A preliminary study of elemental geochemistry and its potential application in Antarctic Seal palaeoecology

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The elemental geochemical composition of sediments influenced by seal excrements in the Antarctic Fildes Peninsula has been examined in order to establish the source of organic matter, identify potential bio-elements and explore their potential palaeoecological implications. The combination of total organic carbon concentration (TOC), total nitrogen concentration (TN), organic carbon isotope ($\delta^{13}$C) and atomic C/N ratio shows that the organic matter in the sediments with many seal hairs has a marine origin, predominantly derived from seal excrements. Among the determined element/oxide concentrations, S, Se, F, Zn, Hg, FeO and P$_2$O$_5$ were found to be remarkably enriched in the sediments influenced by seal excrements with respect to the sediments with few or without seal hairs, and their concentrations displayed strong and positive correlations with organic matter abundance, indicating that they had the same source and transportation mechanism as the in situ organic material. A comparison of these element/oxide concentrations with the seal hair numbers showed that they had similar distribution patterns with depth, and the correlations were positive and statistically significant. Based upon these results, S, Se, F, Zn, Hg, FeO and P$_2$O$_5$ in the seal excrement sediments were identified as potential bio-elements and their concentrations could potentially be used as inorganic geochemical indicators for tracking seal palaeoecological processes in the Antarctic region.

Keywords: elemental geochemistry, sediments influenced by seal excrement, palaeoecology, Antarctica

INTRODUCTION

On the Antarctic continent, ice-free areas, formed due to climate warming and glacial retreat, are important for scientific expeditions even though they comprise approximately 2% of the continent. The sediments from these ice-free areas not only provide good records of the history of regional chemical weathering and environmental variability, but also preserve well global changes of different spatiotemporal scales, and represent ideal proxy materials for studying the palaeoenvironmental evolution of the Antarctic region during the Holocene time period (Ingolfsson et al., 1998). The information recorded in these sediments about palaeoclimate changes and glacier advance and retreat has been extensively studied (e.g., Mäusbacher et al., 1989; Schmidt et al., 1990; Goodwin, 1993; Martinez-Macchiavello et al., 1996; Björck et al., 1996; Hjort et al., 1997; Smith et al., 1999), but comparatively less attention has been given to the palaeoecological processes of Antarctic marine animals, such as seal, penguin, etc. (Baroni et al., 1994; Polito et al., 2002; McDaniel et al., 2002; Emslie et al., 2003). This may be due to the fact that current paleoecological studies strongly rely on fossil relics, such as footprint, moulage, reliquia, bone and other materials, but these materials are rarely available and difficult to preserve. However, in recent studies, Hodgson et al. (1997, 1998), Sun and Xie (2001) and Sun et al. (2000, 2001, 2004) argued that well-preserved animal relics and remnants, such as seal hairs and penguin droppings, in lake sediments near seal or penguin rookeries could be used to estimate the historical populations of seals or penguins, and the sediment profiles containing these biological relics could be useful for examining the ecological responses of these animals to climate changes and human activity.

Elemental geochemical studies are increasingly being used to interpret some of the information on the palaeoclimatic variability and anthropogenic pollution recorded in different materials of the Antarctic environment, such as snow-ice, soil and sediments (Boutron et al., 1986; Bishop et al., 1996; Ciaralli et al., 1998; Ikegawa et al., 1999; Giordano et al., 1999; Sheppard et al., 2000). To our knowledge, however, sediments influenced by seal excrements have rarely been studied with an elemental geochemical approach. This paper presents a complete elemental geochemical study of seal excrement-rich sediment profiles containing seal hairs from the Fildes Peninsula of Antarctic King George Island, fol-
Following a previous study by Sun et al. (2004). The main objectives of this study are to (1) determine the source of organic matter, (2) identify bio-elements based on the analysis of elemental geochemical characteristics, and (3) evaluate the possibilities of the application of bio-elements as inorganic geochemical proxies for seal palaeoecology through the examination of the inter-correlations between the bio-element concentrations and the seal hair abundances.

**STUDY AREA**

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 the South Shetland Islands (Fig. 1). It is hilly with a total surface area 38 km², an elevation less than 200 meters above sea level, a south-north span of 8 kilometers, and a west-east span of 2.5−4.5 kilometers. The bedrock is composed of mostly laminar basaltic lava. The study area 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 630 mm 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 Fildes Peninsula according to annual statistical data (Shen et al., 1999). 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 (Huduruga 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 the second place. 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).

**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) of a depositional basin located in the second marine terrace with an altitude of 8 meters on the west coast of the Fildes peninsula (Fig. 1), during the Eighteenth Chinese Antarctic Research Expedition (Nov. 2001−Mar. 2002). During sampling, a PVC plastic gravity pipe of 12 cm in diameter was pushed down into the bedrock and then quickly retrieved. The sediment core was sectioned every 0.5 cm for the top 18 cm and then every 1.0 cm for the remaining 24.5 cm. The lithological section is illustrated in Fig. 2. Within the overall sediment core stratigraphy, seal hairs could be found at some depth, but no plant remains could be observed. As proposed by Hodgson et al. (1997, 1998), the well preserved seal hairs in the sediments are usually used as a reliable indicator of seal presence. For convenience of discussion, the top 18 cm of HF4 which contained many seal hairs is referred to as HF4-18, whereas the remaining 24.5 cm of sediments are referred to as HF4-24.5.

Each portion of the sediment core was air-dried and homogenized. The number of seal hairs in each section was counted, and the results, expressed as relative abun-
dance in 1 g of dry weight of sediments, are given in Fig. 2. A detailed description of the count and analysis of seal hairs is given in Sun et al. (2004). Total organic carbon concentration (TOC), total nitrogen concentration (TN), loss on ignition (LOI) and carbon isotope ratios of the sediments were analyzed after removal of carbonate and seal hairs. For comparison purposes, the above element contents and isotopic ratios of fresh animal excrements from the maritime Antarctic were also analyzed. The LOI of the subsamples was determined by drying the samples at 105°C and then ashing them for an additional 3 h at 550°C. TN was determined with the Kjeldanl digestion method with an error less than 0.005% (Sun et al., 1991). The chemical volumetric method was used to measure TOC with a duplication error of 0.05% (Loring et al., 1992). The determined TOC, TN and LOI versus depth are plotted in Fig. 2. Carbon isotope analysis was performed using the sealed tube combustion method (Minagawa et al., 1984). Briefly, about 1 g of dried sample was mixed with CuO powder and then placed in a 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 2 h. After cooling the tubes at room temperature, the resulting CO₂ gas was dehydrated, purified, and then separated in a high-vacuum gas transfer system. Isotope measurements were made on a Finnigan-MAT 251 Mass spectrometer and are reported in the ‰ (per mil) notation with respect to Pee Dee Belemnites (PDB) standard. Replicate measurements of internal laboratory standards indicated that the analytical precision of the isotopic measurement was within ±0.05‰.

For chemical element analysis, subsamples were sieved through a 200 mesh after air-drying them. About 0.1–0.5 g of each powder sample was taken, precisely weighed, and then digested by multi-acid in a Pt crucible with electric heating. The digested samples were analyzed for the following 27 elements/oxides: SiO₂, Al₂O₃, FeO, Fe₂O₃, S, F, Sr, Ba, P₂O₅, TiO₂, Cr, V, B, As, Se, Hg, K₂O, Na₂O, CaO, MgO, MnO, Pb, Ni, Cu, Zn, Ga, Cd. Concentrations of SiO₂, Al₂O₃ and Fe₂O₃ were determined by various wet chemical methods. FeO was measured by the potassium dichromate volumetric method. S was analyzed by the KI volume method after combustion in SRJK-2 high-temperature furnace. F was measured by ion selective electrode (ISZ). Trace elements Sr and Ba were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Model Atom Scan Advantage from Thermo Elemental) after digestion by aqua regia/HF/HClO₄. Abundance of P₂O₅, TiO₂, Cr, V and B were determined by ultraviolet visible spectrophotometry (UVS). Concentrations of As, Se and Hg were measured by Atomic Absorption Spectrometer (AFS-2202a) after dissolution in HNO₃-H₂O₂-HClO₄ (in proportion to V:V:V = 5:10:1). Atomic absorption spec-

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**Fig. 2.** Down-core variation profiles of the seal hair abundance, loss on ignition (LOI) percentage, total organic carbon (TOC) and total nitrogen (TN) contents of the sediments impacted by seal excrements. Lithological 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, a rounded gravel covering 15 to 16 cm; 7. Black mud with much well-sorted and rounded fine sand, indicating marine sedimentary environment.
trophotometry (AAS) (Model PZ-1100) was used to de-
terminate K₂O, Na₂O, CaO, MgO, MnO, Ni, Cu, Zn, Pb, 
Cd and Ga. For quality control purpose, the Chinese na-
tional standard sediment and soil samples of 07407, 07402 
(2 replicates), 07403, 07405 were measured as “un-
knowns” with every batch analysis. The results from the 
analyses were consistent with the reference values and 
the differences for most major and trace elements were 
generally within ±0.5% and ±15%, respectively (Fig. 3). 
The quality control in this study is similar to that used in 
our previous studies (Sun et al., 2001; Liu et al., 2004).

RESULTS AND DISCUSSION
The predominant source of organic matter in HF4-18
The average concentrations (n = 30) of TOC and TN 
in HF4-18 are 1.75% (1.23%–3.10%), and 0.29% (0.21%– 
0.54%), respectively. The mean TOC and TN contents 
(n = 6) in other sections of HF4 are 0.37% (0.26%–0.60%) 
and 0.07% (0.057%–0.084%), respectively. The remark-
ably higher TOC and TN concentrations in HF4-18 indi-
cate that the C and N inputs are likely related to seal ac-
tivity. As shown in Fig. 4, TN concentrations are signifi-
cantly correlated with the TOC concentrations, i.e., TN 
(%) = 0.1865 ¥ TOC (%) + 0.004 (r² = 0.964). The small 
intercept of 0.004% indicates a negligible fraction of in-
organic nitrogen in the sediments (Sun et al., 2004). Thus, 
the measured nitrogen is associated with organic matter, 
and the calculated TOC/TN ratios, or C/N values, can be 
employed to determine the origin of organic matter, i.e., 
terrestrial or marine. Marine and terrestrial organic sub-
stances have typical C/N ratios of <8 and >12, respec-

Fig. 3. Comparison between measured values and reference values of the internal standard sample 07405.

Fig. 4. Correlations between total organic carbon (TOC), total nitrogen (TN), loss on ignition (LOI) and seal hair numbers (per 1 g dry weight of sediments).
A preliminary study of elemental geochemistry and its potential application in antarctic Seal palaeoecology

HF4-18 has an average C/N values of 6.99 (5.4–8.96, n = 30), i.e., close to 5.65 ± 1.86 (n = 12) which represents the value of fresh sea bird droppings and seal feces in the Antarctic region. Therefore, the organic matter in HF4-18 is likely of marine origin, originating from seal excrements. 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 Fig. 5, the subsamples of HF4-18 are clustered together, an indication of the common source of organic materials, close to fresh marine animal excrements, and well within the range of marine algae, but far from the C3 and C4 terrestrial plants. Taking into account the presence of seal hairs in the sediments, the measured TOC and TN concentrations and C/N values, as well as the organic carbon isotope compositions, it can be concluded that the organic matter in HF4-18 is most likely from seal excrements of marine origin and transported to the terrestrial ecosystem by seals through the natural food chain. This is also strongly supported by the fact that the contents of TOC, TN and LOI in HF4-18 and seal hair abundances have similar vertical variation patterns as a function of depth (Fig. 2). Linear regression analysis revealed that the TOC, TN contents and LOI percentage in HF4-18 are strongly correlated with the seal hair numbers, i.e., with a correlation coefficients of 0.76, 0.67 and 0.80 (p < 0.001), respectively (Fig. 4).

Identification of bio-elements in HF4-18

The concentrations of 27 elements/oxides in the HF4 sediments are listed in Table 1 and plotted in Fig. 6 as a function of depth. As seen in Fig. 6, most of the concentrations show relatively small changes below the depth of approximately 18 cm in HF4-24.5, but large variations above the depth of 18 cm in HF4-18. The concentrations of FeO, S, P₂O₅, Se, Hg, Cu and Zn have very similar variation patterns, and in HF4-18, they are remarkably higher than those in HF4-24.5. The depth of 18 cm appears to be a kind of critical point. Additionally, the ver-

Table 1. Mean element and oxide concentrations in HF4-18 and HF4-24.5

<table>
<thead>
<tr>
<th>Elements</th>
<th>Range</th>
<th>Mean</th>
<th>Elements</th>
<th>Range</th>
<th>Mean</th>
<th>Oxides</th>
<th>Range</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF4-18 (n = 35)</td>
<td></td>
<td></td>
<td>HF4-24.5 (n = 13)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1.32–2.95</td>
<td>1.67</td>
<td>Se</td>
<td>0.09–1.87</td>
<td>0.96</td>
<td>Al₂O₃</td>
<td>18.6–20.78</td>
<td>19.64</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05–0.17</td>
<td>0.092</td>
<td>Sr</td>
<td>336–442</td>
<td>384</td>
<td>TiO₂</td>
<td>0.636–0.773</td>
<td>0.705</td>
</tr>
<tr>
<td>Cu</td>
<td>98–153</td>
<td>124.4</td>
<td>Ba</td>
<td>106–172</td>
<td>121</td>
<td>P₂O₅</td>
<td>0.209–0.431</td>
<td>0.308</td>
</tr>
<tr>
<td>Ga</td>
<td>16.2–21.6</td>
<td>18.8</td>
<td>Hg</td>
<td>31.5–385</td>
<td>198</td>
<td>Fe₂O₃</td>
<td>7.89–9.04</td>
<td>8.43</td>
</tr>
<tr>
<td>Mn</td>
<td>563–1131</td>
<td>763.5</td>
<td>Cr</td>
<td>11–72</td>
<td>36.7</td>
<td>FeO</td>
<td>1.6–2.97</td>
<td>2.14</td>
</tr>
<tr>
<td>Ni</td>
<td>6–10.5</td>
<td>9.2</td>
<td>B</td>
<td>2.4–73</td>
<td>29.2</td>
<td>K₂O</td>
<td>0.34–0.67</td>
<td>0.47</td>
</tr>
<tr>
<td>Pb</td>
<td>10–29</td>
<td>19.4</td>
<td>V</td>
<td>89.6–270</td>
<td>1394</td>
<td>Na₂O</td>
<td>2.35–3.44</td>
<td>2.80</td>
</tr>
<tr>
<td>S</td>
<td>323–1762</td>
<td>926.3</td>
<td>F</td>
<td>52.3–133</td>
<td>87</td>
<td>MgO</td>
<td>3.32–3.94</td>
<td>3.51</td>
</tr>
<tr>
<td>Zn</td>
<td>80–120</td>
<td>99</td>
<td>SiO₂</td>
<td>44.92–47.91</td>
<td>46.67</td>
<td>CaO</td>
<td>7.15–9.04</td>
<td>8.05</td>
</tr>
</tbody>
</table>

Table 1. Mean element and oxide concentrations in HF4-18 and HF4-24.5

Note: Element and oxide concentrations are in mg kg⁻¹ and 10 g kg⁻¹, respectively, except Hg is in μg kg⁻¹.
tical concentration profiles of $\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}$, $\text{Ba}$, $\text{As}$, $\text{K}_2\text{O}$ and $\text{MnO}$ seem to be opposite of those of $\text{FeO}$, $\text{S}$, $\text{F}$, $\text{P}_2\text{O}_5$, $\text{Se}$, $\text{Hg}$, $\text{Cu}$ and $\text{Zn}$. The abundances of $\text{TiO}_2$, $\text{CaO}$, $\text{MgO}$ and $\text{Cd}$ only show slight fluctuations. The levels of $\text{B}$, $\text{Pb}$, $\text{Ga}$, $\text{Cr}$ and $\text{V}$ display frequent fluctuations of complex pattern.

In order to better compare and understand the vertical concentration profiles of these elements/oxides, the elemental enrichment factors (EFs) in HF4-18 with respect to HF4-24.5 were calculated using the following formula:

$$\text{EF}_i = (X/\text{Al}_2\text{O}_3)_{\text{HF4-18}}/(X/\text{Al}_2\text{O}_3)_{\text{HF4-24.5}}.$$
X and Al2O3 refer, respectively, to the concentrations of the element of interest and to the reference element. (X/Al2O3)HF4-18 and (X/Al2O3)HF4-24.5 represent the ratios derived from the concentrations of element X and Al2O3 in HF4-18 and HF4-23.5, respectively. Al2O3 was chosen as a reference element because Al is a well-defined lithophile element and shows very low chemical reactivity. Moreover, its abundance is directly linked to clay materials and its concentration in sediments is not significantly affected by biogenic cycles (Dellwing et al.,

Fig. 7. Average enrichment factors (EFs) of all elements/oxides in HF4-18 with respect to HF4-24.5.

Fig. 8. The R-mode clustering results for the chemical elements, total organic carbon (TOC), total nitrogen (TN) and loss on ignition (LOI) and seal hair number (SHN) in HF4-18. It is clear that S, Se, F, Hg, P2O5, FeO, Zn, TOC, TN, LOI and the seal hair number (SHN) are clustered into one group (shown in a rectangle with dashed line).
Using the data of Table 1, the average EFs of the 27 elements/oxides were calculated and are plotted in Fig. 7. As illustrated in this figure, the average EFs of As, K\textsubscript{2}O, MnO and Ba are less than 1 or depleted in HF4-18 relative to HF4-24.5. SiO\textsubscript{2}, CaO, Pb, V, TiO\textsubscript{2}, MgO, Fe\textsubscript{2}O\textsubscript{3}, Cu, Ga, Ni, Na\textsubscript{2}O and Sr have an average EF of approximately 1. Zn, FeO, F, Cd, S, B, P\textsubscript{2}O\textsubscript{5}, Hg and Se have an average EF of greater than 1.2, indicating a relatively strong enrichment. In order to further examine the significant enrichment of these elements/oxides, clustering analysis, principle component analysis (PCA) and correlation analysis were performed. The R-clustering results on the data of 27 element and oxide concentrations, TOC, TN, LOI and the seal hair number in HF4-18 are given in Fig. 8 and show that S, Se, F, Zn, Hg, FeO, P\textsubscript{2}O\textsubscript{5}, TOC, TN, LOI and the seal hair number belong to the same group.

The principal component analysis (PCA) of the correlation matrix of the concentrations of all elements/oxides excluding Ga, Pb, Cr, V and B (these elements are either heteroscedastic or do not contribute to any of the factors) (Bennett et al., 1999), after quartimax rotation, was able to account for approximately 80% of the variance of the data. In particular, the first component, which accounted for approximately 40% of the variance, was composed of S, Se, F, Zn, Hg, FeO, P\textsubscript{2}O\textsubscript{5}, TOC, TN and LOI if elements with positive loading over 0.6 are included (Fig. 9). Figure 9 also shows that lithophile elements Al and Si variables are loaded inversely with these elements/oxides in the same component. This suggests that the elements/oxides enriched in HF4-18 originated from a distinct source from Al and Si, but likely had the same origin and transportation mechanism as TOC, TN and LOI, which reflect the organic material abundances (Ruiz-Fernández et al., 2003; El Bilali et al., 2002).

Correlation analysis between the element/oxide con-
centrations and the LOI contents in HF4-18 and HF4-24.5 were conducted to confirm the robustness of the cluster analysis and PCA results. Table 2 lists the correlation coefficients of all the element/oxide concentrations and the LOI in HF4-18 and HF4-24.5. As can be seen in Table 2, S, Se, F, Zn, Hg, FeO and P2O5 concentrations only have significantly positive correlations with LOI in HF4-18, but not in HF4-24.5. The least square fitting results of S, Se, F, Zn, Hg, FeO and P2O5 concentrations in HF4-18 with TOC are given in Fig. 10 and show a strong association between these elements/oxides and organic matter. The significant correlations between the levels of S, Se, F, Zn, Hg, FeO and P2O5 and LOI percentage, TOC content in the sediments influenced by seal excrements contrast with the poor correlations between them in the sediments with few or no seal hairs. This suggests that organic matter might have played a key role in the enrichment of these elements/oxides in HF4-18, as shown by the link between their high affinity with organic matter and their high EFs, as mentioned before. In other words, the notable enrichments of S, Se, F, Zn, Hg, FeO and P2O5 in HF4-18 seem to be caused by their high affinity to organic matter. As indicated above, the organic matter in HF4-18 is predominantly from seal excrements, therefore, it is reasonable to believe that the input of seal excrements into the sediments exerts a major influence on the concentrations of these elements/oxides. Furthermore, as shown in Table 3, most of these elements/oxides, except P2O5, slightly correlated with the other elements, only showed strong correlations between each other in HF4-18, but not in HF4-24.5. The existence of such close relationships among these elements/oxides may be attributed to the incorporation of seal excrements into the sediments, but the lack of correlation between these elements in the sediments without seal excrement inputs may be due to their different chemical activities. Based on these results of elemental geochemical analyses, we propose that S, Se, F, Zn, Hg, FeO and P2O5 could be used as bio-elements, associated with seal activity. Furthermore, we suggest that a significant portion of these elements/oxides in HF4-18 is likely from seal excrements, and that the assemblage of these elements/oxides is an important geochemical characteristic of the sediments influenced by seal excrements. However, further analyses should be performed on more sediment cores before extending our findings to larger areas.

The potential applications of bio-elements for Antarctic seal palaeoecology

According to Sun and Xie (2001) and Sun et al. (2000, 2001), the bio-element concentration changes in the sediments amended by penguin droppings can be used as an indirect measure of historical penguin population changes. For the sediments influenced by seal excrements,
Table 3. Correlations among seven elements/oxides associated with organic matter in HF4-18 and H4F-24.5

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>Zn</th>
<th>Se</th>
<th>Hg</th>
<th>F</th>
<th>P₂O₅</th>
<th>FeO</th>
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<tbody>
<tr>
<td>HF4-18</td>
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<td>S</td>
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<tr>
<td>Zn</td>
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<tr>
<td>Se</td>
<td>0.822**</td>
<td>0.718**</td>
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<tr>
<td>Hg</td>
<td>0.829**</td>
<td>0.777**</td>
<td>0.964**</td>
<td>1</td>
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<tr>
<td>F</td>
<td>0.606**</td>
<td>0.608**</td>
<td>0.656**</td>
<td>0.700**</td>
<td>1</td>
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</tr>
<tr>
<td>P₂O₅</td>
<td>0.368*</td>
<td>0.452**</td>
<td>0.300</td>
<td>0.452**</td>
<td>0.573**</td>
<td>1</td>
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<tr>
<td>FeO</td>
<td>0.839**</td>
<td>0.737**</td>
<td>0.946**</td>
<td>0.948**</td>
<td>0.751**</td>
<td>0.409*</td>
<td>1</td>
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<td>S</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.206</td>
<td>0.411</td>
<td>0.401</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.226</td>
<td>-0.318</td>
<td>-0.485</td>
<td>-0.406</td>
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<td></td>
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</tr>
<tr>
<td>P₂O₅</td>
<td>-0.190</td>
<td>0.003</td>
<td>0.838**</td>
<td>0.203</td>
<td>-0.254</td>
<td>1</td>
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<tr>
<td>FeO</td>
<td>-0.020</td>
<td>-0.237</td>
<td>-0.338</td>
<td>-0.309</td>
<td>0.650*</td>
<td>-0.352</td>
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</tr>
</tbody>
</table>

**Correlation is significant at the 0.01 level (2-tailed); *Correlation is significant at the 0.05 level (2-tailed).

Fig. 11. Relationships between the content of bio-elements and the seal hair numbers in the excrement sediments. Lines correspond to best fit regression lines.

the contents of bio-elements as discussed above may also be applied to evaluate historical seal population. In order to test this hypothesis, the bio-element concentrations in the excrement sediments are compared with the seal hair numbers in Figs. 2 and 6. According to Hodgson et al. (1997, 1998), the varying number of seal hairs in lake sediments can indicate fluctuations in the size of visiting seal populations, i.e., more seal hairs may reflect larger visiting seal populations. As seen clearly from Fig. 2, the seal hair abundances within the sediment sequence influenced by seal excrements display two notable troughs and peaks, probably indicating the significant variations in the historical populations of the seals visiting the coastal terrace on the Fildes peninsula (Sun et al., 2004). As seen in Fig. 6, very similar concentration profiles of the bio-elements in HF4-18 are also observed.

When the concentrations of the bio-elements in HF4-18 are plotted as a function of the seal hair numbers (Fig. 11), a general trend of increasing bio-element contents with seal hair abundances can be observed. A linear regression analysis revealed that all the bio-element contents were significantly correlated with the seal hair numbers ($p < 0.05$). The presence of these significant associations could be interpreted as follows: the organic mat-
ter in HF4-18 is mainly from the seal excrement input and its abundance is proportional to the seal hair numbers. An increase in seal hair numbers in the sediments may imply that elevated seal populations occurred at the study site, and thus more excrements were transported and incorporated into the sediments, resulting in an increase in the organic matter abundance. Since the bio-elements listed above were likely introduced in the sediments through sorptive or complexing reactions with organic matter, increasing organic matter abundance led to relatively high levels of the bio-elements in HF4-18.

Several studies have shown that seal hairs in lake sediments can be successfully used to detect the presence, absence and possibly broad scale changes in historical seal populations (Hodgson et al., 1997, 1998; Sun et al., 2004). Here, our results suggest that the bivariate correlations between the bio-element contents and the seal hair abundances are positive and statistically significant. Thus, we propose that bio-element concentrations in the seal excrement sediments could potentially be used as new markers and paleoecological proxies for historical seal population changes in the Antarctic region. Counting of seal hairs in sediments is time consuming (up to 360,000 seal hairs were enumerated in the present study) and it would be far more advantageous and fast to rely on bio-elements as indicators of their presence in past environments.

CONCLUSIONS

As previously reported, the deposition of seal hairs and bio-elements from penguin droppings have been used as indirect measurement of historical seal and penguin population changes. In this study, geochemical investigations of organic matter and major and trace elements from an excrement sediment profile containing seal hairs have been carried out. According to the results of elemental geochemical analysis, we can draw the following conclusions:

(1) The sediment section containing many seal hairs exhibited much higher total organic carbon (TOC) and total nitrogen (TN) relative to the rest of the sediments where fewer or no seal hairs were present. This, combined with the organic carbon isotopic composition and the atomic C/N values as well as the appearance of significant correlations between organic matter and seal hair numbers, clearly showed that the organic matter was predominantly of marine origin and mainly from seal excrements.

(2) Among the determined elements/oxides, S, Se, F, Zn, Hg, FeO and P2O5 had relatively similar concentration profiles, and they were enriched in HF4-18, the sediment section influenced by seal excrements, as compared to the rest of the sediments with fewer or no seal hairs, indicating that they likely had a common source. This hypothesis is strengthened by the clustering analysis, principle component analysis (PCA) and correlation analysis. These analyses showed that notable enrichments of S, Se, F, Zn, Hg, FeO and P2O5 in HF4-18 may be caused by their high affinity to organic matter and that the input of seal excrements into the sediments exerted a major influence on the geochemical characteristics of these elements/oxides. We therefore propose that these elements could be used as bio-elements, associated with seal activity.

(3) When comparing the bio-element concentrations with the seal hair numbers, it became apparent that they shared a similar trend. A linear regression analysis revealed that all bio-element contents were significantly correlated with the seal hair numbers. The deposition of seal hairs has been successfully used as an index of changes in Antarctic mammal populations. We therefore propose that bio-element concentrations in the seal excrement sediments, such as seal hair numbers, could also be used as paleoecological proxies to estimate historical seal populations and be applied in studies of Antarctic seal palaeoecological processes. However, it is clear that additional sediments cores should be investigated prior to extending our findings to large scale areas.

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