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## A 1300-year Record of Penguin Populations at Ardley Island in the Antarctic, as Deduced from the Geochemical Data in the Ornithogenic Lake Sediments

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#### Abstract

We have reconstructed a continuous high-resolution penguin population record over the past  $\sim \! 1300$  years from the geochemical and  $^{14}\mathrm{C}$  dating data in the ornithogenic lake sediments at Ardley Island in the Antarctic. The concentrations of F, P, Sr, Se, S, Cu, Zn, and Ca in the sediments are notably enriched and significantly correlated with each other, and they have a consistent pattern of change versus depth. These elements, as previously reported, are biomarkers of penguin droppings and population. Over the past  $\sim \! 1300$  years, the penguin population at Ardley Island, as measured by these biomarkers' concentrations, has a decreasing trend, especially during the past century when the penguin population has dropped steeply. Compared with the paleoclimatic records and glacial advance and retreat history in the study area, the pronounced penguin population changes in the absence of human activities appear to be related to climatic changes. The steep decline of the penguin populations in the past century, however, seems to be caused by the abnormally warming climate in the Antarctic Peninsula.

#### Introduction

The populations of Antarctic seabirds, especially penguins, have been extensively studied over the last several decades as reliable bio-indicators of the natural and environmental variability in the Southern Ocean marine ecosystem (e.g., Fraser et al., 1992; Kaiser, 1997; Tatur et al., 1997; Smith et al., 1999; Croxall et al., 2002; Weimerskirch et al., 2003). A number of penguin monitoring programs in the Antarctic ecosystems are currently underway and are expected to provide data for studying penguins' response to climatic and environmental variability. Currently available data and evidence, however, are not very 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; Weimerskirch et al., 2003; Zhu et al., 2005).

Abandoned penguin colonies have become an important way for estimating historical penguin populations and for other paleoenvironmental research. The penguin relics in these colonies, marked by the presence of nest stones, ornithogenic soils, food, and chicks, can provide considerable information about the past population, diet, and migration of penguin species (Baroni and Orombelli, 1994; Emslie et al., 1998; Emslie and McDaniel, 2002; Polito et al., 2002). Furthermore, these data can be compared with other paleoclimatic records to determine whether the population changes are related to climate change. These older relics, however, are generally not well preserved and difficult to obtain. For example, the old ornithogenic soil surfaces containing penguin remains have possibly been entirely eroded and scoured by glacial advances, or dissolved in the wetter climatic zone of maritime Antarctica (Tatur et al., 1997; Emslie, 2001).

In more recent studies, Sun et al. (2000, 2001a, 2004) reported that the remnants of ancient penguin droppings in the lake sediments near penguin colonies can be identified by their geochemical characteristics and provide continuous information about historical penguin population changes. In this paper, we performed detailed geochemical analyses on an ornithogenic lake sediment core from Ardley Island in the Antarctic in order to reconstruct a continuous, high-resolution record of the penguin population on that island over the past ~1300 yr B.P.

#### Study Area

Ardley Island (62°13'S, 58°56'W), declared as an Antarctic Specially Protected Area by the Protocol on Environmental Protection to the Antarctic Treaty and ratified in 1991, is 2.0 km in length and 1.5 km in width (Fig. 1). The island is about 500 m east of the coast of Fildes Peninsula, Maxwell Bay, King George Island, and connected to the Fildes Peninsula through a sandy dam. The Great Wall Station of China is located about 0.5 km to the west (Fig. 1). The study area has a cold oceanic climate, characteristic of maritime Antarctica. According to the meteorological records from the Great Wall Station, the mean annual precipitation is about 630 mm, the annual average relative humidity is about 90%, and the mean annual air temperature is around -2.6°C with a winter low at -26.6°C and a summer high at 11.7°C. It is free of snow and ice during the summer. Geologically, it consists mainly of Tertiary andesitic and basaltic lavas and tuffs together with raised beach terraces. The topography is plain, with the highest elevation at 70 m, and 70% of Ardley Island is covered by vegetation.

Ardley Island is one of the most important penguin colonies in the maritime Antarctic region. The site has the largest concentration of Gentoo penguins (Pygoscelis papua) within the South Shetland Islands. The average number of breeding pairs is estimated at about 4000. In addition, there are also about 1200 breeding pairs of Adélie penguins (Pygoscelis adeliae) and a small number of Chinstrap penguins (Pygoscelis antarctica) (cited from Sun and Xie, 2001). The inter-season fluctuation in the numbers and the breeding success of each penguin species is available from modern census data collected since 1979. In addition to these census data, ancient penguin waste products, accumulated in small and shallow lakes on the island, have recently been proposed as a means to examine ancient penguin populations and paleoclimate (Sun et al., 2000). In the catchment area of the investigated Y4 lake, there are some abandoned colonies of penguins, which are a potential eutrophying factor in this area (Tatur and Myrcha, 1984); the penguin droppings probably have been transferred and deposited into the lake by ice or snowmelt water.

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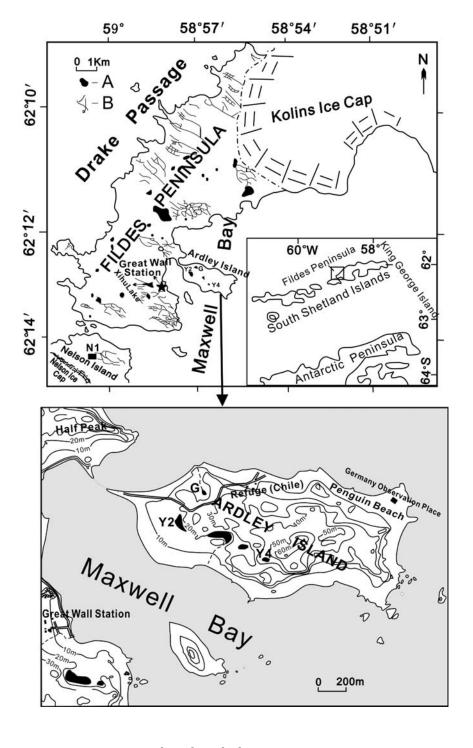


FIGURE 1. Studied area and sampling sites for the cores Y4, N1, and Y2. In the top panel, marker A shows lakes, marker B shows network of meltwater channels. In the bottom panel, the contour interval is 10 m.

#### Materials and Methods

#### **SAMPLING**

A lake sediment core (Y4), 34 cm long, was collected by driving PVC pipe, 12 cm in diameter, into the soft substrate of the Y4 lake floor at an altitude of 28 m during the austral summer of 1999/2000. For the purpose of comparison, we also collected a 66-cm-long weathered sediment sequence from the front margin of Nelson Ice Cap (as marked by N1 in Fig. 1), a 67.5-cm-long sediment core (named as Y2) amended by penguin droppings, and a 54-cm-long lake core from a lake named G using the same method. All the sampling sites are shown in Figure 1. These sediment cores were transported directly to the home laboratory without slicing, and were preserved in cold storage prior to being analyzed. In the laboratory, continuous subsampling for

elemental analyses was done in 2-cm slices for the sediment core Y4. The lithologic section is illustrated in Figure 2. This sediment core discharges an unpleasant smell, and some ancient penguin bones, identified with reference to modern penguin bones from the Fildes Peninsula on the King George Island, are well preserved in it (shown in Fig. 2). For the sediment core N1 and Y2 and the Xihu lacustrine sediments, detailed information about their sediment patterns and geochemical characteristics have been described by Liu et al. (2004), Sun et al. (2000, 2001a), and Zhao (1991), respectively.

#### ELEMENTAL ANALYSIS

All the Y4 subsamples were ground to 200 mesh size after drying in open air. About 0.1–0.5 g of each powder sample was taken,

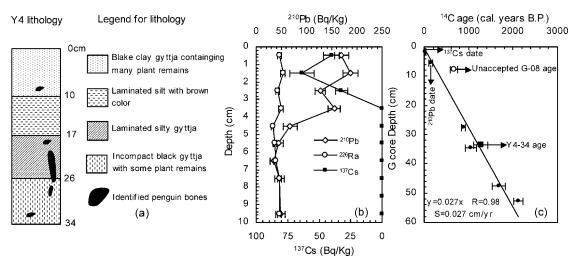


FIGURE 2. (a) Sediment lithostratigraphy for the core Y4; (b) <sup>210</sup>Pb, <sup>137</sup>Cs versus depth in the sediment core G. Highest peak value of <sup>137</sup>Cs corresponds to the 1965 fallout maximum from the atmospheric testing of nuclear weapons, in good agreement with the result of CRS <sup>210</sup>Pb model (Sun et al., 2001b). (c) Linear depth-age model for the core G using the radiometric and calibrated ages, except one with an age of 666 cal. yr B.P. (G-08). The linear sedimentation rate (S) is 0.027 cm a<sup>-1</sup>.

precisely weighed, and then digested by multi-acid in a Pt crucible with electric heating. The digested samples were analyzed for the following 24 elements: Si, Al, Fe, S, F, Sr, Ba, P, Ti, Cr, V, As, Se, K, Na, Ca, Mg, Mn, Pb, Ni, Cu, Zn, Ga, and Ge. Concentrations of Si, Al, and Fe<sub>2</sub>O<sub>3</sub> 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 a 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/HClO<sub>4</sub>. Abundance of P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, Cr, and V was determined by ultraviolet visible spectrophotometry (UVS). Concentrations of As and Se were determined by atomic fluorescent hydrogenation (AFS) (XDY-1 atomic fluorescent spectrometry). Atomic absorption spectrophotometry (AAS) (model PZ-1100) was used to determine K, Na, Ca, Mg, Mn, Ni, Cu, Zn, Pb, and Ge. Precision and accuracy of our results was monitored by analyzing standard sediment reference materials with study samples in every batch of analysis. The analytical values for the major elements and trace elements are within  $\pm 0.5\%$ and  $\pm 5\%$  of the certified ones, respectively.

#### RADIOMETRIC AND RADIOCARBON ANALYSIS

Conventional radiocarbon dating was carried out on two samples of bulk sediments from the core Y4. For the sediment core G,

conventional radiocarbon dating was performed on one sample of moss-rich sediments as well as handpicked moss remains (Amblystegiaceae, *Drepanocladus aduncus*) at four different depths (Table 1). Using tweezers and a needle, the moss materials were separated under a binocular microscope, and mechanically cleaned from other sediment particles. <sup>14</sup>C measurement was conducted on organic carbon components by using a Quantalas-1220 liquid scintillometer, after pretreatment with dilute HCl to remove the minute content of carbonate which may have been included in the samples. The conventional radiocarbon ages were reported here as B.P. (before present, conventionally before 1950). The quoted errors in the dates are based on the reproducibility of measurement.

For the G sediment core, the top 10 cm of sediments were sectioned into 10 samples at 1-cm intervals. About 3 g of each subsample was dried and then ground to fine powder in the laboratory. The analysis for recent radionuclides ( $^{210}$ Pb,  $^{226}$ Ra, and  $^{137}$ Cs) of these subsamples was performed by direct gamma spectrometry using Ortec HPGe GWL series, well-type, coaxial, low background, intrinsic germanium detectors.  $^{210}$ Pb activity was determined via its gamma emissions at 46.5 keV, and  $^{226}$ Ra by the 295 and 352 keV  $\gamma$ -rays emitted by its daughter isotope  $^{214}$ Pb following 3 weeks storage in sealed containers to allow radioactive equilibration.  $^{137}$ Cs was measured by its emissions at 662 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known  $^{210}$ Pb activity. Corrections were made for the effect of self-absorption of low energy  $\gamma$ -rays within the sample. Supported

TABLE 1  $^{14}\mathrm{C}$  conventional and calibrated ages of the samples from G and Y4 lake sediment cores.

	Laboratory			<sup>14</sup> C conventional	Calibrated age (cal. yr B.P)		
Core	number	Dated material	Depth (cm)	age (yr B.P.)	Intercept	2 sigma	
G	G-08	Aquatic moss remains	7–8	720 ± 55	666	559-733	
	G-14	Moss-rich sediments	27-28	$915 \pm 45$	883	930-729	
	G-18	Aquatic moss remains	34–35	$1120 \pm 55$	1051	1173-930	
	G-27	Aquatic moss remains	47–48	$1765 \pm 55$	1695	1822-1537	
	G-31	Aquatic moss remains	52-53	$2120 \pm 55$	2116	2183-1985	
Y4	Y4-01	Bulk sediment	0-1	$420 \pm 40$	modern	modern	
	Y4-34	Bulk sediment	33-34	$1723 \pm 120$	1270	967-1420	

Note: A reservoir correction was applied to the date of sample Y4-34 from the sediment core Y4 by subtracting 420 years, and then calibrated using the INTCAL 98 data set (Stuiver et al., 1998) in the CALIB 4.4 program (Stuiver and Reimer, 1993).

TABLE 2
Chemical element concentrations in the proglacial sediments (N1), the local bedrocks, and the lake sediments Y4, Y2, and Xihu.

		Y4 (n = 18)		Bedrock $(n = 51)^a$	N1 $(n = 35)^b$	$Y2 (n = 24)^c$	Xihu $(n = 26)^d$	
	Range	CV (%)	Mean	Mean	Mean	Mean	Mean	
Major eler	ments (%)							
Na	0.78-1.78	29.38	1.08	1.47	1.84	1.86	1.84	
K	0.22-0.38	15.82	0.27	0.34	0.50	0.54	0.47	
Ca	8.46-14.14	11.91	11.95	8.48	3.99	7.68	2.88	
Mg	0.45-1.13	31.31	0.73	2.20	2.31	1.38	1.43	
Mn	0.10-0.15	84.93	0.12	0.093	0.12	0.073	0.078	
Fe	2.38-4.40	47.23	5.71	5.07	6.71	5.02	4.94	
Ti	0.25-0.56	32.47	0.34	0.48	0.68	0.7	0.63	
Al	3.17-5.96	22.03	4.12	8.05	9.55	6.98	7	
Si	7.95–16.68	16.12	10.60	23.28	23.97	20.43	n/a	
Minor and	trace elements (mg/Kg	(;)						
Zn	490-772	50.95	681.5	60	100	343	65	
Cu	425-866	16.49	682.28	91	99	301	102	
Ge	0.51-1.27	66.21	0.8	n/a	1.1	n/a	n/a	
Ni	4.9-9.8	104.93	7.54	34	21	9	19	
Pb	5.2-51.2	64.61	11.33	0.5	13.8	15.7	20.0	
As	6.6-16.9	38.49	12.41	7.7	5.7	5	n/a	
S	5700-18400	25.64	14205.56	110	190	2190	1297	
F	3491-8313	107.19	7131.67	n/a	270	7700	n/a	
Se	24-54.9	74.05	43.33	7.9	0.2	10.2	n/a	
Sr	1162-1904	31.73	1628.06	495	452	1005	n/a	
Ba	132-169	45.45	150.22	213	196	228	n/a	
Cr	31-60	26.6	45.28	58	55	48	35	
P	32004-60821	16.12	52932.86	551	758	26747	568	
V	60-170	34.61	89.44	159	44	97	180	
Ga	8.6-20.6	25.98	12.03	n/a	n/a	16.65	n/a	

<sup>&</sup>lt;sup>a</sup> Geochemical data for the local bedrocks are from Zhao (1991) and Xie et al. (1992).

Note: CV is coefficient of variation. n/a = not determined.

<sup>210</sup>Pb in each sample was assumed to be in equilibrium with in situ <sup>226</sup>Ra. Unsupported <sup>210</sup>Pb activity at each depth was calculated by subtracting <sup>226</sup>Ra activity from total <sup>210</sup>Pb activity. A more detailed description of the equipment and method was given by Wu et al. (2004). In this study, both the radiometric and conventional radiocarbon dating were performed at Nanjing Institute of Geography & Limnology, Chinese Academy of Sciences (CAS).

#### **Results and Discussion**

#### CHRONOLOGY

As reviewed by Björck et al. (1991a) and Ingólfsson et al. (1998), there are a number of problems associated with dating Antarctic lacustrine deposits that can result in inaccurate chronologies. In particular, marine sources can contaminate freshwater sediments, and therefore dates can be influenced by the Antarctic marine reservoir effect, which yields older radiocarbon dates (Hodgson et al., 2001). As discussed in this section, marine material from the input of penguin droppings contaminated lake Y4, and thus the radiocarbon dates for the bulk organic carbon in the sediments require a reservoir correction. However, the reservoir effect for marine-originated penguin droppings in the study area is unknown to date. Because there was no terrestrial material suitable for <sup>14</sup>C dating in the Y4 lake sediments, we only determined two conventional <sup>14</sup>C dates on bulk organic materials from the surface and base of the core Y4 (Table 1). Assuming that the

surface date could be used to estimate the local marine reservoir effect (McMinn, 2000; Hodgson et al., 2001), the base date can be reasonably corrected by subtracting the surface from it to give the reservoir-corrected date of about 1300 yr B.P. We cannot establish a more high resolution chronology for this core since no other radiocarbon dates were available in the present study.

The adjacent lake G contains large amounts of aquatic mosses. Since moss remains in lake sediments can give the most reliable <sup>14</sup>C ages in the Antarctic Peninsula (Björck et al., 1991a, 1991b), ages of mosses in lake G from conventional radiocarbon dating were taken to be those of the sediments.

As shown in Figure 2, <sup>137</sup>Cs is present in the uppermost 3-cm sediment layer of the lake G core, with a peak activity at the depth of 1.5 cm, likely indicating that the 1965 fallout maximum from the atmospheric testing of nuclear weapons pertains to this depth (Appleby et al., 1995). Significant levels of unsupported <sup>210</sup>Pb were detected in the top 5 cm, and the total <sup>210</sup>Pb activities were in equilibrium with the <sup>226</sup>Ra activity below 6 cm, which produces supported <sup>210</sup>Pb. The oldest <sup>210</sup>Pb-datable sediments in the core are located at 4.5 cm and correspond to an age of 134 yr B.P. based on a constant rate of supply (CRS) dating model (Appleby et al., 1995). Further information on <sup>210</sup>Pb and <sup>137</sup>Cs chronology has been published elsewhere (Sun et al., 2001b).

Five samples from the lake G core were measured for radiocarbon dates, out of which four are aquatic mosses (Amblystegiaceae, *Drepanocladus aduncus*) extracted from the bulk sediments, and one

<sup>&</sup>lt;sup>b</sup> Data for the proglacial sediments (N1) are from Liu et al. (2004).

<sup>&</sup>lt;sup>c</sup> Data for the Y2 lake sediments are from Sun et al. (2001a).

<sup>&</sup>lt;sup>d</sup> Geochemical data for the Xihu lake sediments are from Zhao (1991).

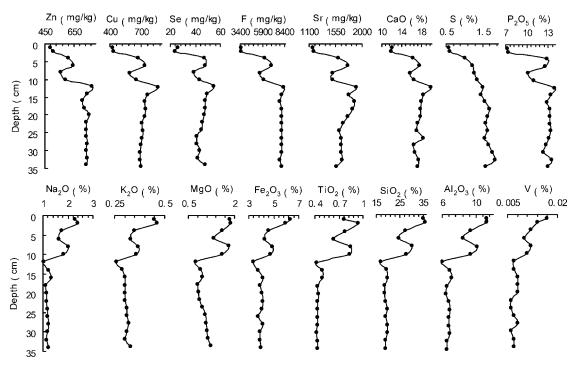


FIGURE 3. Concentrations of some elements versus depth in the Y4 lake sediments.

is moss-rich sediments (G-08 listed in Table 1). All the radiocarbon dates were transformed into calibrated radiocarbon years before present (cal. B.P.) using the INTCAL98 calibration data set (Stuiver et al., 1998) in the CALIB 4.4 program (Stuiver and Reimer, 1993); the results are shown in Table 1. All the <sup>14</sup>C dates, the <sup>137</sup>Cs peak, and the oldest <sup>210</sup>Pb date are illustrated in Figure 2 versus depth. As can be seen from Figure 2, the radiocarbon date of the moss-rich sediment sample G-08 is apparently too old in comparison with the <sup>210</sup>Pb dating results, and this is consistent with the results of Björck et al. (1991a, 1991b) and Shen et al. (1998), who suggested that the dates on aquatic moss samples were more reliable than those of the bulk sediments themselves. If G-08 is removed from the age-depth modeling, we see a good correlation between the dates and the sediment depth with a slope or average sedimentation rate of 0.027 cm a<sup>-1</sup>, in good agreement with 0.029 cm a<sup>-1</sup> of the adjacent lake Y2 as reported by Sun et al. (2000). Because the lakes Y2, G, and Y4 are in the same geographical area and have similar limnological features, it is reasonable to believe that they should have consistent average sedimentation rates. As shown in Figure 2, the basal date for the sediment core Y4 (sample Y4-34) is in line with the age-depth model of the G lake sediment profile. Therefore, we could use this age-depth model to establish the chronology of the sediment core Y4.

#### GEOCHEMICAL CHARACTERISTICS

According to the results of Sun et al. (2000, 2001a, 2004), nine "bio-elements"—sulfur (S), phosphorus (as  $P_2O_5$ ), calcium (as CaO), copper (Cu), zinc (Zn), selenium (Se), strontium (Sr), barium (Ba), and fluorine (F)—were enriched and significantly correlated with each other in the soils or sediments amended by penguin guanos. These element levels in the sediments or soils impacted by penguin guanos are significantly higher than those in the unaffected ones (Tatur et al., 1997; Sun et al., 2000; Liu et al., 2004). They have not been reported together in high concentration in any organic material except penguin droppings, and they were typical elements of penguin guanos. Without remnants of penguin guanos, these elements cannot be accumulated together since their chemical properties are very different (Sun et al.,

2000, 2001a; Sun and Xie, 2001). Moreover, these typical elements from penguin guanos are almost immobile in the sediments of Antarctic lakes and depressions, according to Sun et al. (2000, 2001a). Therefore, the assemblage of P, Sr, Cu, Zn, Se, Ca, F, Ba, and S is an important geochemical marker for penguin droppings or the soils and sediments impacted by them in the maritime Antarctic.

Table 2 gives the arithmetic mean, variable range, and coefficient of variation (CV) for the chemical concentrations of elements in the Y4 lake sediments. For comparative purposes, the average element concentrations in the local bedrock, N1 proglacial sediments, Y2 lake sediments, and Xihu lacustrine sediments are also given in this table. As seen from the Table 2, the mean concentrations of major elements, with the exception of Ca, in Y4 and Y2 were obviously lower than those in local bedrock and N1, but the concentrations of the minor elements, such as Zn, Cu, P, S, Se, Sr, and F, in Y4 and Y2 were much higher. These significant differences in the mean element concentrations among the local bedrock, N1, Y2, Y4, and Xihu lake sediments may be attributed to their different sediment patterns. The Y2 lake sediments were found to be impacted by penguin droppings, thus resulting in remarkable enrichment of S, P, Ca, Cu, Zn, Se, Sr, Ba, and F and significant intercorrelations (Sun et al., 2000, 2001a; Sun and Xie, 2001). The Xihu lacustrine sediments were not amended by penguin droppings, but affected by biogenic materials such as moss, lichens, etc. (Zhao, 1991). The N1 proglacial sediments were not affected by penguin droppings or by biological action, and they were considered to be the naturally weathered products of the local bedrocks (Liu et al., 2004). The Y4 lake sediments, having remarkably higher concentrations of F, P, Sr, Se, S, Cu, Zn, and Ca, are apparently similar to the Y2 lake sediments and very likely impacted by penguin droppings.

The impact of penguin droppings on Y4 is also supported by the vertical concentration profiles of major and minor elements versus depth and the results of clustering and correlation analysis. As illustrated in Figure 3, the vertical distributions of F, P, Sr, Se, S, Cu, Zn, and Ca concentrations display almost the same pattern, but opposite that of lithophile elements such as Na, K, Al, Mg, Ti, Si, Fe, etc. The results of R-clustering performed on the intercorrelation

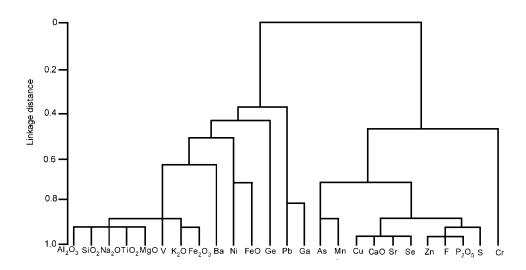


FIGURE 4. R-cluster analysis result for the chemical elements in the Y4 lake sediments.

coefficients of 24 element concentrations in Y4 are given in Figure 4. As seen from the dendrogram, Sr, Cu, P, Zn, S, F, Ca, Se, As, Mn, and Cr belong to the same group, and the rest of the elements belong to the other group. A Pearson correlation analysis also gave significantly positive correlations among the concentrations of Sr, Cu, P, Zn, S, F, Ca, and Se in Y4 (Table 3). All these results indicated that Sr, Cu, P, Zn, S, F, Ca, and Se are likely to be of the same origin.

As indicated above, Antarctic penguin droppings are notably rich in P, Sr, Ba, Cu, Zn, Se, Ca, F, and S, and the assemblage of these bioelements is an important geochemical marker or biomarker for the lake sediments impacted by penguin droppings or guano soil (Sun et al., 2000, 2001a; Sun and Xie, 2001). For Y4, nevertheless, Ba does not belong to this assemblage probably due to the difference of its geochemical behavior in Y2 and Y4. In Y2, Ba was considered to be associated with a bio-source, but in Y4, it seems to be a lithogenic element. Table 4 gives the correlation coefficients of Ba and other elements in Y4 and shows that Ba has significantly positive correlations with lithophile elements such as Na, K, Fe, Al, Si, and V, but negative with P, Cu, Zn, Se, Ca, F, and S. Further investigations suggested that Ba is mainly controlled by minerals such as potassium feldspars. As illustrated in Figure 5, there is a strong correlation between K and Ba concentrations. This correlation may be attributed to the mineralogical control of K-feldspar as a result of poor chemical weathering processes under extremely low temperatures of the Antarctic (Liu et al., 2004), since K-feldspar is the main carrier for these elements (Kim et al., 1998). Furthermore, we found excellent correlation between Ba/Mg versus Al/Mg ratios (Figure 5), indicating the presence of feldspars (Kim et al., 1999).

TABLE 3

The correlation coefficients between the eight elements in the Y4 lake sediments.

Elements	Zn	Cu	Se	F	Sr	Ca	P	S
Zn	1.000							
Cu	0.873	1.000						
Se	0.764	0.958	1.000					
F	0.980	0.911	0.829	1.000				
Sr	0.823	0.955	0.917	0.873	1.000			
Ca	0.854	0.978	0.930	0.901	0.943	1.000		
P	0.916	0.947	0.909	0.950	0.903	0.932	1.000	
S	0.899	0.782	0.688	0.933	0.758	0.793	0.846	1

Note: All the correlations listed in this table are significant at the 0.001 level (2-tailed).

Therefore, the assemblage of P, Cu, Sr, Zn, Se, Ca, F, and S is the biomarker of the amendment by penguin droppings or guano soil in Y4. Penguin rookeries are present around the lake Y4, and its excreta are probably deposited in the lake by catchment snow-melt or directly in the water, as evidenced by the presence of ancient penguin bones in the sediments. The input of penguin droppings enriched the Y4 sediments with the bio-elements of P, Cu, Sr, Zn, Se, Ca, F, and S and resulted in the dilution of the lithophile elements. Additionally, as shown in Table 2, the contents of the bio-elements in Y4 are much higher than those in Y2, probably indicating a greater influence of penguin droppings.

### RECONSTRUCTION OF HISTORICAL PENGUIN POPULATION OVER THE PAST $\sim$ 1300 YEARS

With the evidences that geochemical characteristics of Y4 are controlled mainly by the influence of penguin droppings or guano soil, Q-mode factor analysis (Sun et al., 2000), a method for decomposing multiple factors, was utilized to analyze the concentration of P, Cu, Sr, Zn, Se, Ca, F, and S in Y4. The results revealed that more than 99% of the variance in the data could be explained by two factors (51.54% for factor1 and 48.43% for factor2). As illustrated in Figure 6, the change pattern of the first factor is very close to the profiles of the bio-element concentrations versus depth. Therefore, this factor can be used to measure the input of penguin droppings in the sediments and thus penguin population for the last  $\sim$ 1300 years. The profile of factor 1, as given in Figure 6, shows that the historical penguin population, while relatively stable, has a decreasing trend. Two troughs appear around 1000 yr B.P. and during the period of  $\sim$ 450–200 yr B.P. Especially, in the past century, the penguin population declined steeply, and the trend still continues. This is consistent with the recently documented decreases in the total number of penguins on Ardley Island (citing from Xie, 2001). The trough of  $\sim$ 450–200 yr B.P., as shown in Figure 6, is comparatively shallow, but the t-test result showed that there existed significant differences between the data within the period of  $\sim$ 450–200 yr B.P. and the rest (*t*: –3.85; *p*: 0.00093; confidence level: 95%). Therefore, we suggested that the fluctuation of the factor 1 curve during the period of ~450-200 yr B.P. did represent a significant decline of the penguin population.

What is responsible for the declining penguin population? In order to answer this question, we tentatively compared the relative penguin populations with the paleoclimatic records and glacial advance and retreat history. According to the work of Sun et al. (2000), Sun and Xie (2001), Xie (2001), and Zhao (1991, 1997), the period of 1100–1300 yr B.P. was characterized by warm and humid climatic conditions with

TABLE 4

The correlation coefficients between element Ba and lithological elements and bio-elements in the Y4 lake sediments.

Na	K	Fe	Al	Si	V	Zn	Cu	Se	F	Ca	P	S
0.526*	0.573*	0.593*	0.500*	0.520*	0.628*	-0.506*	-0.538*	-0.517*	-0.577*	-0.508*	-0.527*	-0.701*

<sup>\*</sup> Correlation is significant at the 0.05 level (2-tailed).

relatively high precipitation. After that, there was a glacial advance at about 1000 yr B.P. in the South Shetland Islands (Barsch and Mäusbacher, 1986), and this is in agreement with the decreasing penguin populations around 1000 yr B.P.

The trough of the relative penguin population from  $\sim$ 450 to 200 yr B.P. coincides well with the onset of the Little Ice Age. The Little Ice Age, a widespread cooling climate event that also occurred on the Antarctic Peninsula, has been supported by evidence from ice cores, marine sediments, lake sediments, and penguin occupation history (Kreutz et al., 1997; Goodwin, 1998; Emslie et al., 1998; Smith et al., 1999; Emslie and McDaniel, 2002). The ice-core and oxygen isotope record from Siple station indicate that the Antarctic Peninsula did experience colder climates than today during the Little Ice Age (Emslie, 2001; citing Mosley-Thompson et al., 1990). Emslie et al. (1998), based on the investigation of the penguin occupation history on the Antarctic Peninsula, suggested that a brief gap occurred during the period of the Little Ice Age (A.D. 1500-1850). During climatic deterioration, Ardley Island could have been covered with more ice or a glacier, making it harder for penguins to nest and breed and thus leading to a reduction in the populations of breeding penguins (Smith et al., 1999; Emslie et al., 1998; Emslie, 2001; Emslie and McDaniel, 2002). Other causes for the reduction of penguin populations may include changes in marine food availability and/or sea-ice conditions that precluded breeding penguins from existing in the study area (Fraser et al., 1992), since lower surface air temperature could increase sea ice extent in the Antarctic Peninsula (Smith et al., 1999).

With the available data in the present study, the cause for the significant decrease in the penguin population over the past  $\sim 100$  years, however, cannot be fully understood. According to reliable climatic records and other evidences, the recent warming on the Antarctic Peninsula has resulted in a profound climatic change, an order of magnitude greater than global mean warming (Fraser et al., 1992; Stark, 1994; King, 1994; Turner et al., 2002). This abnormally warming climate period may hold more moisture and cause heavier snowfall (Kaiser, 1997). Moreover, as discussed by Zhu et al. (unpublished data), the north, north-west, and west winds are more frequent than the east wind on Ardley Island; therefore, more snow should have accumulated on the northwest, west, and southwest sides of the island over the past  $\sim 100$  years, making it harder for penguins to breed. Therefore, we speculated that the sharp reduction of penguin populations in the past century in the catchment of Y4 lake is possibly

due to interactions between the effects of increased snow deposition and decreasing egg and/or chick survival due to predation and flooding (Kaiser, 1997; Patterson et al., 2003). To confirm this hypothesis, however, sampling of additional sediment cores from the northwest, west, and southwest sides of the Ardley Island is apparently necessary.

#### CONCLUSIONS

Compared with the local bedrock, natural weathered sediments, Xihu lake sediments, and ornithogenic lake sediments, the Y4 lake core from the Antarctic Ardley Island has a distinct geochemistry, characterized by notably high concentrations of F, P, Sr, Se, S, Cu, Zn, and Ca and significantly positive inter-correlation. The vertical distribution patterns of F, P, Sr, Se, S, Cu, Zn, and Ca concentrations are almost identical, but opposite to those of lithophile elements such as Na, K, Al, Mg, Ti, Si, Fe, etc. The assemblage of P, Cu, Sr, Zn, Se, Ca, F, and S suggests that the Y4 lake sediments have been impacted by penguin droppings or guano soil, and this is further confirmed by the presence of well-preserved penguin bones in the sediments. Using Q-mode factor analysis, we have determined the factor responsible for the input of penguin droppings, and its changes are considered to be representative of the population dynamics of penguin species. Our results show that the penguin population on the Ardley Island over the past ~1300 years, while relatively stable, has a decreasing trend, especially in the past century, when the penguin population declined steeply. The comparison between the historical penguin population changes in Y4 and the paleoclimatic records suggests that the decline, prior to the past two centuries, is likely due to climatic deterioration. The cause for the significant decrease in penguin population over the past  $\sim 100$  years, however, remains to be further studied.

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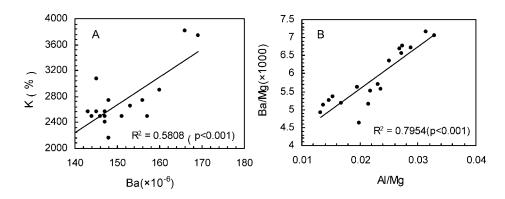


FIGURE 5. Plots of element K versus Ba (A) and element ratio Al/Mg against Ba/Mg (B).

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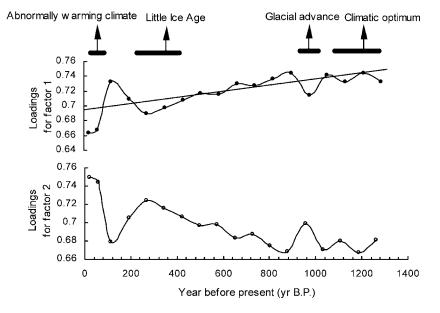


FIGURE 6. The change of penguin populations during the past -1300 years obtained by Qfactor analysis for the sediment core Y4 on the Ardley Island. The factor 2 is opposite to the factor 1; variation in loadings of factor 1 represents the variation in penguin population during the past 1300 years. At the top of the graph, the climatic optimum is based on the work of Sun et al. (2000), Sun and Xie (2001), Xie (2001), and Zhao (1991, 1997); the period of glacial advance is from Barsch and Mäusbacher (1986); the Little Ice Age is derived from the work of Kreutz et al. (1997), Goodwin (1998), Emslie et al. (1998), Smith et al. (1999), and Emslie and Mc-Daniel (2002). The abnormally warming climate period is from the work of Fraser et al. (1992). Stark (1994), King (1994), and Turner et al. (2002). With regard to the correlation between the climatic change and penguin population fluctuation, see text for detailed discussion.

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