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HCl-soluble $^{87}Sr/^{86}Sr$ ratio in sediments impacted by penguin or seal excreta as a proxy for historical population size in the maritime Antarctic

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ABSTRACT: The strontium (Sr) isotopic compositions in the HCl-soluble and insoluble fractions of sediments impacted by penguin and seal excreta in the maritime Antarctic were analyzed. The HCl-soluble phase of the sediments impacted by penguin guano has a high $^{87}Sr/^{86}Sr$ ratio (average 0.7087), close to the ratio in seawater (average 0.7092), suggesting that the $^{87}Sr/^{86}Sr$ ratios in the sediments are significantly impacted by penguin guano. The $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble phase of the sediments impacted by seal excreta vary between 0.705066 and 0.706117, with an average of 0.705507, higher than those of the local bedrock, but lower than the ratio in modern seawater; they are interpreted to be a mixture of Sr from seal excreta (30 to 50%) and the weathering products of the local bedrock (50 to 70%). The Sr contributions from penguin guano and seal excreta were calculated using the 2-member isotope mixing equation, and they have a significant correlation with the historical penguin population size as estimated from other geochemical analyses and the seal hair density in the sediments, respectively. These results suggest that the $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble fraction of sediments impacted by penguin or seal excreta can potentially be used as an indirect and new proxy for the historical population size of these sea animals in the maritime Antarctic.

KEY WORDS: Strontium isotope · Antarctica · Penguin guano · Seal excreta · Sediment

INTRODUCTION

Penguins and seals have been considered to be the ideal 'bio-indicators' of the ecosystem and environmental changes in the maritime Antarctic (Ainley et al. 1995, Smith et al. 1999, Sun et al. 2000, Croxall et al. 2002). Abandoned colonies, bones, feathers, egg fragments, guano in relic ornithogenic soils, hairs, and other samples of these species have been scrutinized in recent years to (1) reconstruct the historical changes of their populations and colonies; (2) investigate the factors responsible for more drastic changes; (3) study their responses to regional and even global climatic and sea-level changes; and (4) reconstruct the paleoenvironments in the maritime Antarctic (Baroni & Orombelli 1994, Zale 1994, Hodgson & Johnston 1997, Tatur et al. 1997, Emslie et al. 1998, 2003, Sun et al. 2000, Sun & Xie 2001, Zhu et al. 2005). It has been suggested that the changes in the population of penguins or seals are caused by climate-related factors such as sea-ice coverage and atmospheric temperature. Currently available data and evidence, however, are not consistent with each other and remain equivocal and debatable, and one of the major reasons is the difficulty in obtaining long-term and continuous *in situ* data (Croxall et al. 2002, Kato et al. 2002, Weimerskirch et al. 2003).

The concentrations of Cu, S, Sr, Zn, P, Ca, Ba, F and Se in sediments impacted by penguin guano and seal hair density have recently been proposed and used as the long-term *in situ* data and the proxy for the size of historical penguin and seal populations (Hodgson & Johnston 1997, Sun et al. 2000, 2004a,b, Sun & Xie 2001, Zhu et al. 2005). The results from these methods,

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however, could be impacted by a number of factors, such as elements from the sources for local bedrock and the dilution, grain-size effects and preservation conditions of penguin guano and seal hair.

During the 15th and 18th Chinese Antarctic Research Expeditions (CHINARE-15th and CHINARE-18th), we investigated the ecological environments of penguin and seal colonies on Ardley Island and Fildes Peninsula, on King George Island, maritime Antarctic. We collected sediment samples in the catchments close to penguin and seal colonies, and we analyzed the $^{87}Sr/^{86}Sr$ ratios in the sediments impacted by penguin or seal excreta. In this paper, we propose to utilize the $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble fraction of the sediments impacted by penguin or seal excreta as an indirect and new proxy for the size of historical penguin or seal populations.

Strontium (Sr) isotopes are generally used as sensitive geochemical traces. They differ from other isotopes (H, C, N, O and S) in that they are unaffected by biological or chemical processes and the mass-dependent isotope fraction (Miller et al. 1993). In addition, they provide 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, Capo et al. 1998, Barbieri 2002, Lyons et al. 2002). In recent years, Sr isotope compositions have been increasingly applied to the studies of earth-surface processes and sedimentary environments. The $^{87}Sr/^{86}Sr$ ratios in various ecosystem pools and sedimentary environments are the results of mixing of Sr derived from different sources (Gosz et al. 1983, Derry et al. 1992, Ingram & Sloan 1992, Miller et al. 1993). Based upon the differences in the compositions of various sources, Sr isotopes can be used as the source indicators and the tracers for the cycles of nutrients in the ecosystems (Graustein 1989, Palmer & Edmond 1992, Blum et al. 1994, Blum & Erel 1995, Bailey et al. 1996, Capo et al. 1998, Barbieri 2002, Lyons et al. 2002).

MATERIALS AND METHODS

One study site was located on Ardley Island (62° 13′ S, 58° 56′ W), which is linked to the Fildes Peninsula through a sandy dam with an area of about 2 km^2 (Fig. 1). The topography is even and has a highest elevation of 70 m. Mosses and lichens cover 70 to 80% of this island. It is one of the most important penguin colonies in the maritime Antarctic. During the breeding period every summer, the number of penguins on this island is estimated to be 10 218; the major species are gentoo *Pygoscelis papua* (74%), Adélie *P. adeliae* (21%), and chinstrap *P. antarctica* (5%) (Trivelpiece et al. 1987). A large amount of guano is deposited in the lakes on the island by ice or snowmelt water every year. For this study, a 67.5 cm lake core was collected from a lake (Y2) using a 12 cm PVC pipe during CHINARE-15. The sediments in this lake were amended and strongly impacted by penguin guano (Sun et al. 2000, 2001). The sediment core was divided into 64 sections of 1 cm each for the upper 64 cm and 1 additional section for the bottom 3.5 cm (from 64 to 67.5 cm depth) in the laboratory. Sr isotope composition analysis was performed at 5 cm intervals.

The other sampling site was located on the Fildes Peninsula (62° 12′ S, 58° 58′ W), in an ice-free area on King George Island, the largest of South Shetland Islands (Fig. 1). On the west coast there are some established colonies of marine mammals. Large marine mammals include 5 pinnipeds: Weddell seal *Leptonychotes weddellii*, southern elephant seal *Mirounga leonine*, leopard seal *Hudrurga leptonyx*, Antarctic fur seal *Arctocephalus gazella*, and crabeater seal *Lobodon carcinophagus*. Of those species, the elephant seal is the most abundant (71.4% of total seal populations). The fur seal follows with a population size of ~1600 (14.8%) (Liu et al. 2004a). During the molting and breeding period each summer, seal hairs and excreta are deposited in the sediments by snowmelt water. During CHINARE-18, a 42.5 cm sediment core (HF4) was collected from a terrestrial catchment (62° 11′ 57″ S, 59° 58′ 48″ W) on the western coast of Fildes Peninsula (Fig. 1). The sediment core was sectioned at 0.5 cm intervals for the top 18 cm (HF4-18). Within the overall sediment core stratigraphy, seal hairs were found at various depths, but no plant

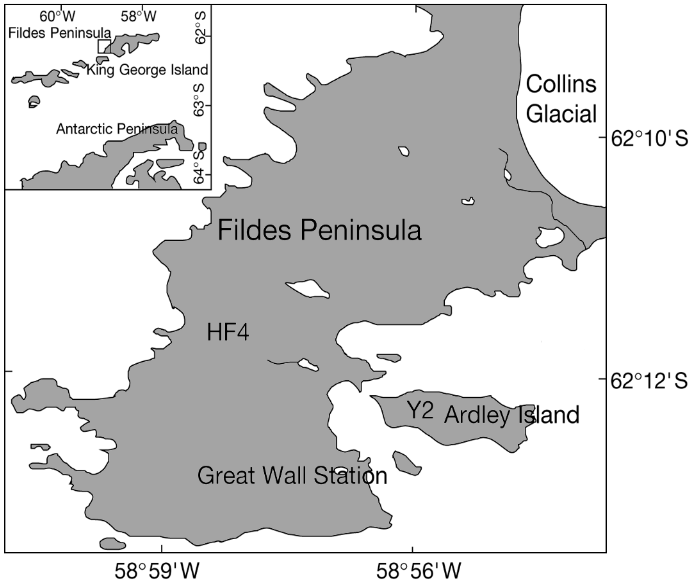

Fig. 1. Study area and sampling sites. Lake Y2 and HF4 catchments are shown

remains were observed. The study areas and sampling methods also have been described by Sun et al. (2001, 2004a,b).

All the air-dried subsamples were ground into powder using an agate mortar and pestle, and the >120-mesh fractions were separated from the powder and analyzed. The dried samples with precise weight were treated with 0.1 mol l^{-1} hydrochloric acid (HCl), and the silicate fraction was not significantly dissolved at this concentration (Barbieri 2002). The HCl-soluble and insoluble phases were separated via filters. The HCl-soluble phase represents the soluble marine-source fraction, and the insoluble one approximately represents the siliceous fraction (Barbieri 2002). The filtrate was transferred into a 25 ml vessel, and 15 ml of the filtrate was removed to a Teflon crucible and evaporated to dryness at 200°C. The insoluble phase was washed 3 times with Millipore water then put into a porcelain crucible and incinerated for 1 h at 450°C and 1.5 h at 550°C in the muffle. About two-thirds of the insoluble fraction was placed in a Teflon crucible and 0.5 ml of 6 mol l^{-1} HCl, 0.5 ml HNO_3 and 3 ml HF was added, sealed and then heated for 24 h at 160°C. The cap was taken out and washed with Millipore water; HF was evaporated at 230°C. All the samples of the insoluble phase were then dissolved in 2.0 mol l^{-1} HCl and centrifuged at 2000 rpm for 3 min. The supernatant was pipetted off and dried.

All the samples were re-dissolved in 2 ml of 2 mol l^{-1} HCl. They were eluted on a quartz cation exchange column loaded with Biorad AG 50 × 8 resin for Sr separation. Sr isotopic compositions were determined in a Finnigan-MAT 262 thermal ionization instrument with static multi-collection. The $^{86}Sr/^{88}Sr$ ratios were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.1194. NBS987 standards run with each sample magazine yielded an average value of 0.710257 ± 21 (2σ, n = 20) during the course of this work. The $^{87}Sr/^{86}Sr$ ratios in the soluble and insoluble phases of tundra vegetation, fresh penguin and seal excreta were also determined using the same method.

In addition, we analyzed the concentrations of Zn, Cu, Ca, Sr, P, Se, Ba, S in the Y2 lake sediment profiles and the concentrations of S, Se, F, TOC (total organic carbon) and TN (total nitrogen) contents and seal hair density in HF4-18. Zn, Cu, Ca (as CaO) were determined using atomic absorption spectrometry (AAS); Sr and Ba were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES); P (as P_2O_5) was determined using ultraviolet visible spectrometry (UVS); Se was determined using atomic fluorescent spectrometry (AFS); S was determined by volume method (VOL) after fusion with KI. TOC content in the sediments was measured using the chemical volumetric method; TN content was determined by the Kjeldahl method. The seal hairs were counted following the method of Hodgson & Johnston (1997). These data have been published, and the methods have been described by Sun et al. (2000, 2001, 2004a).

RESULTS

The strontium isotope compositions in the sediments from the Lake Y2 are given in Table 1 and Fig. 2a. The $^{87}Sr/^{86}Sr$ ratios in the HCl-insoluble phase range from 0.703416 to 0.705759, with an average of 0.704302 (n = 15), close to the $^{87}Sr/^{86}Sr$ ratios (0.70314 to 0.70396) of the bedrock and the silicate phase for the sediments (Zheng et al. 1988, Li et al. 1992, Chen et al. 1997, Xing et al. 1997). This suggests that the Sr in the HCl-insoluble phase is predominantly derived from the weathering products of local bedrock. The $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble phase range from 0.708191 to 0.709077, with an average of 0.708743 (n = 25), close to 0.7092 (Burke et al. 1982, Capo & DePaolo 1992), the average $^{87}Sr/^{86}Sr$ ratio of fresh penguin guano and modern seawater. This indicates that the Sr in the HCl-soluble phase is predominantly derived from the deposition of penguin guano, and the marine Sr is transferred into terrestrial ecosystems via the food chains. The $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble phase are determined by the amount of the penguin guano transported and deposited into the Lake Y2, and they reflect the relative size of the penguin population in the catchment of the lake.

Table 1. $^{87}Sr/^{86}Sr$ ratios (± error) in the Y2 lake sediments and the natural materials around the study site

Natural material	$[^{87}Sr/^{86}Sr]_{insoluble}$	$[^{87}Sr/^{86}Sr]_{soluble}$
Tundra moss Y2M	0.706316 ± 24	0.708913 ± 22
Tundra moss Y3M	0.705895 ± 19	0.708676 ± 18
Penguin guano GWP	0.709384 ± 19	0.709223 ± 20
Penguin guano BDP	0.707794 ± 22	0.709238 ± 16
Seal excreta ZHS	0.709265 ± 22	0.709175 ± 17
Y2 lake sediments		
5 cm	0.704527 ± 27	0.708967 ± 25
7 cm	0.704484 ± 26	0.708745 ± 42
10 cm	0.704200 ± 35	0.708957 ± 22
15 cm	0.704408 ± 32	0.708820 ± 20
20 cm	0.703815 ± 30	–
25 cm	0.703416 ± 24	0.709048 ± 24
30 cm	–	0.708760 ± 24
35 cm	0.704509 ± 92	0.709367 ± 20
40 cm	0.704949 ± 40	0.709077 ± 19
45 cm	0.705353 ± 23	0.709044 ± 93
50 cm	0.704502 ± 53	0.708909 ± 43
56 cm	0.703717 ± 25	0.708209 ± 21
58 cm	0.703789 ± 19	0.708191 ± 23
59 cm	0.703549 ± 23	0.708191 ± 79
60 cm	0.703551 ± 42	0.708597 ± 24

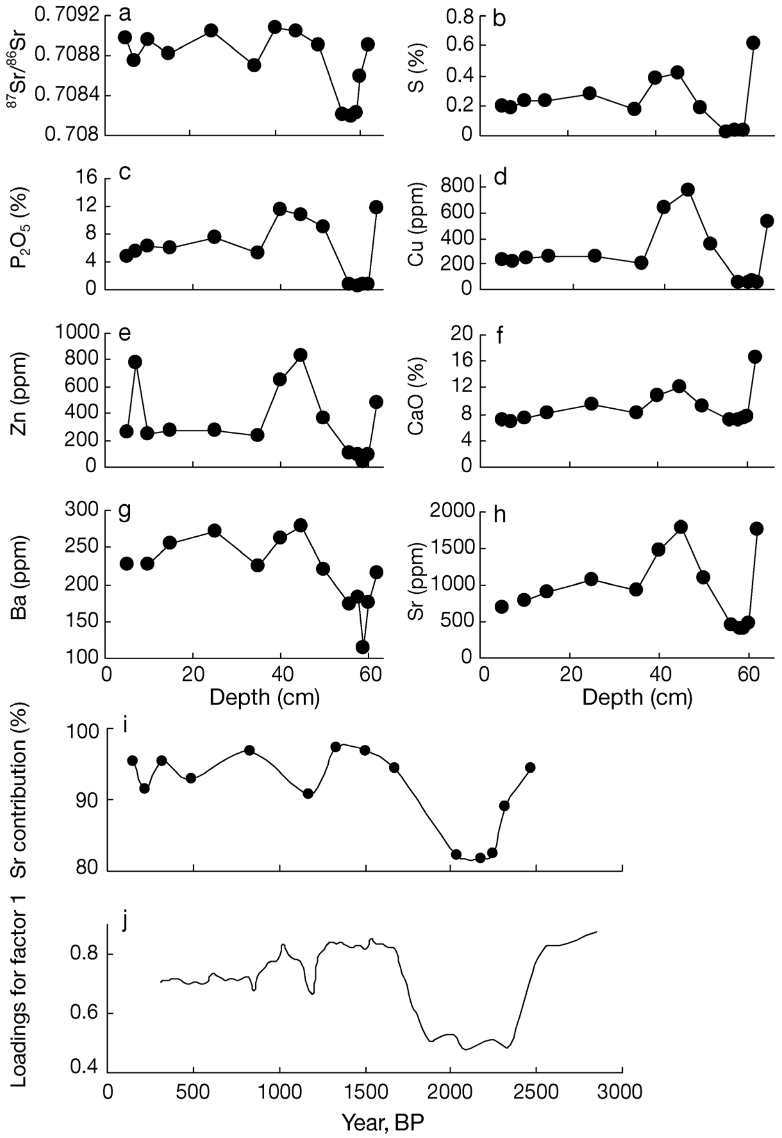

Fig. 2. Profiles of (a) $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble fractions; (b–h) the concentrations of S, P_2O_5, Cu, Zn, CaO, Ba and Sr in the sediments (cited from Sun et al. 2000); (i) the Sr contribution from penguin guanos in the HCl-soluble fractions and (j) the changes of 3000 yr penguin population as obtained from typical elements (cited from Sun et al. 2000)

For the purpose of comparison, the concentration-versus-depth profiles (Fig. 2b–h) of 7 elements (S, P_2O_5, Cu, Zn, CaO, Ba and Sr) (Sun et al. 2000, Sun & Xie 2001) and the profile (Fig. 2j) of the loading factor in the Y2 lake sediments are also given. As reported in our previous work (Sun et al. 2000, 2001, Sun & Xie 2001), these elements in the Y2 lake sediments have a high concentration; their levels show a similar fluctuation against depth; and they are clustered into the same group according to the correlation coefficients between their profiles. The assemblage of these elements is an important geochemical characteristic of the lake sediments impacted by penguin guano. The loading factor (Fig. 2j), derived from *Q*-mode factor analysis of these elements' concentration-versus-depth profiles, represents the relative size of historical penguin populations.

As shown in Fig. 2, the profile of the $^{87}Sr/^{86}Sr$ ratios versus depth is very consistent with those of the 7 elements. The $^{87}Sr/^{86}Sr$ ratio in the soluble phase is significantly correlated with the concentrations of S, P_2O_5, Cu, Ba, and Sr (Table 2). Therefore the $^{87}Sr/^{86}Sr$ ratio in the HCl-soluble phase of the sediments impacted by penguin guano can provide a useful indicator for the size of historical penguin population. The lack of such a correlation between the $^{87}Sr/^{86}Sr$ ratio and Zn, CaO, and Se is likely caused by the incorporation of the latter elements from weathering products into the Y2 lake sediments.

The $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble and insoluble phases of HF4-18 are given in Table 3 and Fig. 3a. The $^{87}Sr/^{86}Sr$ ratios in the HCl-insoluble phase are between 0.703283 and 0.703947, with an average of 0.703445 (n = 12). These values are in good

Table 2. Correlations between the $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble phases and the typical elements in Y2 lake sediments (n = 15). Significant correlations: *0.05 level (2-tailed) and **0.01 level (2-tailed)

	$[^{87}Sr/^{86}Sr]_{soluble}$	S	P_2O_5	Cu	Zn	CaO	Se	Ba	Sr
$[^{87}Sr/^{86}Sr]_{soluble}$	1.00	0.59*	0.68**	0.57*	0.43	0.36	0.38	0.73**	0.61*
S		1.00	0.93**	0.87**	0.68**	0.89**	0.57*	0.67**	0.94**
P			1.00	0.92**	0.76**	0.77**	0.73**	0.76**	0.96**
Cu				1.00	0.81**	0.76**	0.70**	0.70**	0.96**
Zn					1.00	0.48	0.51	0.72**	0.93**
Ca						1.00	0.66**	0.38	0.88**
Se							1.00	0.34	0.73**
Ba								1.00	0.70**
Sr									1.000

Table 3. $^{87}Sr/^{86}Sr$ ratios (± error) in the HCl-soluble and insoluble phases of HF4-18 sediments

Depth (cm)	$[^{87}Sr/^{86}Sr]_{insoluble}$	$[^{87}Sr/^{86}Sr]_{soluble}$
1.5 to 2	–	0.705995 ± 32
2 to 2.5	0.703367 ± 63	0.705155 ± 16
2.5 to 3	0.703392 ± 22	–
4 to 4.5	0.703947 ± 55	–
5 to 5.5	0.703338 ± 13	0.705503 ± 18
6 to 6.5	0.703367 ± 17	0.706117 ± 62
7 to 7.5	0.703341 ± 15	–
8.5 to 9	0.703283 ± 19	0.705404 ± 32
10 to 10.5	0.703379 ± 22	0.705236 ± 50
12 to 12.5	0.703516 ± 24	0.705254 ± 40
13 to 13.5	0.703330 ± 15	0.706083 ± 30
13.5 to 14	0.703546 ± 14	–
16.5 to 17	0.703528 ± 16	0.705121 ± 38
17 to 17.5	–	0.705201 ± 15

agreement with the Sr isotope composition of the bedrock around the study site (Zheng et al. 1988, Li et al. 1992, Xing et al. 1997). The $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble phase, however, 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 the value of 0.70918 from modern sea water. This suggests that the Sr in the HCl-soluble phase of HF4-18 sediments is a mixture of the isotopically distinct Sr from both marine and weathering sources.

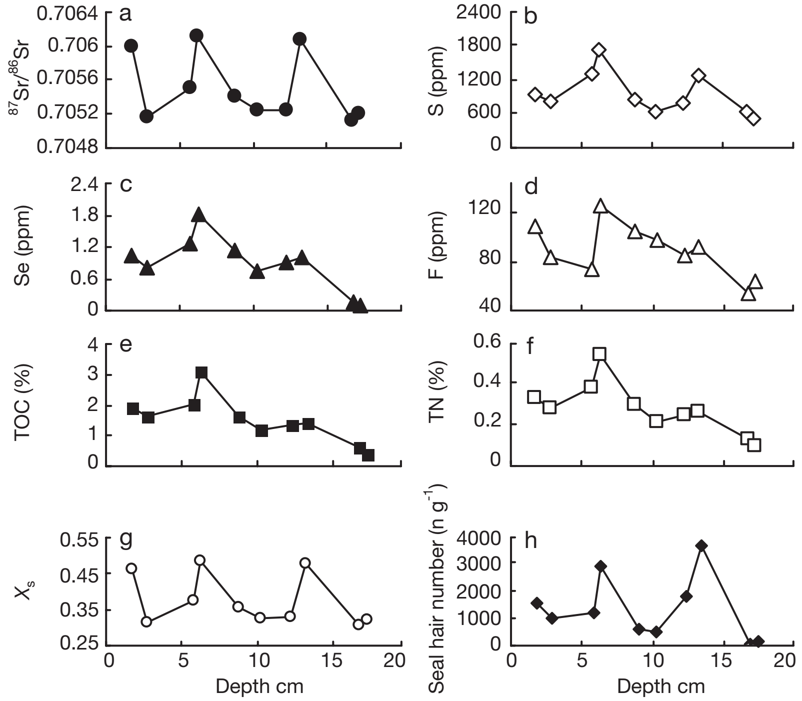

Fig. 3. Profiles of (a) the $^{87}Sr/^{86}Sr$ ratios in the HCl-soluble fractions; (b–f) the concentrations of S, Se, F, TOC (total organic carbon) and TN (total nitrogen) in the HF4-18 sediments (cited from Sun et al. 2004a); (g) the Sr contribution from seal excreta in the HCl-soluble fractions; and (h) the historical seal population as obtained from seal hair number preserved in the HF4-18 sediments (cited from Sun et al. 2004a)

The profile (Fig. 3a) of the $^{87}Sr/^{86}Sr$ ratio versus depth in the HCl-soluble phase of HF4-18 is shown together with the profiles (Fig. 3b–f) of S, Se, F, TOC, TN and seal hair density (Fig. 3h). As seen in this figure, the profile of the $^{87}Sr/^{86}Sr$ ratio in the HCl-soluble phase is consistent with those of the seal hair density and the levels of S, Se, F, TOC and TN. The seal hair density in lake sediments has been used as the proxy for the size of seal population (Hodgson & Johnston 1997, Sun et al. 2004a), and the $^{87}Sr/^{86}Sr$ ratio in the HCl-soluble phase of lake sediments can be another good proxy for the size of historical seal population in the maritime Antarctic.

DISCUSSION

Strontium in terrestrial lake sediments usually has various sources. According to the Sr isotopic compositions determined in this study (Fig. 2, Table 1), the Sr in the HCl-insoluble phase of the Y2 lake sediments is predominantly derived from the weathering products of local bedrock. This is also supported by the $^{87}Sr/^{86}Sr$ ratios in the HCl-insoluble phase of the local tundra vegetation (Table 1). The Sr in the HCl-soluble fractions was predominantly derived from penguin guano. Field observations showed that many abandoned penguin colonies are distributed in the areas around the Y2 lake (Sun et al. 2000, 2001), and the deposition of penguin guano strongly influences the physical and chemical properties of tundra soils via the effects of microbes and thus the sediments in the lake (Ugolini 1972, Tatur et al. 1997).

There are other 2 likely sources of Sr for the Y2 lake sediments. The first is atmospheric precipitation, since Y2 is close to the Southern Ocean. Precipitation has a Sr isotopic composition similar to that of seawater, but the Sr concentration in Antarctic precipitation (less than 1 ppb) is lower than that in the seawater (about 8 ppm) by several orders of magnitude (Graustein & Armstrong 1983, Gosz & Moore 1989, Åberg et al. 1990, Capo et al. 1998, Burton et al. 2002). Thus the contribution of Sr from atmospheric precipitation is insignificant. Tundra vegetation could be another source, since it flourishes around the lake. However, Sr isotopes are generally not fractionated by biological processes (Miller et al. 1993, Capo et al. 1998), and the

^{87}Sr/^{86}Sr ratios of tundra vegetation reflect the sources of Sr (and other nutrients) in the local environment. As listed in Table 1, the ^{87}Sr/^{86}Sr ratios in the HCl-soluble phase of local moss vegetation are close to those in fresh penguin guano; and the Sr available to local tundra vegetation is predominantly derived from penguin guano.

It seems highly likely that the Sr in the Y2 lake sediments, as well as the tundra vegetation, is derived from penguin guano and the local bedrock around the lake, and the ^{87}Sr/^{86}Sr ratio in the sediments is controlled by the amount of penguin guano and weathering products from local bedrock. Therefore we can use the following 2-member isotope mixing equation to estimate the contribution (X_p) of the penguin guano-derived Sr in the HCl-soluble fractions (Graustein & Armstrong 1983, Graustein 1989, Miller et al. 1993, Capo et al. 1998):

$$X_p=[(^{87}Sr/^{86}Sr)_m-(^{87}Sr/^{86}Sr)_w]/[(^{87}Sr/^{86}Sr)_p-(^{87}Sr/^{86}Sr)_w]$$

where $(^{87}Sr/^{86}Sr)_m$ is the determined Sr isotope ratios in the HCl-soluble phase of the Y2 sediments; $(^{87}Sr/^{86}Sr)_w$ and $(^{87}Sr/^{86}Sr)_p$ are the isotopic ratios of the weathering-derived and penguin guano-derived Sr in the soluble phases, respectively.

The HCl-soluble Sr in the weathering products of the study area is most likely derived from the calcium carbonate of primary origin and has the same isotopic ratio as the insoluble phase. Geologically, our study area consists mainly of Tertiary andesitic and basaltic lavas and tuffs together with raised beach terraces; the local rock is compositionally dominated by feldspar, pyroxene, apatite, etc. But an insignificant amount of HCl-soluble carbonate mineral is present in this region (Zheng et al. 1988, Li et al. 1992, Chen et al. 1997, Xing et al. 1997), and its distribution has been investigated in detail in 274 samples of 84 local soil profiles. Calcium carbonate, belonging to grainy and crystal calcite, was found in only 17 samples of 5 soil profiles, and its content ranges from 1.09 to 6.15% (Zhao 1995, Zhao & Li 1995, 1996). Since secondary calcium carbonate with stalactitic, tuberculoid or farinose structures was not observed in this region, and biogenic $CaCO_3$ is insignificant due to low temperature (Zhao 1995, Zhao & Li 1995, 1996), $CaCO_3$ in the local soils and thus the HCl-soluble Sr in weathering products is predominantly derived from the parent material, i.e. local bedrock. Therefore HCl-soluble phase of weathering products has the same Sr isotopic ratio as the insoluble phase.

According to the isotope mixing equation above, the calculated contributions (X_p) of the Sr from penguin guano in the soluble phase of the Y2 lake sediments are given in Fig. 2i, and they are in the range of 81.8 to 97.4%, with an average of 91.5%. The correlation between X_p and the loading factor (the proxy for penguin population) is striking and statistically significant ($r = 0.88$; $p < 0.001$). According to Sun et al. (2000), the penguin population was lowest at 1800 to 2300 yr BP, a period of low temperature (Clapperton et al. 1989). After this, the population increased and peaked between 1400 and 1800 yr BP (Fig. 2a,i), and the peak corresponds almost exactly to the period of high precipitation (Zhao 1990).

The relative contribution (X_s) of seal excreta to the Sr isotope composition in the HCl-soluble phase of HF4-18 is given in Fig. 3g and is between 30 and 40%. The correlation between X_s and the seal hair density is also striking and statistically significant ($r = 0.86$, $p = 0.001$). According to Sun et al. (2004a), the seal population exhibited dramatic fluctuations with 2 peaks in the depths from 5 to 8 cm (750 to 500 yr BP) and from 12 to 15 cm (1400 to 1100 yr BP), as illustrated in Fig. 3a,g.

The concentrations of Cu, S, Sr, Zn, P, Ca, Ba, F and Se in the sediments impacted by penguin guano and the seal hair density have been successfully used as the proxy for the size of historical populations of penguins and seals (Hodgson & Johnston 1997, Sun et al. 2000, Sun & Xie 2001, Sun et al. 2004a,b, Zhu et al. 2005). The results from these methods, however, could be impacted by a number of factors, such as the dilution, grain-size effects, inorganic sources, and preservation conditions. Compared with these methods, the ^{87}Sr/^{86}Sr ratio has a number of advantages. First, it is not affected by these factors, although their determination requires serious chemical analyses. Second, it is not affected by post-depositional diagenesis. Third, it helps in determining whether or not the sediments of a terrestrial lake are affected by the excreta of penguins or seals in the maritime Antarctic (Liu et al. 2004b) and in estimating the corresponding Sr contribution from the excreta. Therefore the ^{87}Sr/^{86}Sr ratio in the HCl-soluble phase of lake sediments and the calculated contribution of the Sr from penguin or seal excreta provides a more accurate and sensitive proxy for the relative size of historical penguin or seal populations in the maritime Antarctic.

In conclusion, we propose a novel method to estimate the relative size of historical penguin or seal populations in the maritime Antarctic based upon the analyses of the HCl-soluble ^{87}Sr/^{86}Sr ratios in the lake sediments impacted by these marine animals. The obtained historical record, combined with ^{14}C dating, can provide more accurate and valuable information about the changes of these marine animal populations, and thus the paleoenvironments, paleoclimates and their evolution in the maritime Antarctic.

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LITERATURE CITED

Åberg G, Jacks G, Wickman T, Hamilton PJ (1990) Strontium isotope in trees as an indicator for calcium availability. Catena 17:1–11

Ainley DG, Nur N, Woehler EJ (1995) Factors affecting the distribution and size of Pygoscelid penguin colonies in the Antarctic. Auk 112:171–182

Bailey SW, Hornbeck JW, Driscoll CT, Gaudette HE (1996) Calcium inputs and transport in a base-poor watershed as interpreted by Sr isotopes. Water Resour Res 32:707–719

Barbieri M (2002) Use of the ^{87}Sr/^{86}Sr isotopic ratio as an environmental tracer: an example of the application to the Fossil Forest of the Dunarobba (FFD) sedimentary system near Avigliano Umbro (Terni-Central Italy). Appl Geochem 17:1543–1550

Baroni C, Orombelli G (1994) Abandoned penguin rookeries as Holocene paleoclimatic indicators in Antarctica. Geology 22:23–26

Blum JD, Erel Y (1995) A silicate weathering mechanism linking increases in marine ^{87}Sr/^{86}Sr with global glaciation. Nature 373:415–418

Blum JD, Erel Y, Brown K (1994) ^{87}Sr/^{86}Sr ratios of Sierra Nevada stream waters: Implications for relative mineral weathering rates. Geochim Cosmochim Acta 58: 5019–5025

Burke WH, Denison RE, Hetherington EA, Koepnick RB, Nelson HF, Otto JB (1982) Variation of seawater ^{87}Sr/^{86}Sr throughout Phanerozoic time. Geology 10:516–519

Burton GR, Morgan VI, Boutron CF, Rosman KJR (2002) High-sensitivity measurements of strontium isotopes in polar ice. Anal Chim Acta 469:225–233

Capo RC, DePaolo DJ (1992) Homogeneity of Sr isotope in the oceans. EOS Trans Am Geophys Un 73:272

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

Chen YW, Gui XT, Wei GJ, Luo YL (1997) C, O, Sr and Pb isotope geochemistry of sediment core NG93–1 from Maxwell Bay, West Antarctic, and their paleoenvironmental implications. Geochimica 26:1–10 (in Chinese with English abstract)

Clapperton CM, Sugden DE, Birnie J, Wilson MJ (1989) Lateglacial and Holocene glacier fluctuations and environmental change on South Georgia, Southern Ocean. Quatern Res 31:210–228

Croxall JP, Trathan PN, Murphy EJ (2002) Environmental change and Antarctic seabird populations. Science 297: 1510–1514

Derry LA, Kaufman AJ, Jacobsen SB (1992) Sedimentary cycling and environmental change in the Late Proterozoic: evidence from stable and radiogenic isotope. Geochim Cosmochim Acta 56:1317–1329

Emslie SD, Fraser WR, Smith RC, Walker W (1998) Abandoned penguin colonies and environmental change in the Palmer station area, Anvers Island, Antarctic Peninsula. Antarct Sci 3:257–268

Emslie SD, Berkman PA, Ainley DG, Coats L, Polito M (2003) Late-Holocene initiation of ice-free ecosystems in the southern Ross Sea, Antarctica. Mar Ecol Prog Ser 262:19–25

Gosz JR, Moore DI (1989) Strontium isotope studies of atmospheric inputs to forested watersheds in New Mexico. Biogeochemistry 33:23–30

Gosz JR, Brookin DG, Moore DI (1983) Using strontium isotope ratios to estimate input to ecosystems. Bioscience 33(1):23–30

Graustein WC (1989) ^{87}Sr/^{86}Sr ratios measure the sources and flow of strontium in terrestrial ecosystems. In: Rundel PW, Ehleringer JR, Nagy KA (eds) Stable isotopes in ecological research. Springer-Verlag, New York, p 491–512

Graustein WC, Armstrong RL (1983) The use of strontium-87/strontium-86 ratio to measure atmospheric transport into forested watersheds. Science 219:289–292

Hodgson DA, Johnston NM (1997) Inferring seal populations from lake sediments. Nature 387:30–31

Ingram BL, Sloan D (1992) Strontium isotope composition of estuarine sediments as paleosalinity-paleoclimate indicator. Science 255:68–72

Kato A, Ropert-Coudert Y, Naito Y (2002) Changes in Adélie penguin breeding populations in Lützow-Holm Bay, Antarctica, in relation to sea-ice conditions. Polar Biol 25: 934–938

Li ZD, Zhen XS, Liu XH, Shang RX, Jin QM, Wang BX (1992) Volcanic rock of the Fildes Peninsula, King George Island, West Antarctica. Science Press, Beijing, p 50–89 (in Chinese)

Liu XD, Sun LG, Yin XB, Zhu RB (2004a) Paleoecological implications of the nitrogen isotope signatures in the sediments amended by Antarctic seal excrements. Prog Nat Sci 14:71–77

Liu XD, Sun LG, Xie ZQ, Zhu RB, Yin XB, Zhao JL (2004b) Geochemical evidence for the influence of historical sea bird activities on Mochou Lake sediments in the Zhongshan Station area, East Antarctica. Chin J Polar Res 16: 294–309 (in Chinese with English abstract)

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. Aquat Geochem 8:75–95

Miller EK, Blum JD, Friedland AJ (1993) Determination of soil exchangeable-cation loss and weathering rates using Sr isotope. Nature 362:438–441

Palmer MR, Edmond JM (1992) Controls over the strontium isotope compositions of river water. Geochim Cosmochim Acta 56:2099–2111

Smith RC, Ainley D, Baker K, Domack E, Emslie S and 6 others (1999) Marine ecology sensitivity to climate change. Bioscience 49:393–404

Sun LG, Xie ZQ (2001) Relics: penguin population programs. Sci Prog 84(1):31–44

Sun LG, Xie ZQ, Zhao JL (2000) A 3,000-year record of penguin populations. Nature 407:858

Sun LG, Xie ZQ, Zhao JL (2001) The sediments of lake on the Ardley Island, Antarctic: identification of penguin-dropping soil. Chin J Polar Sci 12:1–8 (in Chinese with English abstract)

Sun LG, Liu XD, Yin XB, Zhu RB, Xie ZQ, Wang YH (2004a) A 1,500-year record of Antarctic seal populations in response to climate change. Polar Biol 27:495–501

Sun LG, Zhu RB, Yin XB, Liu XD, Xie ZQ, Wang YH (2004b) A geochemical method for the reconstruction of the occupation history of penguin colony in the Maritime Antarctic. Polar Biol 27:670–678

Tatur A, Myrcha A, Niegodzisz J (1997) Formation of abandoned penguin rooker ecosystems in maritime Antarctic. Polar Biol 17:405–417

Trivelpiece WZ, Trivelpiece SG, Volkman NJ (1987) Ecological segregation of Adelie, Gentoo, and Chinstrap penguins at King George Island, Antarctica. Ecology 68: 351–361

Ugolini FC (1972) Ornithogenic soils of Antarctica. In: Llano GA (ed) Antarctic terrestrial biology. Antarct Res Ser 20: 181–193

Weimerskirch H, Inchausti P, Guinet C, Barbraud C (2003) Trends in birds and seal populations as indicators of a system shift in the Southern Ocean. Antarct Sci 15: 249–256

Xing GF, Shen WZ, Wang DZ, Tao KY, Jin QM (1997) Sr-Nd-Pb isotopic compositions and source features of Mesozoic to Cenozoic magmatic rocks on King George Island, Antarctica. Acta Petrol Sin 13:473–486 (in Chinese with English abstract)

Zale R (1994) Changes in size of the Hope Bay Adelie penguin colony as inferred from Lake Boeckella sediments. Ecography 17:297–304

Zhao JL (1990) The features of environmental evolution in the area of Fildes Peninsula, King George Island, Antarctic. Chin Sci Bull 35:661–666 (in Chinese with English abstract)

Zhao Y (1995) An analysis of the origin of $CaCO_3$ in soils on Fildes Peninsula of King George Island, Antarctica. Chin Sci Bull 40:1120–1124 (in Chinese with English abstract)

Zhao Y, Li TJ (1995) Analysis of the chemical weathering characteristics of soil-minerals on Fildes Peninsula of King George Island, Antarctica. Antarct Res (Chinese edn) 7: 18–24

Zhao Y, Li TJ (1996) The pedogenic groups and diagnostic characteristics in the Fildes Peninsula of King George Island, Antarctica. Antarct Res (Chinese edn) 17:70–78

Zheng XS, Liu XH, Yang RY (1988) Characteristics of prtrology of the Cenozoic volcanic rocks in the southwestern Great Wall Station area. Acta Petrol Sin 1:33–47 (in Chinese with English abstract)

Zhu RB, Sun LG, Yin XB, Xie ZQ, Liu XD (2005) Geochemical evidence for rapid enlargement of gentoo penguin colony on Barton Peninsula in the Maritime Antarctic. Antarct Sci 17:11–16

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