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The identification and comparison of the bio-elements of the penguin ornithogenic sediments sample from Davis Station and Great Wall Station

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Abstract During CHINARE-22 in austral summer of 2005-2006, a lake sediment core named DG4, which is impacted by penguin droppings, was retrieved from a lake catchment in Gardner Island of Vestfold Hills, East Antarctica. In this study, the concentrations of characteristic elements in the core, local bedrocks and fresh penguin guanos were determined. P, Se, F, S, As, Sr and Cu in DG4 were identified as the bio-element assemblage by R-clustering analysis and compared with those in the local bedrocks and fresh guanos, the results are similar to Y2 in Ardley Island, Antarctic Peninsula. On this basis, P and Se were identified as the optimum bio-elements in DG4 and F, P and S were identified in Y2, respectively. This work will provides the foundation for reconstructing the past penguin populations in Gardner Island of Vestfold Hills, East Antarctica and comparing the penguin population dynamics between East Antarctica and Antarctic Peninsula.

Key words ornithogenic sediment. bio-element. environmental background. penguin diet. Vestfold Hills. Antarctic Peninsula.

1 Introduction

The ebb and flow of the ice-free area surrounding Antarctica and the corresponding climatic and environmental changes since Holocene can be well recorded in lake sediments, and different methods have been proposed to extract such information. Zhao[1] used biogeochemical method to analyze the sediments of West Lake near Great Wall Station, located on the King George Island in the Antarctic Peninsula, and reconstructed a 4000 yr record of precipitation in this area, after comparing the precipitation changes with the environmental changes of South Chile over a time span of 16000 yr, Zhao suggested that the climate of King George Island was impacted by the Antarctic Convergence Zone. Roberts and McMinn[2,3] and Roberts et al.[4] reconstructed the palaeosalinity history of three lakes in Vestfold Hills and Bunger Hills from the diatom-salinity signal preserved in the sediment cores. Hodgson and Johnston[5] and Sun[6] successfully utilized well-preserved animal rel-

ics and remnants such as hairs, droppings or feces in lake sediments to infer historical population dynamics of sea animals and examine the responses of ecological systems to climatic changes and human activities. The bio-element assemblage, $^{87}Sr/^{86}Sr$ proxy and bio-markers from ornithogenic sediments were extracted and used to reconstruct the historical populations of seabird[7-9].

In this study, a sediment core DG4 amended by penguin droppings was collected on the Gardner Island near Davis Station, East Antarctica. The concentrations of characteristic elements in the ornithogenic sediments, local bedrocks and fresh penguin guanos were determined. The bio-element assemblage in DG4 was extracted, and the optimum bio-elements in DG4 and Y2 were identified by comparing the concentrations of the bio-elements in the fresh guanos and local bedrocks. It provides the foundation for studying the past penguin population dynamics and its response to climatic and environmental changes in Gardner Island of Vestfold Hills and comparing the variation patterns of the penguin populations between East Antarctica and Antarctic Peninsula.

2 Environmental background, sample collection and analysis

2.1 Environmental background

The Gardner Island is in the vicinity of Davis Station (Fig. 1) which is located on the edge of the Vestfold Hills of the eastern side of Prydz Bay in the Ingrid Christensen Coast of Princess Elizabeth Land. The Vestfold Hills is an ice-free area of about 400 km^2; it is bounded by the Sorsdal Glacier in the south, by the steep ice-covered slopes in the east, and by the sea in the northwest; it consists of Long peninsula, Broad peninsula and Mule peninsula; and it is bare, low-lying hilly country deeply indented by sea-inlets and studded with lakes and tarns of varying salinity[10]. The climate of this area is cold, dry and windy. Mean summer maximum temperatures rise to about +9 ℃. As is typical of continental antarctic localities, temperatures are below 0 ℃ for most of the year, falling to as low as −40 ℃ in winter[11].

The Gardner Island is about 2 km long, 1 km wide, and 4 km west of Davis Station in the Vestfold Hills. The topography of this island is plainness with a maximum 49 m height above sea level. No moss and lichen, which are popular in Antarctica Oasis, were found on this island. Large number of Adelie penguins as well as some skuas and Giant Petrels were occupying on this island. Krill, fish, shellfish and mollusk make up of the diets of penguins. Krill comprises 81.79% of the diets for Adelie penguins in Fildes Peninsula, Antarctic Peninsula[12], but penguins in East Antarctica, however, were primarily fed on fish, krill comprises no more than 40% of the diets for Adelie penguins in Windmill Islands[13,14].

2.2 Sample collection and analysis

The lake sediment core DG4 of 83 cm was collected from the Gardner Island near Davis Station, East Antarctica during the 22nd Chinese Antarctic Research Expedition. The coring site as shown in Fig. 1, was dry when sampled. A 12 cm diameter PVC pipe was

pushed vertically into the lake catchment center to excavate the sediment core. After the PVC pipe was retrieved, its bottom and top was hermetically sealed with lids. The bedrocks, fresh penguin guanos and modern penguin bones and feathers from a dead penguin were also collected in the island. All the samples were preserved in cold storage prior to analysis. In the laboratory, the core was opened, photographed, described, and then sectioned at 1cm intervals and the obtained 83 subsamples were stored in freezer prior to analysis.

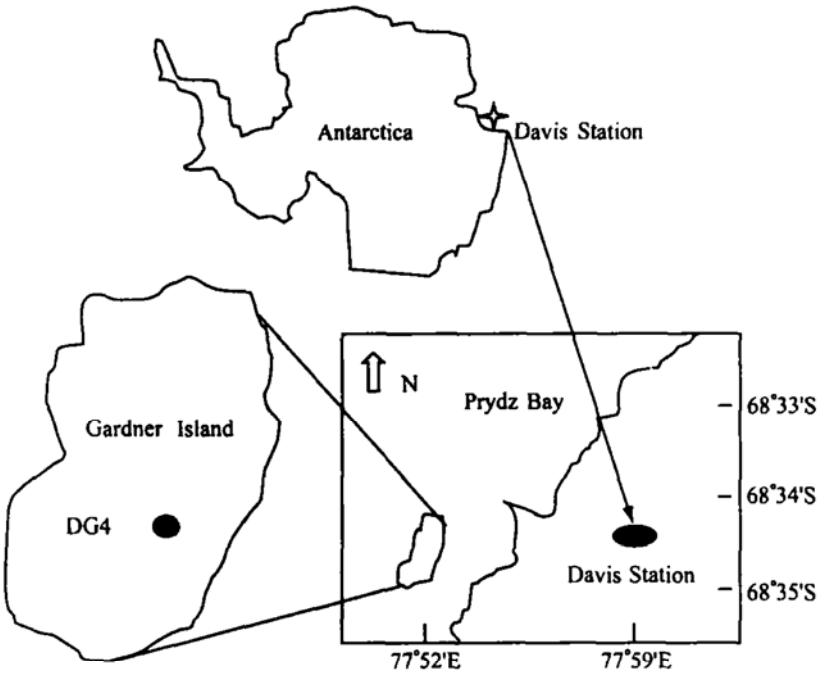

Fig. 1 Map for Gardner Island and sampling location for DG4.

Before chemical analyses, each subsample was air-dried in a clean laboratory and homogenized. All the subsamples from DG4 as well as the local bedrocks and fresh penguin guanos were analyzed for their characteristic elemental concentrations, total organic carbon (TOC), total phosphorus (TP) and total sulfur (TS), and these analyses were completed at the Institute of Polar Environment, University of Science and Technology of China.

For chemical element analysis, subsamples were sieved though a 70 μ mesh, and then ground to powder after removal of large rock pieces and animal remains. About 0.25g of each powder sample were taken, precisely weighed, and then digested by multi-acids in a Teflon crucible with electric heating. The digested samples were analyzed by AAS novAA400 for K, Na, Ca, Mg, Fe, Mn, Pb, Ni, Cu and Zn, by ICP-OES DV2100 for Sr, Ba, Ti and Al, by UV-VIS 8500 for TP and by atomic fluorescence spectrophotometer AFS-930 for Hg, As and Se. F was determined by fluoride ISE and TS was analyzed by H_2O_2 volume method after combustion in SRJK-2 high temperature furnace. The chemical volumetric method was used to measure TOC content with a duplicate error of 0.05%.

3 Results and discussion

3.1 Identification of bio-element assemblage in DG4

The concentrations of 21 elements in the ornithogenic sediments DG4 were listed in Table 1. The factors influencing elemental concentrations of lake sediments are complex, the geological explanations for behavior of a single element are usually complex, but an assemblage of elements can be specific and used as an indicator of their material source[15]. In order to understand the vertical concentration profiles of elements in sediment core better and to obtain an assemblage of bio-elements, R-clustering analysis and Peason correlation analysis were conducted.

Table 1. The means values and the variant coefficients for 21 elements of DG4 sediment core

Element		TOC	F	P_2O_5	Se	As
Concentration (ppm)	Mean	14800	1444	11000	3.09	7.48
	Range	5500 ~ 29400	479 ~ 4914	1500 ~ 42500	0.59 ~ 10.48	1.63 ~ 19.16
Variance coefficient (%)		38.18	70.84	95.45	75.08	66.04
Element		S	Cu	Zn	MnO	Ni
Concentration (ppm)	Mean	7500	81.2	103.87	1700	108.01
	Range	2500 ~ 70400	37.9 ~ 164.1	51.40 ~ 239.50	300 ~ 3800	23.4 ~ 205.2
Variance coefficient (%)		132.00	35.10	39.28	33.53	30.12
Element		Sr	CaO	Ti	Fe_2O_3	MgO
Concentration (ppm)	Mean	475.22	124600	3340.97	55000	36000
	Range	198 ~ 750.5	58200 ~ 214600	594 ~ 4798	6900 ~ 82300	20600 ~ 47000
Variance coefficient (%)		36.19	39.00	23.43	27.09	17.92
Element		Na_2O	K_2O	Ba	Al_2O_3	Pb
Concentration (ppm)	Mean	40400	16600	446.99	72770	8.77
	Range	28800 ~ 238600	6800 ~ 21200	68.2 ~ 602.7	20000 ~ 108000	1.5 ~ 14.1
Variance coefficient (%)		66.10	12.35	23.86	33.88	22.09
Element		Hg	/	/	/	/
Concentration (ppm)	Mean	0.0084	/	/	/	/
	Range	0.0038 ~ 0.0221	/	/	/	/
Variance coefficient (%)		42.41	/	/	/	/

The R-clustering results for the element concentrations in DG4 (Fig. 2) show that F, P, Se, As, S, Sr, Cu, Zn, Ni, Mn and Ca belong to the first group, and K, Na, Ba, Fe, Ti, Mg, Pb and Al the second. Element Cu, Zn and As in the first group are generically elements relative to Cu; while Sr and Se are generically scattered elements; S, F and P are bio-elements; Ni and Mn are generically iron family elements and Ca is generically petrogenic element[16].

To reduce the influences of the local environmental background on the extracted bio-element assemblage, the concentrations of 11 elements from the first group in local bedrocks and penguin guanos were analyzed. As shown in Table 2, the concentrations of F, P, Se, As, S, Cu and Sr in local penguin guanos are much higher than those in local bedrocks, but Zn, Ni, Mn and Ca have a reverse geochemical character. It indicates that F, P, Se, As, S, Cu and Sr in DG4 have a common source of penguin guanos, and they should be the bio-elements of the ornithogenic sediment. Zn, Ni, Mn and Ca have a very lower level in penguin guanos, Zn, Mn and Ni can be easily enriched by organic materials during the course of surface action[16,17], and their co-occurrence with F, P, Se, As, S, Cu and Sr are most likely ascribed to the high level of organic materials in the ornithogenic sediments

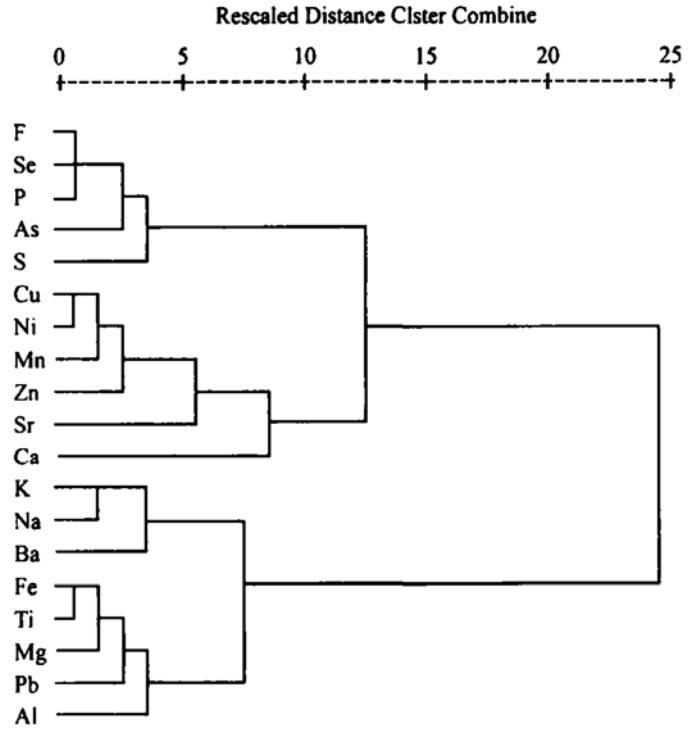

Fig. 2 R-mode clustering results for the elements in the sediment core DG4, East Antarctica.

of DG4. Ca is usually associated with Sr in the sediments because both Ca and Sr usually come from biological calcareous deposition[18], and this may explain why Ca is in the first group. The high concentrations of Ca in local bedrocks, however, could disturb its message; and Ca is a less than idea bio-element for DG4. Therefore, F, P, Se, As, S, Cu and Sr were identified as the bio-element assemblage in DG4. Peason correlation analysis on the concentrations of these bio-elements was performed to corroborate the clustering results. In Table 3 the correlation coefficients are listed and significant correlations among the 7 bio-elements in the ornithogenic sediment are shown.

Table 2. The concentration of some elements of the local bedrock and fresh droppings, on the Gardner Island[1] and Ardley Island[2]

unit	ppm	%	ppm	ppm	%	ppm	ppm	ppm	ppm	%	%
element	F	P_2O_5	Se	As	S	Cu	Sr	Zn	Ni	MnO	CaO
bedrock[1]	330	0.29	0.63	0.71	0.46	144	116	209	52	0.19	9.64
guano[1]	1760	6.33	7.73	1.78	2.11	310	418	130	22	0.03	4.21
guano/bedrock[1]	5.3	21.8	12.3	2.5	4.6	2.1	3.6	0.62	0.42	0.16	0.44
unit	ppm	%	ppm	ppm	%	ppm	ppm	ppm	%		
element	F	P_2O_5	Se	Ba	S	Cu	Sr	Zn	CaO		
bedrock[2]	361	0.055	7.95	98-188	0.011	90.63	263-556	59.79	8.47		
guano[2]	14725	6.08	13.87	276	0.72	316	2164	314	10.89		
guano/bedrock[2]	40.8	110.5	1.74	1.5-2.8	65.5	3.5	3.8-8.2	5.3	1.3		

Note: The data of bedrock[2] cited from [1, 21, 22]. The data of guano[2] cited from [23].

The elements in the second group such as K, Na, Mg and Al are primarily related to

the weathering action of the mother rock. They reflect the characters of the chemical composition of mother rock and the course of weathering on Gardner Island. The chemical weathering action in this area was very weak because of the low temperature and the scarce biologic activity, as testified by elements Ti and Mg whose variance of concentration-versus-depth is very small[19]. Ba and K have very similar trends because Ba is usually enriched in unweathered potassic feldspar[20] and DG4 has high levels of potassic feldspar debris.

Table 3. The results of correlation analysis of the bio-elements and TOC

	F	P_2O_5	Se	As	S	Cu	Sr	TOC
F	1.00							
P_2O_5	0.97**	1.00						
Se	0.97**	0.95**	1.00					
As	0.87**	0.91**	0.88**	1.00				
S	0.62**	0.69**	0.65**	0.60**	1.00			
Cu	0.89**	0.84**	0.94**	0.46**	0.46**	1.00		
Sr	0.67**	0.67**	0.72**	0.88**	0.44**	0.72**	1.00	
TOC	0.58**	0.56**	0.75**	0.72**	0.44**	0.75**	0.87**	1.00

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

3.2 The comparison and optimization of the bio-elements between East Antarctica and Antarctic Peninsula

As above discussion, the bio-element assemblage of the sediment core DG4 from Davis Station, East Antarctica was identified as P, Se, F, S, As, Cu and Sr. In the Previous research, the bio-element assemblage of the Y2 sediment core from Great Wall Station, Antarctic Peninsula was identified as Sr, F, Cu, P, Zn, S, Ca, Se and Ba[24]. The bio-element assemblages from two different areas were consistent although there were several differences.

In the ornithogenic sediments DG4 from East Antarctica, Zn, Ca and Ba were not in the bio-element assemblage, and this could be explained by the high background levels of Zn and Ca in the local bedrocks of the sampling area of DG4. The abundances of Zn and Ca in lake sediments are mainly controlled by local biological source and mother rock. Ba and K are associated in unweathered potassic feldspar, the significant correlation between their concentration-versus-depth profiles in DG4 indicates that Ba primarily comes from potassic feldspar rather than biological sources, and this gives explanations for their absence in the bio-element assemblage.

As a bio-element in DG4 of Vestfold Hills, however, As was not in the bio-element assemblage of Y2 from Antarctic Peninsula. As could be enriched in the organic-rich and sulfur-rich environments[16], its concentration in the bedrocks from Gardner Island of Vestfold Hills is 0.71 ppm, and it is as high as 7.16 ppm in the basalt of Ardley Island in Antarctic Peninsula[21]. The signal of As in the ornithogenic sediments from Ardley Island is apparently overwhelmed by its high background level or noise and environmental background levels of elements have a significant impact on the identification of bio-element assemblage.

Remarkable correlation between the bio-elements from penguin ornithogenic sediments also exist in the unaffected weathered soil (unpublished). To reduce such background noises, it is necessary to further optimize the bio-element assemblage such as the bio-elements which have a very low level in unaffected weathered soils[23]. In this study, it is proposed to use 'guano/bedrock ratio' or the ratio of concentrations of bio-elements in guanos over those in bedrocks and defined a bio-element as optimum bio-element if it has a guano/bedrock ratio $\geqq 10$. According to this criterion, P and Se were considered as the optimum bio-elements in DG4 from Davis Station and F, P and S in Y2 from Great Wall Station (Table 2).

These optimum bio-elements are greatly impacted by local and ecological environments. Krill, fish, shellfish and mollusk make up of the diets of penguins. In the Fildes Peninsula, Antarctic Peninsula, krill comprises 81.79% of diets for Adelie penguins[12]. Penguins in East Antarctica, however, primarily feed on fish and krill makes up no more than 40% of diets for Adelie penguins[13,14]. F was only identified as the optimum bio-element in Y2 from Antarctic Peninsula, apparently due to the fact that it is much enriched in krill[25]. The concentrations of S and Se in the bedrocks of Ardley Island near Great Wall Station were 0.011% and 7.95 ppm, respectively, and on Gardner Island near Davis Station they were 0.46% and 0.63 ppm, respectively. The concentration of S in the bedrock of Gardner Island was some 40 times higher than that on Ardley Island, and the level of Se in the bedrocks of Great Wall Station was 12.8 times higher than that in Gardner Island near Davis Station. Most likely, it is the huge differences in the environmental background that make S the optimum bio-element of Ardley Island, Antarctic Peninsula and Se of Gardenr Island in East Antarctica. The optimum bio-elements will provide more accurate proxy for studying the past penguin populations and climatic and environmental changes in the areas surrounding Antarctica.

4 Conclusions

(1) P, Se, F, S, As, Cu and Sr were identified as the bio-element assemblage in the ornithogenic sediment core DG4 sample from Gardner Island near Davis Station, the assemblage is similar to those in Y2 near Great Wall Station, but there are differences which indicate the influences of different environmental background and penguin diets for extracting the bio-elements.

(2) To reduce the influences of the environmental background accurately, it is therefore necessary to further optimize the bio-element assemblage, and the optimum bio-elements not only show the biological significance but also have a very low concentrations as well as a very small fluctuation in the unaffected weathered soils. On the basis of the comparative research on the concentrations of bio-elements in penguin guanos and local bedrocks, P and Se were identified as the optimum bio-elements in DG4 while in Y2 those were F, P and S.

(3) The identification of bio-element assemblage of DG4 from Davis Station will provides a foundation for studying the past penguin populations and their responses to the climatic and environmental changes.

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