresh water lake sediments on Fildes Peninsula (Liu *et al* 1998), the Xihu lake sediments in the area of Great Wall Station (Li *et al.* 2002), the lichens, mosses and alga (Galimov 2000), the soil of penguin rookeries at Cape Bird (Mizutani and Wada 1988), the soil from Nunataks with breeding snow petrels (Cocks *et al.* 1998b), the planktonic grazers and phytoplanktons in the Antarctic Ocean (Kaehler *et al.* 2000), the krill from Maxwell Bay (Huang *et al.* 1998) and the C3 and C4 plants (O'Leary 1988).
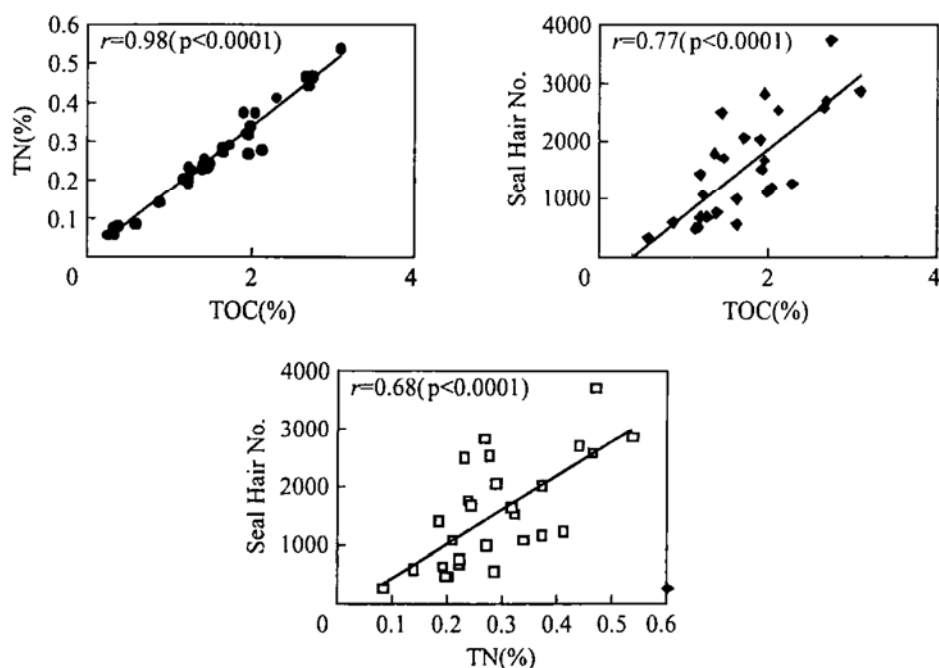

Fig. 4   Correlations among total organic carbon (TOC), total nitrogen (TN) and seal hair numbers (per 1g dry weight).

We also made the cross plot of atomic C/N and organic $\delta^{13}C$ values, as proposed

by Meyers *et al.* (1994) and Arnaboldi *et al.* (2003), to identify the origin of organic matter in HF4-18. As shown in Figure 5, the spots of the subsamples of HF4-18 are
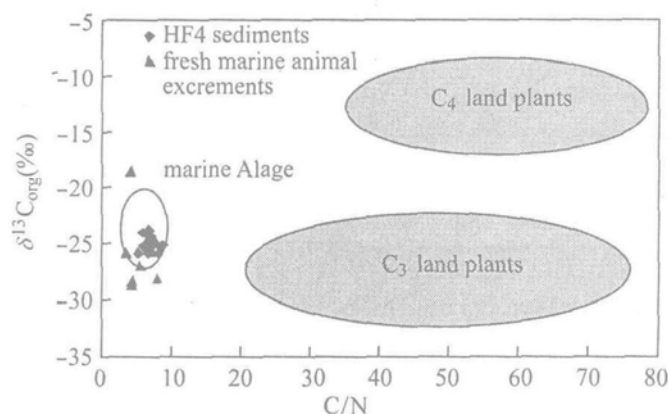

Fig. 5 δ^{13}Corg and atomic C/N values of the organic matters in HF4 sediment samples, marine algae, C$_3$ and C$_4$ land plants. Apparently, the organic matter in HF4 is predominantly marine in origin. The data for marine algae and C$_3$ and C$_4$ plants are from Meyers (1994) and Arnaboldi *et al.* (2003).

Table 2.   The determined δ13Corg values and atomic TOC/TN or C/N ratios in the fresh marine animal excrements, mosses and mosses-covered soils

Sample No.	BG-01	AP-01	AP-02	ES-01	WS-01	FS-01	GP-01	SP-01
δ^{13}C(‰)	−18.53	−28.37	−27.11	−28.02	−28.19	−25.72	−28.63	−25.97
C/N	5.01	5.19	6.56	n.d	9.32	8.41	5.23	4.31
Sample No.	AP-03	ES-02	SK-01	SP-02	BG-02	MS-01	MS-02	MSS-01
C/N	4.46	7.49	3.90	3.80	4.18	39.99	10.37	15.45

Notes: BG-01 and BG-02: black-backed gull (*Larus dominicanus dominicanus*); AP-01, AP-02 and AP-03: Adelie Penguin (*Pygoscelis adelie*); ES-01 and ES-02: elephant seal (*Mirounga leonina*) ; WS-01: Weddell seal (*Leptonychotes Wedellii*); FS-01: fur seal (*Arctocephalus gazella*); GP-01: Gentoo Penguin (*Pygoscelis Gentoo*); SP-01 and SP-02: Southern giant petrel (*Macronectes giganteus*); SK-01: Skua(*Catharacta lonnbergi*); MS-01 and MS-02: mosses(*Bryum Pseudotriquetrum* and *Bryum muelthenbeckii*); MSS-01: soil covered with mosses. n.d.: not determined.

clustered together, indicating the common source of organic materials, close to those of fresh marine animal excrements, and fall well within the range of marine algae, but far from the C3 and C4 terrestrial plants. Taking into account the appearance of seal hairs, TOC and TN concentrations and C/N values, the organic matters in HF4-18 are most likely from the seal excrements of marine origin and transported to the terrestrial ecosystem by seals through the natural food chain.

The identification of the organic matter source in HF4-18 has some paleoecological applications. Since the organic carbon and nitrogen in HF4-18 are mainly from the seal excrement inputs, the TOC and TN contents in HF4-18 are expected to be proportional to the historical seal populations, like the seal hair numbers. Indeed, as shown in Figure 4, the TOC and TN contents in HF4-18 are strongly correlated with the seal hair numbers with the correlation coefficients of 0.77 and 0.68 ($P<0.001$), respectively.

]5.2   *The δ^{15}N values in HF4-18 and their paleoecological implications*

The δ^{15}N values of HF4-18 are close to the highest one recorded so far in the ornithogenic soil of Antarctica (Wada *et al.* 1981; Mizutani *et al.* 1985a). The δ^{15}N

values in the ornithogenic soil on Nunataks are in the range of 13. ‰-25. 9‰ ($n=7$) (Cocks *et al.* 1998b). Those in the soil of penguin rookeries at Cape Bird are between 26. 8‰-38. 1‰ ($n=6$) (Mizutani *et al.* 1986). These high $\delta^{15}N$ values have been commonly used as a reliable marker to identify whether a soil or plant sample is influenced by animal-derived nitrogen (Mizutani *et al.* 1986; Cocks *et al.* 1998a, 1998b; Erskine 1998). Also, the nitrogen isotopic compositions of sediment samples reflect the source's 15N signatures and remain relatively stable after the deposition (Bergstron *et al.* 2002). The high $\delta^{15}N$ values in HF4-18 thus confirm its origination of seal excrements.

The high $\delta^{15}N$ values of HF4-18, like those of ornithogenic soils, can be explained by two mechanism: trophic enrichment and NH_3 volatilization (Lindeboom 1984; Mizutani *et al.* 1986; Wainright *et al.* 1998; Liu *et al.* 2004). Trophic enrichment refers to the 15N enrichment in organic matters as they pass up the food chain to the consumer that excretes the nitrogen (Wainright *et al.* 1998). In the Antarctic food chain, $\delta^{15}N$ generally displays a stepwise increment of about 3‰ at each successive trophic level, and the $\delta^{15}N$ value of an animal's excrement is proportional to its position in the food chain (Erskine *et al.* 1998). In light of this, Antarctic seals have $\delta^{15}N$ values higher than other animals due to its top position in the food web of the Southern Ocean ecosystem. For example, penguins, small fish and krill have a mean $\delta^{15}N$ value of 10. 6‰, 10‰ and 3‰, respectively, whereas Antarctic seals have an average $\delta^{15}N$ value of 13‰ (Wada *et al.* 1991).

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 (Lindeboom 1984). Urea or uric acid can be rapidly transformed into ammonia through aerobic decomposition, as has been demonstrated in field animal rookeries as well as in laboratory experiments (Mizutani *et al.* 1985a, 1985b, 1988; Lindeboom 1984; Wainright *et al.* 1998; Erskine *et al.* 1998, Cocks *et al.* 1998a, 1998b). The ammonia is depleted in 15N and easily lost to the atmosphere by volatilization, leading to the loss of lighter isotope and thus the enrichment of heavier isotopes in the sediments (Heaton 1988; Legrand and Ducroz 1998).
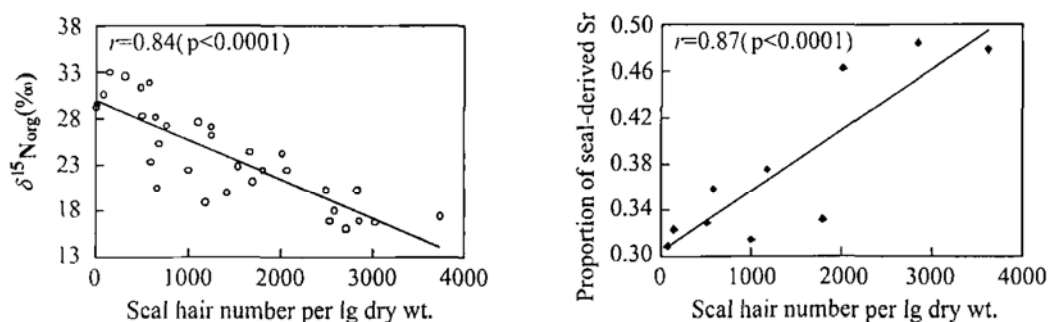

Fig. 6   The correlations between the seal hair numbers (per 1g dry weight), nitrogen isotope composition and the proportion of seal-derived Sr to the total Sr in the acid-soluble fractions of HF4 sediments.

The $\delta^{15}N$ values in HF4-18 also exhibit a large variation with a VC of 23. 1%. This may reflect the historically variable volatilization rates of ammonia produced in the seal excrements before deposition at sampling site (Mizutani *et al.* 1991; Cocks *et al.* 1998a). A Pearson correlation analysis gives a significantly negative correlation between the determined $\delta^{15}N$ values and the seal hair abundances ($r=-0. 84, P<0.$

0001, $n=33$) (Fig. 6A). This negative correlation perhaps can be explained by the observations that cold climates increase the volatilization rate of ammonia but reduce the historical seal population, and vice versa (Liu *et al*. 2004). This finding also suggests the potential of $\delta^{15}N$ signatures in the sediments as the proxy records of historical seal populations. Comparing with the method of counting seal hair numbers-a time-consuming and boring work, the nitrogen isotopic analysis may be faster and more accurate.

5.3   The Sr isotope ratios and their paleoecological implications

In the acid-insoluble fraction of HF4, the $^{87}Sr/^{86}Sr$ ratios are close to those in the local basaltic bedrock, suggesting that the acid-insoluble Sr has been predominantly derived from geological materials around studied site. In the acid-soluble fraction of HF4, the $^{87}Sr/^{86}Sr$ ratios range between the relatively high value for the current sea water (0.70918) and the lower for the local volcanic rocks (0.70314-0.70396) (Sun *et al*. 2005). This suggests that the marine-derived Sr or weathering-derived Sr with a bedrock $^{87}Sr/^{86}Sr$ signature can not be the sole source of acid-soluble Sr. Here, we interpreted the Sr in acid-soluble fraction as a mixture of the above isotopically distinct Sr point sources. The marine original Sr probably has two primary transport pathways: from atmospheric dry and wet deposition and from the seal excrement. The atmospheric deposition of Sr is usually lower than 1ppb as inferred from the data in the polar ice core (Capo *et al*. 1998; Burton *et al*. 2002). Comparing with the Sr concentrations in the fresh excrements (222-2164 ppm, $n=6$) and in the acid-soluble fraction of HF4 (169-563 ppm, $n=7$), the atmospheric deposition is apparently negligible.

In order to evaluate the relative contributions of seal excrements and weathered local volcanic rock to the Sr isotope composition in the acid-soluble fraction of the sediments, the isotope mixing equation based on the mass balance were applied (Graustein 1983; 1989; Miller *et al*. 1993; Capo *et al*. 1998). We use the following mass balance equation to estimate the fractional contribution X_{marine} of the marine-derived Sr:

$$X_{marine} = [(^{87}Sr/^{86}Sr)_{mixture} - (^{87}Sr/^{86}Sr)_{weathering}] / [(^{87}Sr/^{86}Sr)_{marine} - (^{87}Sr/^{86}Sr)_{weathering}]$$

Where $(^{87}Sr/^{86}Sr)_{mixture}$ is the determined Sr isotope ratios in the acid-soluble fraction of HF4; $(^{87}Sr/^{86}Sr)$ weathering and $(^{87}Sr/^{86}Sr)$ marine are the ratios in the weathering-derived and marine-derived sources, respectively. Assuming $(^{87}Sr/^{86}Sr)$ weathering is close to the average measured ratios in the acid-insoluble fraction, $(^{87}Sr/^{86}Sr)$ marine is an average of the acid-soluble fractions of fresh marine animal excrements near the study site, which has an average value of 0.709166, very close to 0.70918, the ratio of the present-day seawater (Table 3).

The calculated X_{marine} is about 30-50% (Table 3). Although the Sr isotope ratios in the acid-soluble fraction of only ten samples were analyzed, very interestingly, a linear regression analysis reveals a good correlation between X_{marine} and the seal hair abundances with a correlation coefficient of 0.86 (Figure 6B). Since X_{marine} is proportional to $(^{87}Sr/^{86}Sr)_{mixture}$, the $^{87}Sr/^{86}Sr$ ratios in the acid-soluble fraction of the

sediments, it is reasonable to believe that they both can provide a useful marker for the historical seal populations in the Antarctic region.

6 Conclusions

In this study, we determined seal hair numbers, total organic carbon (TOC),

Table 3.   The determined $^{87}Sr/^{86}Sr$ ratios in the acid-soluble and acid-insoluble fractions of HF4-18

Depth (cm)	$^{87}Sr/^{86}Sr$ a	Depth (cm)	$^{87}Sr/^{86}Sr$ b	X_{marine}	No.	$^{87}Sr/^{86}Sr$ c
2-2.5	0.703367±63	1.5-2	0.705995±32	0.463	1	0.709223±20
2.5-3	0.703392±22	2.5-3	0.705155±16	0.313	2	0.709219±20
4-4.5	0.703947±55	5-5.5	0.705503±18	0.375	3	0.709238±16
6-6.5	0.703338±13	6-6.5	0.706117±62	0.485	4	0.70918±16
7-7.5	0.703367±17	8.5-9	0.705404±32	0.357	5	0.709175±17
8.5-9	0.703341±15	10-10.5	0.705236±50	0.327	6	0.708963±16
10-10.5	0.703283±19	12-12.5	0.705254±40	0.330		
12-12.5	0.703379±22	13-13.5	0.706083±30	0.479		
13-13.5	0.703516±24	16.5-17	0.705121±38	0.307		
13.5-14	0.703330±15	17-17.5	0.705201±15	0.321		
16.5-17	0.703546±14					
17-17.5	0.703528±16					

Notes: a . b and c are for the acid-insoluble and acid soluble fractions of the HF4 sediments, and the acid-soluble fraction of fresh marine animal excrements, respectively.

total nitrogen (TN) and the isotope compositions of C, N and Sr in the sediments containing seal excrements and hairs. From the results, we can draw the following conclusions:

(1) The seal hair abundances exhibit remarkable fluctuations in HF4 sediments against depths, indicating similar changes in the historical populations of the seals visiting the marine terrace on Fildes peninsula.

(2) The combination of $\delta^{13}C$, C/N values, TOC and TN clearly show that the organic matters in HF4-18, the sections of HF4 containing seal hairs, are predominantly derived from seal excrements.

(3) The determined $\delta^{15}N$ values in HF4-18 are not only remarkably high, but also exhibit large variations. These high $\delta^{15}N$ values can be attributed to trophic enrichment and NH3 volatilization. The large variation and the observed negative correlation between $\delta^{15}N$ values and seal hair abundances seem to be related to the changes in the palaeoclimates and the volatilization rates of the ammonia produced in the seal excrements. The time-integrated $\delta^{15}N$ signatures in the sediments with nitrogen source predominantly derived from seal excrements have the potential as a paleoecological tool for reconstructing the historical seal population fluctuations.

(4) The determined $^{87}Sr/^{86}Sr$ ratios in the acid-insoluble fraction of HF4 are close to the Sr isotopic compositions in the local basaltic bedrock and show little variations. The $^{87}Sr/^{86}Sr$ ratios in the acid-soluble fraction, however, have some variation (0.705066- 0.706117) with a mean value of 0.705507; and they can be interpreted as a mixture of those of the weathered local bedrocks and seal excrements. The

fractional contribution of marine origin Sr, X_{marine}, is estimated to be about 30-50%. The estimated X_{marine} has a significant positive correlation with the seal hair abundances in sediments, suggesting that X_{marine} and the $^{87}Sr/^{86}Sr$ ratios in the acid-soluble fraction of sediments can be used to estimate the historical seal populations in the Antarctic region.

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