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

Liu Xiaodong(刘晓东)¹, Sun Liguang(孙立广)¹*, Yin Xuebin(尹雪斌)¹, Xie Zhouqing(谢周清)¹, Zhu Renbin(朱仁斌)¹, Wang Yuhong(王玉宏)¹-²

1 Institute of Polar Environment, University of Science and Technology of China, Hefei 230026, China
2 National Institutes of Health, Maryland, U. S. A. 20892

Received September 13, 2005

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 δ¹³C, 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 δ¹⁵N values in sediments are attributed to trophic enrichment and NH₄ volatilization processes. The large variations in the δ¹⁵N values and the negative correlation between the δ¹⁵N 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 ⁸⁷Sr/⁸⁶Sr 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%-60%). The calculated proportion of seal-derived Sr based on the ⁸⁷Sr/⁸⁶Sr ratios has a significant correlation with seal hair abundances in sediments. These results suggest that δ¹⁵N values and the ⁸⁷Sr/⁸⁶Sr 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 elements, 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 trophic 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 palaeoecological 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 Fildeles Peninsula (longitude 59°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 algae. A total of 10772 animals live on the Fildeles 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 (Hudsurga 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 molting 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 intervals of 0.5 cm for the top 18 cm and 1.0 cm 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 Kjeldahl 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 CO2 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. H2SO4. The digestion test was extended to 5h after the supernatant solution turned clear. The distillate was collected in 5ml 0.1M H2SO4 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 N2 by Ritenberg method. Resultant CO2 and N2 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 δX = [(Rsample/Rstandard)−1]×1000, where X is 13C or 15N and R is the corresponding ratio 13C/12C or 15N/14N. The Rstandard values were based on the PeeDee Belemnite (PDB) for 13C and atmospheric N2 (AIR) for 15N. 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 Finnigun-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 87Sr/86Sr ratios were normalized to an 87Sr/86Sr ratio of 0.1194. Reproducibility of the 87Sr/86Sr measurement values was tested by replicate analysis of the NBS 987 standard, with a mean value obtained of 0.710257 ± 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 situ 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 ($\delta^{15}$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 $-25.96$ 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 $\delta^{15}$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 $\delta^{13}$Corg values and atomic TOC/TN or C/N ratios in the HF4 sediments

<table>
<thead>
<tr>
<th>Depth(cm)</th>
<th>Depth(cm)</th>
<th>$\delta^{13}$C(‰)</th>
<th>$\delta^{13}$C(‰)</th>
<th>C/N</th>
<th>C/N</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-1.0</td>
<td>6.5-7.0</td>
<td>-24.00</td>
<td>-25.3</td>
<td>5.94</td>
<td>6.94</td>
<td>6.88</td>
</tr>
<tr>
<td>1.0-1.5</td>
<td>7.0-7.5</td>
<td>-23.87</td>
<td>-25.6</td>
<td>6.98</td>
<td>6.98</td>
<td>7.18</td>
</tr>
<tr>
<td>1.5-2.0</td>
<td>7.5-8.0</td>
<td>-24.42</td>
<td>-24.91</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>2.0-2.5</td>
<td>8.0-8.5</td>
<td>-24.42</td>
<td>-25.2</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>2.5-3.0</td>
<td>8.5-9.0</td>
<td>-24.42</td>
<td>-24.91</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>3.0-3.5</td>
<td>9.5-10</td>
<td>-24.42</td>
<td>-25.01</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>3.5-4.0</td>
<td>10-10.5</td>
<td>-24.42</td>
<td>-25.1</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>4.0-4.5</td>
<td>10.5-11</td>
<td>-24.42</td>
<td>-24.7</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>4.5-5.0</td>
<td>11-11.5</td>
<td>-24.42</td>
<td>-25.05</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>5.0-5.5</td>
<td>11.5-12</td>
<td>-24.42</td>
<td>-25.77</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>5.5-6.0</td>
<td>12-12.5</td>
<td>-24.42</td>
<td>-25.48</td>
<td>7.01</td>
<td>7.01</td>
<td>7.01</td>
</tr>
</tbody>
</table>

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 $\delta^{13}$C values of HF4-18 do not fall in the range of the $\delta^{13}$C values of other samples, and thus the $\delta^{13}$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).

![Graph showing δ13C values](image)

**Fig. 3** The variable range of δ13C 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 Filde 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 (Misutani 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 (OLeary 1988).

![Correlation plots](image)

**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 δ13C 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 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 $\delta^{15}N$ values in HF4-18 and their paleoecological implications

The $\delta^{15}N$ 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 $\delta^{15}N$
values in the ornithogenic soil on Nunataks are in the range of 13. 3%–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 δ^{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 (Bergström et al. 2002). The high δ^{15}N values in HF4-18 thus confirm its origination of seal excrements.

The high δ^{15}N values of HF4-18, like those of ornithogenic soils, can be explained by two mechanism: trophic enrichment and NH₃ 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, δ^{15}N generally displays a stepwise increment of about 3% at each successive trophic level, and the δ^{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 δ^{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 δ^{15}N value of 10. 6%, 10% and 3%, respectively, whereas Antarctic seals have an average δ^{15}N value of 13% (Wada et al. 1991).

NH₃ 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 NH₄ 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).

![Diagram](image)

**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 δ^{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 δ^{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 1 ppb 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 $X_{\text{marine}}$ of the marine-derived Sr:

$$X_{\text{marine}} = \left[ \left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{mixture}} - \left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{weathering}} \right] / \left[ \left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{marine}} - \left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{weathering}} \right]$$

Where $\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{mixture}}$ is the determined Sr isotope ratios in the acid-soluble fraction of HF4; $\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{weathering}}$ and $\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{marine}}$ are the ratios in the weathering-derived and marine-derived sources, respectively. Assuming $\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{weathering}}$ is close to the average measured ratios in the acid-insoluble fraction, $\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{marine}}$ 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 $X_{\text{marine}}$ 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 $X_{\text{marine}}$ and the seal hair abundances with a correlation coefficient of 0.86 (Figure 6B). Since $X_{\text{marine}}$ is proportional to $\left( \frac{^{87}Sr}{^{86}Sr} \right)_{\text{mixture}}$, 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 | Depth (cm) | $^{87}$Sr/$^{86}$Srb | $X_{marine}$ | No. |
| 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 | 0.708219±20 |
| 4.4.5 | 0.703047±55 | 5.5, 5 | 0.705603±18 | 0.375 | 3 | 0.706238±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 | 0.70917±17 |
| 8.5-9 | 0.703341±15 | 10-10.5 | 0.705235±50 | 0.327 | 6 | 0.708963±16 |
| 10-10.5 | 0.703283±19 | 12-12.5 | 0.70525±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 the 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, $X_{\text{marine}}$, is estimated to be about 30-50\%. The estimated $X_{\text{marine}}$ has a significant positive correlation with the seal hair abundances in sediments, suggesting that $X_{\text{marine}}$ and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the acid-soluble fraction of sediments can be used to estimate the historical seal populations in the Antarctic region.

**Acknowledgements** We would like to thank Polar Office of National Oceanic Bureau of China for support and assistance and 24 USTC students who counted a total of 360,000 seal hairs, a time-consuming and boring work. This study was supported by the National Natural Science Foundation (Grant No. 40476001 and 40231002), China Postdoctoral Science foundation and KC Wang Educational Foundation, Hong Kong.

**References**

Arnaboldi M, Meyers P (2003); Geochemical evidence for paleoclimatic variations during deposition of two Late Pliocene sapropels from the Vrica section, Calabria. Palaeogeography Palaeoclimatology Palaeoecology, 190; 257 - 271.

Barbieri M (2002); Use of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio as an environmental tracer; an example of the application to the Fossil Forest of the Dunabarba (FPD) sedimentary system near Avigliano Umbro (Teruel-Central Italy). Applied Geochemistry, 17; 1543 - 1550.


Blum JD, Taliaferro EH, Holmes RT (2001); Determining the sources of calcium for migratory song birds using stable strontium isotopes. Oecologia, 126; 569 - 574.

Bordovskiy OK (1965); Accumulation and transformation of organic substances in marine sediments. Marine Geology, 3; 3 - 114.

Burns JM, Trumblt MA, Castellini MA (1998); The diet of Weddell seals in McMurdo Sound, Antarctica as determined from scat collections and stable isotope analysis. Polar Biology, 19; 272 - 282.


Capo RC, Stewart BW, Chadwick OA (1998); Strontium isotopes as tracers of ecosystem processes; theory and methods. Geoderma, 82; 197 - 225.

Chamberlain CP, Blum JD, Holmes RT, Xiaohong Feng, Sherry TW, Graves GR (1997); The use of isotope tracers for identifying populations of migratory birds. Oecologia, 109; 132 - 141.


Cocks MP, Newton IP, Stock WD (1998b); Bird effects on organic processes in soils from five microhabitats on a nunatak with and without breeding snow petrels in Dronning Maud Land, Antarctica. Polar Biology, 20; 112 - 20.


Graustein WC (1989); $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measure the sources and flow of strontium in terrestrial ecosys-
Elemental and Isotopic Signatures in the Sediments Influenced... 133


Harrington RR, Kennedy BP, Chamberlain CP, Blum JD, Folt CL (1998); 15N enrichment in agricultural catchments; field patterns and applications to tracking Atlantic Salmon (Salmo Salar). Chemical Geology, 147; 281–294.

Heaton THE (1988); Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere; a review. Chemical Geology, 59; 87–102.

Hobson KA (1999); Tracing origins and migration of wildlife using stable isotopes; a review. Oecologia, 120; 314–326.

Hobson KA, Welch HE (1992); Determination of trophic relationships with a high Arctic marine food web using 13C and 15N analysis. Mar. Ecol. Prog. Ser., 84(1); 9–18.


Legrand M, Ducros F (1998); Ammonium in coastal Antarctic aerosol and snow: role of polar ocean and penguin emissions. Journal of Geophysical Research, 103(D3); 11043–11056.


Li XM, Yuan BY, Zhao JL (2002); Holocene environmental change delivered from lake core in Fildes Peninsula of King George Island, Antarctic. Chinese Journal of Polar Science, 14; 35–43.

Lyons WB, Nezat CA, Benson LV, Bullen T, Graham EY, Kidd J, Welch KA, Thomas JM (2002); Strontium isotopic signatures of the streams and lakes of Taylor Valley, Southern Victoria Land, Antarctica; chemical weathering in a polar climate. Aquatic Geochemistry, 8; 75–95.


Mizutani H, Kabaya Y, Wada E (1985a); Ammonia volatilization and high 15N/14N ratio in a penguin...
Oelbermann K., Scheu S. (2002); Stable isotope enrichment (δ15N and δ13C) in a generalist predator (Paradosa Iugubris, Araneae; Lycosidae); effects of prey quality. Oecologia, 130; 337–344.
Rau GH., Ainley DG., Bengson JL., Torres J., Hopkins T. (1992); δ15N/δN and δ13C/δ13C in Weddell Sea birds, seals, and fish: implications for diet and trophic structure. Marine Ecology Progress Series, 84; 1–8.
Sun LG and Xie ZQ. (2001); Relics; penguin population programs. Science progress, 84(1); 31–44.
Sun LG, Zhu RB, Liu XD, Xie ZQ, Yin XB, Zhao SP, Wang YH. (2005); HCl-soluble 87Sr/86Sr ratio in the sediments impacted by penguin or seal excreta as a proxy for the size of historical population in the maritime Antarctic. Marine Ecology-Progress Series, 303; 43–80.