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Eco-environmental implications of elemental and carbon isotope distributions in ornithogenic sediments from the Ross Sea region, Antarctica

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Abstract

Seabirds have substantial influence on geochemical circulation of elements, serving as a link for substance exchange between their foraging area and colonies. In this study, we investigated the elemental and carbon isotopic composition of five penguin-affected sediment profiles excavated from Ross Island and Beaufort Island in the Ross Sea region, Antarctica. Among the three main constituents of the sediments (including weathered bedrock, guano and algae), guano was the main source of organic matter and nutrients, causing selective enrichment of several elements in each of the sediment profiles. In the 22 measured elements, As, Cd, Cu, P, S, Se and Zn were identified as penguin bio-elements in the Ross Sea region through statistical analysis and comparison with local end-member environmental media such as weathered bedrock, fresh guano and fresh algae. Carbon isotopic composition in the ornithogenic sediments showed a mixing feature of guano and algae. Using a two-member isotope mixing equation, we were able to reconstruct the historical change of guano input and algal bio-mass. Compared with research in other parts of Antarctic, Arctic, and South China Sea, we found apparent overlap of avian bio-elements including As, Cd, Cu, P, Se, and Zn. Information on the composition and behavior of bio-elements in seabird guano on a global scale, and the role that bio-vectors play in the geochemical circulation between land and sea, will facilitate future research on avian ecology and paleoclimatic reconstruction.

1. INTRODUCTION

Seabirds are an important link for nutrient cycling between land and sea. Their relatively high trophic position and foraging behavior allow seabirds to enrich and transport marine-derived elements and nutrients to the terrestrial environment in the form of guano, egg shells, feathers, dropped food and carcasses (Blais et al., 2005, 2007). In polar coastal areas where oligotrophic environments naturally occur, seabird nesting sites usually become biological hot spots with higher productivity than surrounding areaswithout guano influx (Hadley et al., 2010). In isolated tropical islands, seabird droppings may even become the driving force for the evolution of islet ecosystems (Liu et al., 2006a; Xu et al., 2011). Besides nutrients, marine-derived contaminants such as heavy metals and persistent organic pollutants (POPs) are also concentrated in seabird colonies due to the bio-magnification effects up the food chain (Keatley et al., 2009; Choy et al., 2010; Michelutti et al., 2010). Very high levels of As and Cd in the sediments of seabird-affected ponds were reported at Cape Vera, Devon Island, Arctic Canada, exceeding local guidelines set for environment protection (Brimble et al., 2009a). High concentrations of POPs are also found in Antarctic penguin colonies. Under such circumstances, these sites may serve as secondary pollution sources in the local environment (Roosens et al., 2007; Corsolini, 2009). Thus, numerous

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investigations have documented the elements that guano tends to enrich at various locations, in both polar and tropical regions (Liu et al., 2008; Huang et al., 2009; Brimble et al., 2009b; Xu et al., 2011), providing a greater understanding of the possible impact that guano might bring to local ecosystems.

Marine-derived elements enriched by seabirds can be well preserved in ornithogenic soils and sediments with the accumulation of deposited guano, making it an ideal medium for geochemical study (Xu et al., 2011). A bio-element assemblage can provide us an overall perspective from which to trace the source of multiple elements without being hindered by the specific geochemical behavior of an individual element (Huang et al., 2009). These assemblages also have been used to explore historical seabird ecology recorded in ornithogenic soils and sediments. Sun et al. (2000) inferred penguin population change at Ardley Island, Antarctic Peninsula, for the last 3000 years using bio-elements as markers. Similar research on long-term seabird population dynamics was conducted in Vestfold Hills, East Antarctica (Huang et al., 2009, 2011) and Xisha Islands, South China Sea (Liu et al., 2006a, 2008).

Besides elemental analysis, carbon isotopic composition is also a powerful tool to trace the source, circulation, and transportation of multiple bio-materials. It has been successfully applied in determining the traveling route and food source of migrating animals, especially in the land-sea interface (Chamberlain et al., 1996; Hobson, 1999) and the origin of material in ornithogenic sediments (Liu et al., 2006b). Emslie and Patterson (2007) used carbon isotope values in eggshells of Adélie penguins (*Pygoscelis adeliae*) to infer a possible historic shift in their diet. Lorenzini et al. (2009, 2010) investigated $\delta^{13}C$ in both eggshells and guano to reconstruct the paleo-diet of Adélie penguins in Northern Victoria Land. $\delta^{13}C$ in bat guano deposited in caves was well studied for the historical change in vegetation of the surrounding area (dominance of C_3 over C_4 plants or vice versa), and further insights into climate change in the past (Mizutani et al., 1992; Bird et al., 2007; Wurster et al., 2008). Carbon isotopes in marine sediments were evidently associated with global eustatic sea-level variations, oceanic "anoxic events", and sea basin methane releases, making it an important proxy for paleoenvironmental research (Scholle and Arthur, 1980; Boetius et al., 2000; Kennett et al., 2000).

The Ross Sea region has some of the largest Adélie penguin colonies in Antarctica and research on the paleoenvironment and paleoecology of this region has been conducted (Emslie et al., 2003), yet studies on sediments that accumulate in ponds and lakes near penguin colonies in this area are still scarce. Efforts are needed to interpret the environmental implications of the elemental and isotopic signals preserved in these sediments, and to reconstruct the penguin paleoecology in this region. In this study, we analyzed the elemental and carbon isotopic compositions in five sediment profiles collected from Ross Island and Beaufort Island in the southern Ross Sea to identify the material origin and the penguin bio-element assemblage through multiple statistical methods. Additionally, carbon isotopic composition in the bulk sediments was determined as an effective proxy to identify the influence of penguin guano on the sediments. Combined with previous studies by other researchers on seabird-affected sediments, a comparison of guano-derived bio-elements among Antarctic, Arctic, and South China Sea was conducted. We found overlap of avian bio-elements in these three distinct regions and discuss the possible factors for this overlap.

2. SAMPLING SITES AND ANALYTICAL METHODS

In January 2010, geochemical surveys were conducted in the ice-free areas of the southern Ross Sea region. The Ross Sea is the southernmost sea partly covered by the Ross Ice Shelf and this region is highly sensitive to climate change due to its location with influence from land, sea and ice shelf. The weather here is abrupt and severe due to the conjunction of three different air masses from Victoria Land, the Ross Sea, and the Ross Ice Shelf (Monaghan et al., 2005). The sampling sites of the sediment profiles included in this study were located on Ross and Beaufort Islands (Fig. 1). Ross Island (~2460 km^2) is of volcanic origin and offshore of Victoria Land in McMurdo Sound. Most parts of Ross Island are covered by ice, leaving three ice-free areas where penguins breed at Cape Crozier (~18 km^2), Cape Bird (~15 km^2), and Cape Royds (~13 km^2). A large number (>200,000 pairs) of Adélie penguins reside in these three areas, collectively forming one of the largest Adélie penguin concentrations in Antarctica. Beaufort Island (~18.4 km^2) is 21 km north of Ross Island with Adélie penguins breeding in its ice-free areas on the eastern and southern part. Besides the modern penguin colonies, there are also numerous abandoned penguin breeding sites in the ice-free areas mentioned above, allowing study of penguin paleoecology. Freshwater algae are widely distributed in the ponds and catchments near the penguin colonies (Broady, 1989). The mean annual temperature of this area is −18 °C; temperatures may reach 8 °C in summer and −50 °C in winter. The average wind speed is 12 knots, but may exceed 100 knots on occasion.

The MB4, MB6, CL2 and CC sediment samples were collected from Cape Bird and Cape Crozier of Ross Island, and BI core from Beaufort Island (Fig. 1). The detailed description of sampling sites and sectioning of the sediment profiles used in this study were presented in Nie et al. (2012). All the sediment samples are influenced by penguin guano, and some samples contain algal remains. The lithological characteristics of these five sediment profiles are illustrated in Fig. 2. For comparison, end-member environmental media such as fresh guano, fresh algae and weathered bedrock were also collected in our study area. Sediment subsamples and weathered bedrock were air-dried, while fresh algae and guano samples were freeze-dried. All the samples were homogenized by grinding after the removal of large rock fragments and biological remains through a 74 μm mesh sieve.

Analysis of nitrogen, hydrogen, and sulfur contents was conducted on an element analyzer (Vario EL III) with a relative standard deviation (RSD) less than 1%. The chemical volumetric method was employed to measure total organic

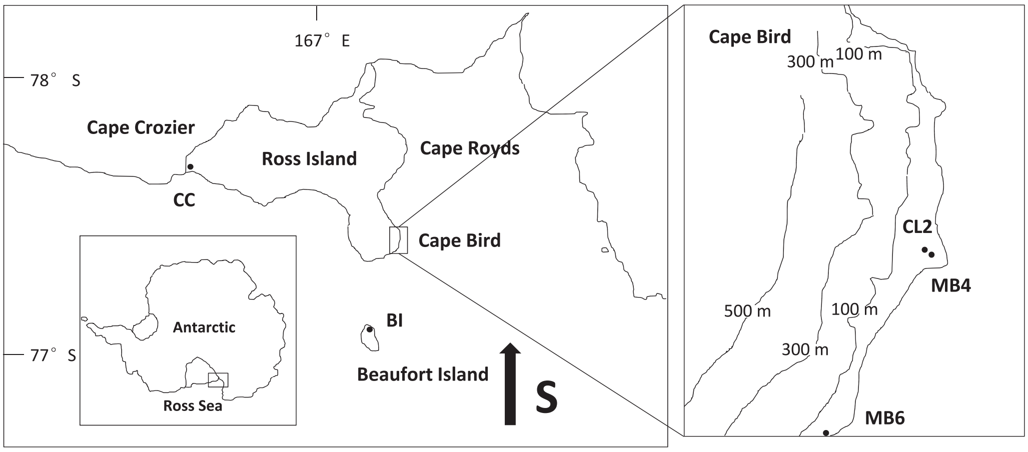

Fig. 1. Sampling sites in the Ross Sea region.

carbon (TOC). Arsenic and selenium contents were determined by Atomic Fluorescence Spectrometry (AFS-930, Titan Instruments Co., Ltd.). For As and Se, 0.25 g subsamples were precisely weighed and digested (HNO_3–HCl–$HClO_4$) in colorimeter tubes with electric heating. Ba, Cd, Co, Cr, Cu, Mn, Ni, P, Pb, Sr, Ti, Zn in all five profiles and Al, Ca, Fe, K, Mg, Na in CL2, BI and CC were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer 2100DV). For these elements, 0.25 g subsamples were precisely weighed and digested (HNO_3–HF–HCl–$HClO_4$) in Teflon tubes with electric heating. Measurements were made at constant solution volume. Reagent blanks and standard reference materials (SRMs) were included in every batch of samples for quality control (Chinese standard reference material GBW 07302 for As and Se; GBW 07415 for TOC; GBW 07401, 07405 and 07406 for Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sr, Ti and Zn on ICP-OES). Certified and observed values of each element measured in SRMs were listed in the Supplementary material, and their consistency shows the reliability of our tests. Al, Ca, Fe, K, Mg, Na, Si in MB4 and MB6 were measured on X-ray fluorescence analyzer (XRF-1800, Shimadzu) in the Instruments' Center for Physical Science of University of Science and Technology of China with an RSD less than 0.5%. Organic carbon isotope analyses of acid-treated (HCl about 1 mol/L) sediment samples were performed using the sealed tube combustion method at G.G. Hatch Isotope Laboratories, University of Ottawa. Stable isotope abundances were expressed in δ notation as the deviation from standards in parts per thousand:

$$\delta^{13}C\ (‰) = [(R_{sample}/R_{standard}) - 1] \times 1000$$

where R is the corresponding $^{13}C/^{12}C$. The $R_{standard}$ values were based on the Vienna Pee Dee Belemnite (V-PDB). Replicate measurements of Canadian internal standard (C55) indicate that the analytical precision of organic carbon isotopic measurements was within ±0.2‰ (see Supplementary material). PCA was performed by the software PASW Statistics 18.

3. RESULTS AND DISCUSSION

3.1. Material source

Several physical/chemical proxies including dry density, total organic carbon (TOC), total nitrogen (TN), total hydrogen (TH) and carbon isotopic composition ($\delta^{13}C_{org}$) for MB4, MB6, CL2, BI and CC are plotted in the profiles with lithology (Fig. 2). Using TOC as the marker for organic matter (OM) input, apparent fluctuations in the five profiles can be observed. Also, TOC, TN, and TH display highly identical distribution patterns in each profile. Significant positive correlations ($R > 0.8$, $p < 0.01$) were obtained between TOC and TN through Pearson correlation tests (Fig. 3), and the same result can be expected between TOC and TH. TN and TH have strong affinity to OM, and could also be used as indicators for OM input in the sediments.

Field observations and laboratory analyses indicate that weathered product of bedrock, penguin guano, and freshwater algae are the three dominant components of the sediments in this area, and the lithological records show that high TOC values always coincide with the appearance of algal mats and ornithogenic layers. Elemental analysis on end-member environmental media including weathered bedrock, fresh guano, and fresh algae was performed, demonstrating that guano and algae contained up to 30% and 11% TOC, respectively, while TOC in weathered bedrock was lower than 1% (Fig. 4). Thus, of the three dominant components, penguin guano and algae are the main OM sources, while weathered bedrock acts as the matrix of inorganic substances. As shown in Fig. 3, dry density is negatively correlated with TOC and this is attributed to the increasing content of guano and lake algae with relatively low density that dilutes inorganic materials from weathered bedrock in the bulk sediments.

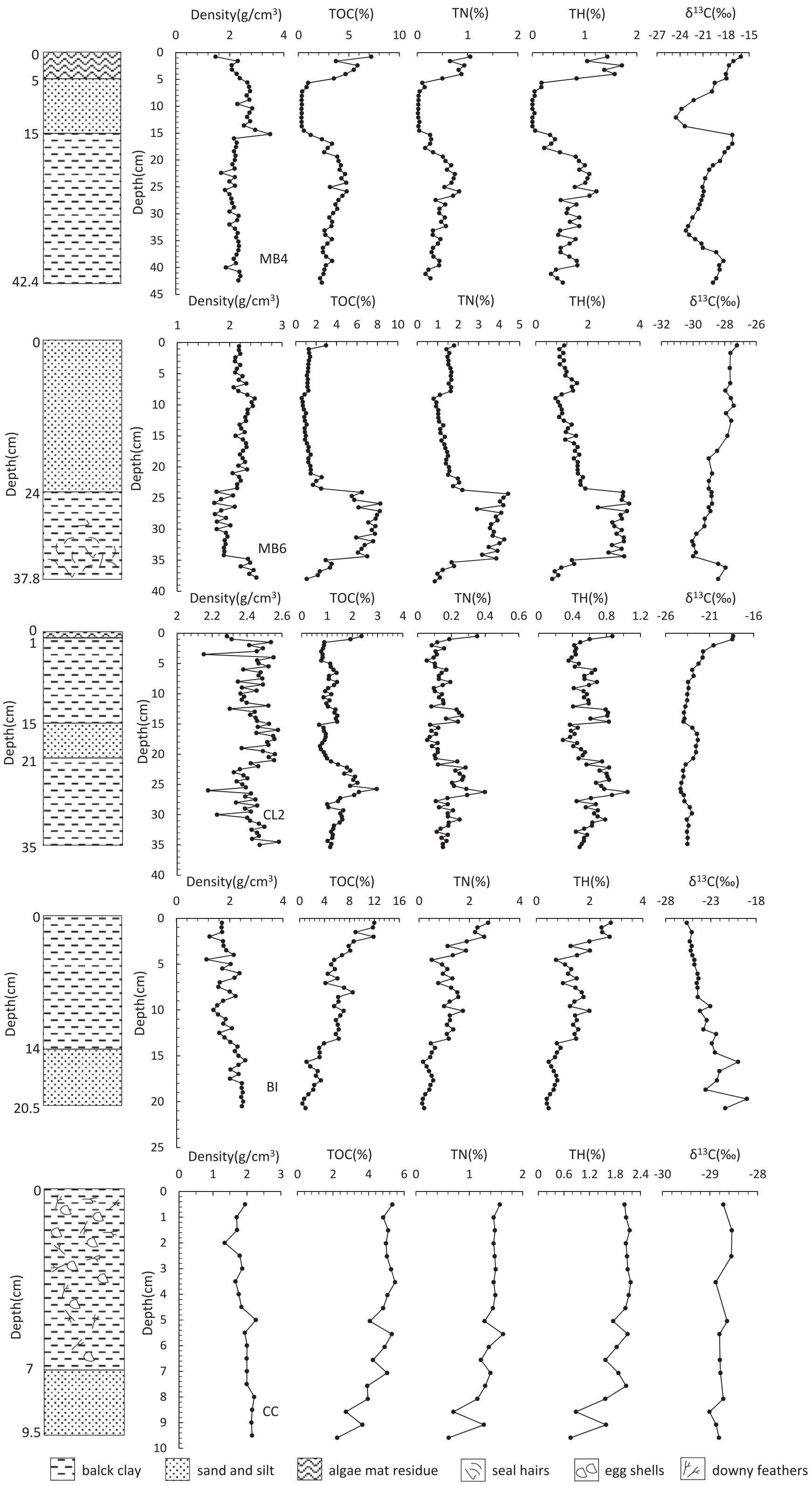

Fig. 2. Vertical distributions of density, TOC, TN, TH and $\delta^{13}C_{org}$ with lithology for sediment profile MB4, MB6, CL2, BI and CC.

To further study the influence of the three components on the sediment profiles, carbon isotopic composition and C/N (TOC/TN, molar ratio) were employed due to their wide usage in material source determination (Hassan

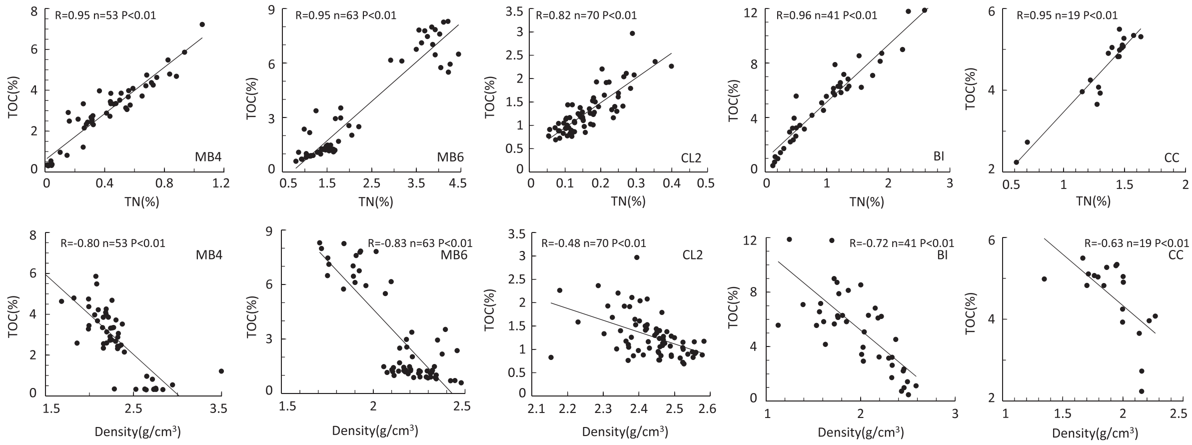

Fig. 3. Correlation analysis of TOC–TN and TOC–density for sediment profile MB4, MB6, CL2, BI and CC.

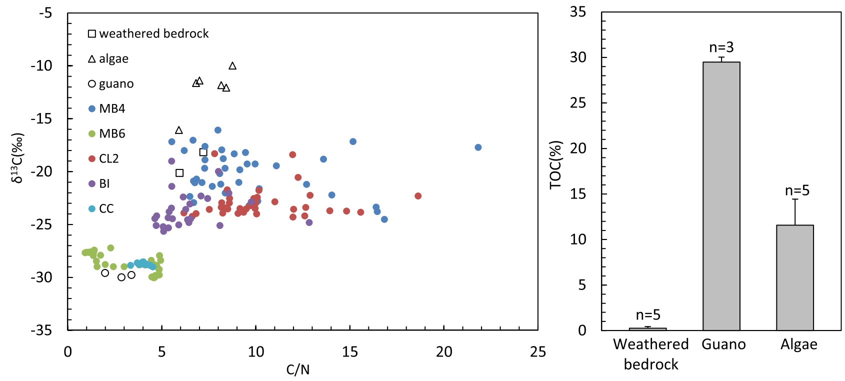

Fig. 4. $\delta^{13}C_{org}$ and C/N of profile MB4, MB6, CL2, BI and CC with environment media including weathered bedrock, penguin guano and aquatic algae (TOC contents given in the right diagram).

et al., 1997; Liu et al., 2006a). Since carbon circulation and isotopic fractionation in different environments and life forms are distinguishable from one another, the two proxies of the bulk sediments may reflect the feature of OM composition. $\delta^{13}C_{org}$ and C/N in the five sediment profiles and environmental media (Fig. 4) indicate that guano has very low $\delta^{13}C$ at about −30‰, which is similar to the data of Adélie penguin guano reported in the neighboring Northern Victoria Land (Lorenzini et al., 2010) and Antarctic Peninsula (Liu et al., 2006b; Zhu et al., 2009). Algae in Antarctica usually has $\delta^{13}C_{org}$ values at about −29‰, significantly lower than the dissolved carbon source in the water column due to the strong isotopic fractionation effects during photosynthesis (Doran et al., 2000), but our samples yielded a much higher $\delta^{13}C_{org}$, reaching −10‰. The algae samples for environmental media were collected in shallow watersheds free from penguin influence. We assume that accelerated photosynthesis efficiency can cause a CO_2 diffusion-limited environment (severe depletion of ^{12}C due to the preferential utilization of $^{12}CO_2$ by the algae for photosynthesis) in the small water bodies, and therefore force the algae to assimilate more ^{13}C, resulting in highly positive $\delta^{13}C_{org}$ values (Doran et al., 1998; Bishop et al., 2001). Weathered bedrock samples have $\delta^{13}C_{org}$ values at about −20‰, but considering its very low TOC content, it is not likely to have much influence on the carbon isotopic composition of the sedimentary organic matter. It is generally considered sediments with marine influence have lower C/N (<12) compared with those affected by terrestrial-derived substances (>20, Schöeninger and DeNiro, 1984). C/N values of guano and algae are about 2.5 and 7.5, respectively (Fig. 4). Guano has lower C/N ratios than algae owning to its abundant N-containing compounds, such as uric acid, while the higher C/N in algae is attributed to the rich C-containing celluloses (Lindeboom, 1984; Speir and Cowling, 1984). MB6 and CC sediment samples overlap with the data of fresh guano, showing clear dominance of guano in TOC. BI, MB4 and CL2 have higher $\delta^{13}C_{org}$, and C/N values, indicating relatively strong influence from algae. Among the three profiles, MB4 is closer to the "algae" end, BI is closer to the "guano" end, and CL2 lies between them, reflecting different intensity of guano influence compared to algae, and the guano displayed stronger influence on the BI sediments. Unlike any of the three components, some MB4 and CL2 subsamples with relatively higher C/N ratios are found to have low TOC and TN values in the bulk sediments (mainly from the sand layer between 15 and 5 cm of MB4 and low-OM layer of CL2).

We believe these subsamples receive minor ornithogenic and algal influences which account for their low OM content, yet their C/N ratios are different from the weathered bedrock samples as environment media. The C/N values (6–7) in the weathered bedrock collected in the surface layer near the sampling sites are clearly under marine influence (Fig. 4), and they are similarly low as in surface soils from the coastal area of the Ross Sea region reported by Barrett et al. (2006). But in more primitive soils with very low OM content, C/N would be much higher (Burkins et al., 2000), which might be the case for these subsamples from MB4 and CL2. Thus we assume in the low-OM layer of MB4 and CL2 with the lack of guano and algae input, the bulk sediments with high C/N feature might show a more primitive characteristic.

According to the environmental media analysis, guano and algae are the main OM sources in the sediment profiles in our study (CC is free from algae influence), and $\delta^{13}C_{org}$–C/N data show that MB6, BI, and CC are strongly influenced by guano, while such effect is weaker in MB4 and CL2 due to the relatively low guano input.

3.2. Bio-element identification of ornithogenic sediments

Geological factors that influence a single element in the sediments are usually complex and hard to trace, but using statistical methods to study element assemblages can provide a clear view on the source of several elements and the geochemical features of the sediments (Sun et al., 2000; Liu et al., 2006a; Huang et al., 2009). To identify the bio-element assemblage for the sediments of the Ross Sea region, 22 elements including Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Si (measured only in MB4 and MB6), Sr, Ti and Zn were measured (Fig. 5) with R-mode cluster analysis performed in each profile (Fig. 6). Phosphorus (P) is a major component of feces and a typical bio-element of ornithogenic soils in Antarctica (Sun et al., 2000). High P concentration in fresh guano than the other two constituents (Fig. 7) makes it a valid marker for bio-element assemblage determination. Table 1 shows the elements in the same clustering group with P.

Though generally located in the same region, bio-element assemblages seem to differ slightly among profiles due to their specific sedimentary environments. Seven common bio-elements in the sediments from the Ross Sea region including As, Cd, Cu, P, S, Se and Zn were identified owing to their presence in the target groups (clustering groups including P) in no less than four out of five profiles. Concentrations of these elements in the environmental media (Fig. 7) indicate that, except for As, all the elements have much higher values in guano than in algae and weathered bedrock, evincing their common source and validating the result of cluster analysis. According to Tatur and Keck (1990), high levels of Cu, P and S mainly originate from krill: the main prey of Adélie penguins, while Cd is enriched in guano through food chain bio-magnification and the upwelling of deep water in the foraging area of the penguins (Fitzwater et al., 2000; Ancora et al., 2002). Zn was also reported to be bio-magnified in marine food webs (Campbell et al., 2005). As for arsenic, its concentration in guano is not as enriched as the other bio-elements comparing to algae and weathered bedrock, but the statistical analysis clearly deemed it as a bio-element. We assume As would be immobilized and enriched in the waxy ornithogenic soils in the penguin rookeries, and then transported by water flow to our sampling sites. The high values in the sediments are a result of continuous input of guano-derived As from penguin rookeries over extended periods. Indeed, at Ardley Island, Antarctic Peninsula, and the Vestfold Hills, East Antarctica, As was also identified as one of the typical bio-elements in the sediments influenced by penguin guano, and can be used to signify the historical change of penguin populations (Xie and Sun, 2008; Huang et al., 2009).

Pearson correlation tests were performed between As, Cd, Cu, S, Se, Zn and the pre-confirmed bio-element P to corroborate the results of cluster analysis. Except for the absence of Zn in MB4 and As in CL2, all elements were significantly correlated with P ($p < 0.01$; Table 2). Sulfur in the surface layer of MB6 has extremely high values, lowering its correlation with P from $R = 0.91$ to $R = 0.47$. Higher values of TOC and TN can also be observed in the same layer, but not as abrupt as S. We believe that the high S concentration in the uppermost section of MB6 is caused by the shift of redox environment. High values of As contents were observed at the depth from 19 to 15 cm in BI, creating a distribution pattern different from the other bio-elements. Although the mechanism behind this is not clear, the abnormally high content of As in the sediments may indicate the influence from factors like redox condition, iron and aluminum minerals, and sulfur in the post-depositional processes (Farmer and Lovell, 1986). Zn is absent in the bio-element group of MB4. This absence may be caused by the abrupt shift from sediments influenced by penguin guano to a total inorganic sand layer in lithology between 15 and 5 cm. Compared with the weathered bedrock samples collected as environmental media, guano enriches Zn to a great magnitude (Fig. 7). However, according to the P content and material source identification of $\delta^{13}C_{org}$–C/N, guano input in MB4 is relatively low. So it is likely that the guano-derived Zn is severely diluted by the terrestrial weathered minerals in the MB4 profile, weakening its discrimination against the sand layer. After removing the sediment samples between 15 and 5 cm, the correlation between P and Zn becomes significant ($R = 0.57$, $p < 0.01$; Table 2). Thus we believe that Zn is still a valid guano bio-element in the Ross Sea region despite its absence in the bio-element group of MB4. Lack of significant co-relation between As and P in CL2 is also a result from low guano input suggested by the analysis above.

Principal component analysis (PCA) was applied to the data for separating element assemblages and identifying the controlling factors on the chemical composition of the sediments. Three components accounting for 72% of the total variance were acquired and their loadings plotted with standardized scores of each sediment subsample (Fig. 8). PC-1 with $\lambda = 0.4$ was the main controlling component. As, Ca, Cd, Cu, Mg, S, Se, P, and Zn were found to have positive loadings on PC-1, coinciding with the bio-elements identified by cluster analysis in Table 1. Thus, PC-1 was deemed

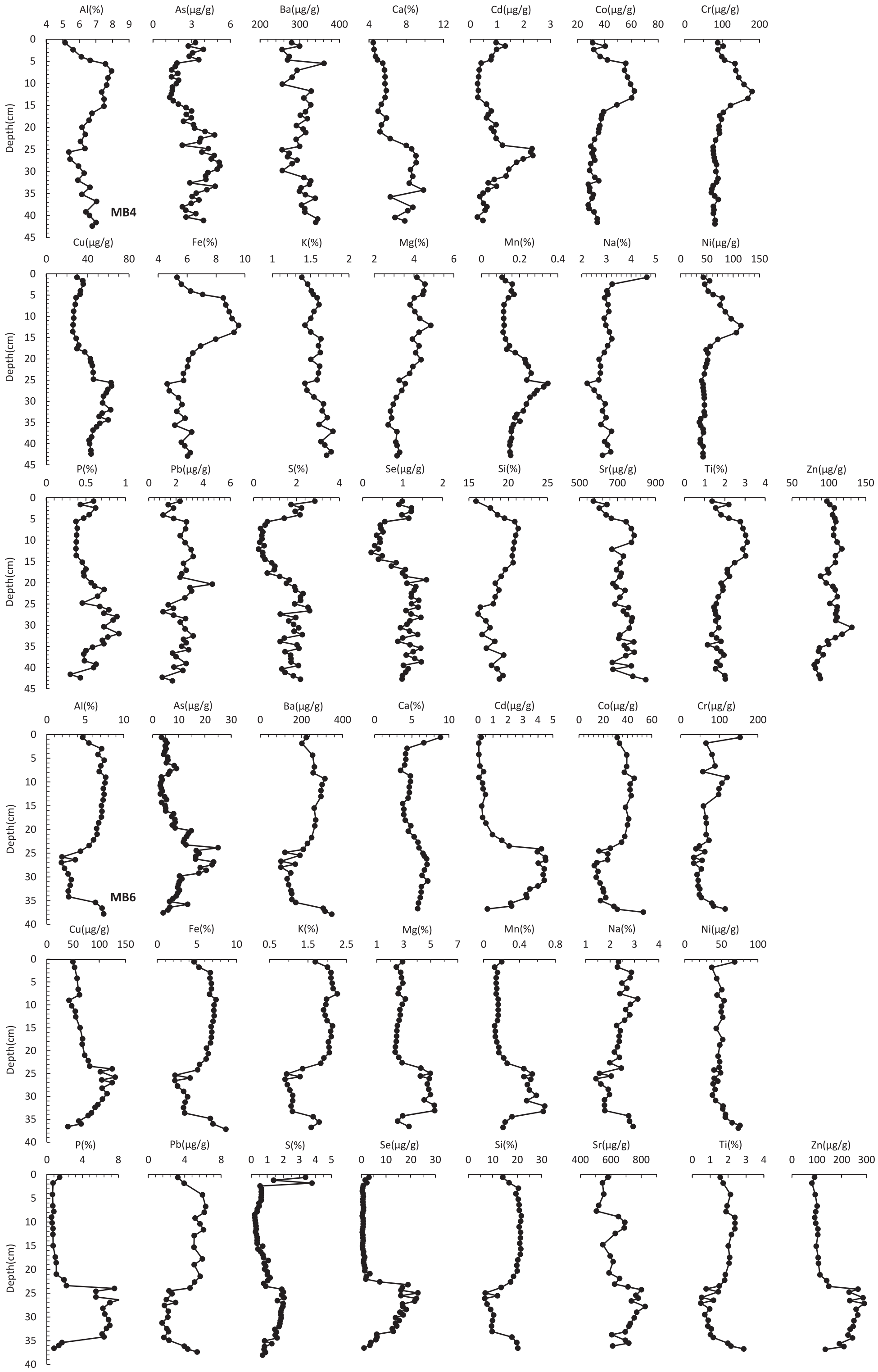

Fig. 5. Vertical distributions versus depth of all analyzed elements including Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Si (measured only in MB4 and MB6), Sr, Ti and Zn in profile MB4, MB6, CL2, BI and CC.

to represent the input of guano and the negative loadings of Al, Fe, Ti, K, Na and Ba derived from the weathered bedrock were caused by the dilution effect that the guano imposed on their concentrations. Fig. 8 indicates MB6 and CC have higher scores on PC-1, BI, MB4 and CL2 are lower by order, corresponding to the intensity of guano influence in the profiles we concluded previously. Since weathered bedrock constituents comprise the bulk of the

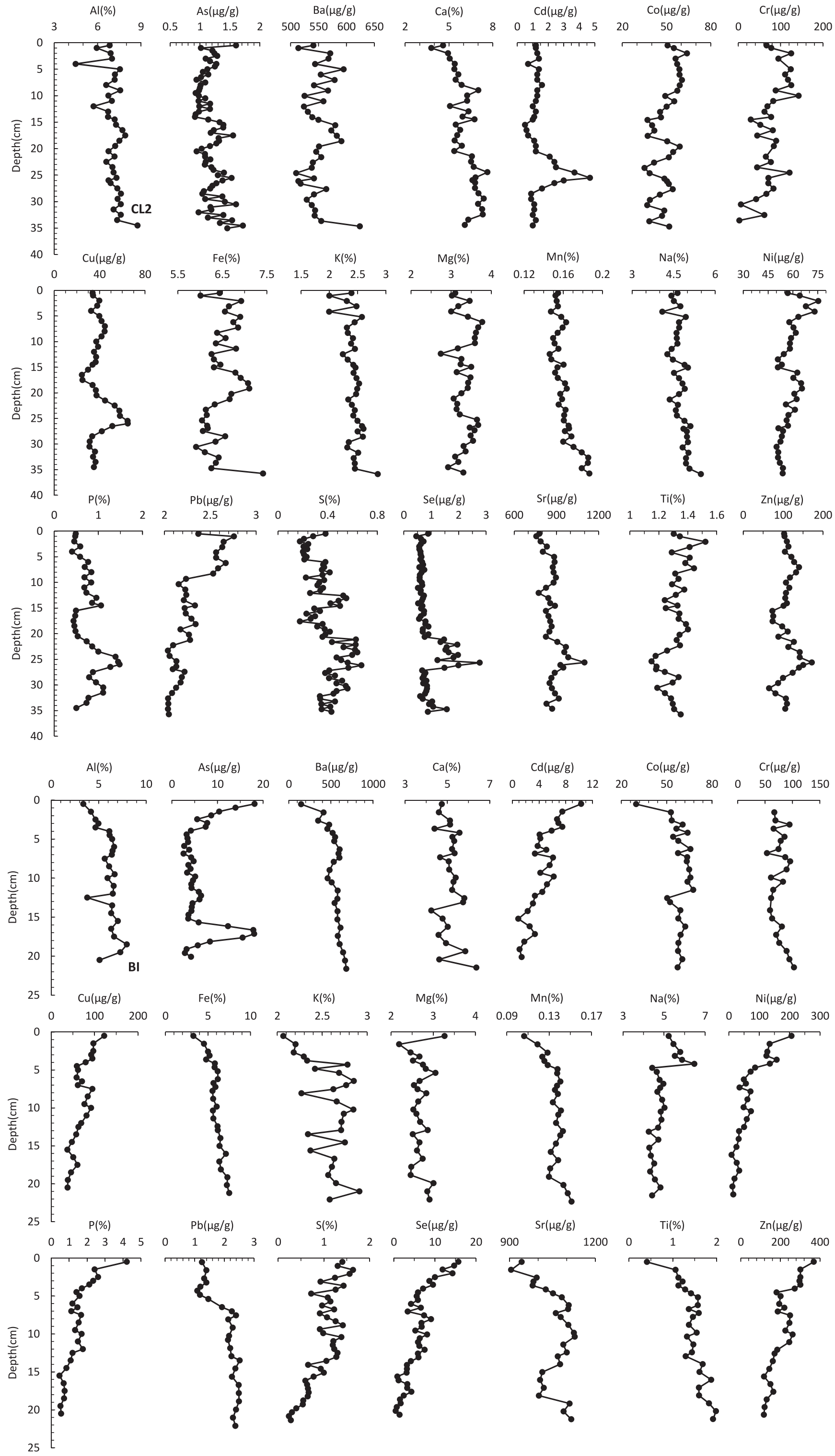

Fig. 5. (*continued*)

sediments, it is then understandable that only high guano-containing subsamples in MB6, BI and CC gained high scores on PC-1, and the rest of the subsamples had low and even negative PC-1 scores, reflecting the relatively greater influence from weathered bedrock than the penguin guano. Guano-derived bio-elements determined in PC-1 were slightly different from the result of cluster analysis, with the lithological elements Ca and Mg included by PCA, since PCA was performed on all data in the five profiles, while R-mode clustering was applied to each profile.

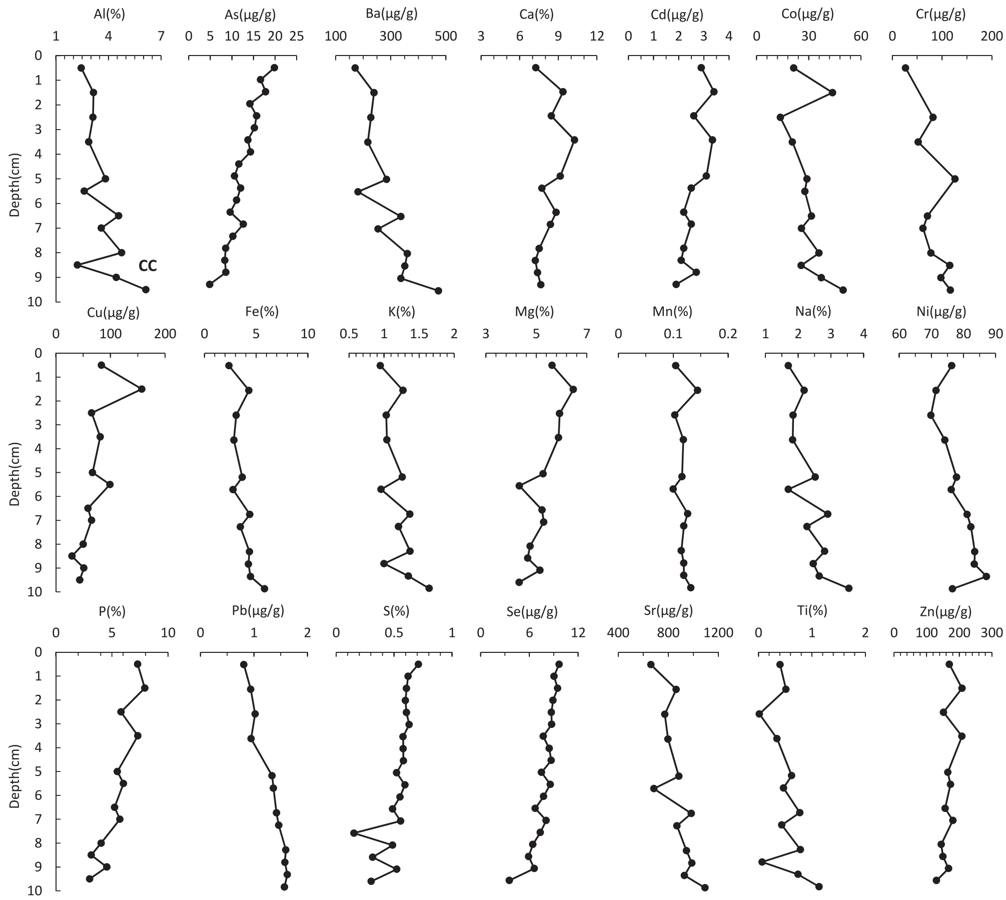

Fig. 5. (*continued*)

For example, Ca and Mg also appear in certain clustering bio-element groups such as CC and MB6 profiles (Fig. 6). From a regional view, we believe labeling As, Cd, Cu, P, S, Se and Zn from the selective result of R-clustering as bio-elements is a more comprehensive and accurate practice.

In the Ross Sea region, similar element bio-magnification of As, Ca, Cd, Cu, Hg, Mg, P, S and Zn in the penguin guano were also reported at Edmonson Point, Terra Nova Bay and Cape Hallett, northern Victoria Land (Ancora et al., 2002; Hofstee et al., 2006). Enrichment of Ca and Mg are often connected with the mineralization of phosphorus (struvite for example, Tatur and Keck, 1990), but they are likely limited in specific sites in our study. Thus, it is reasonable to consider As, Cd, Cu, P, S, Se and Zn as the bio-elements in the entire Ross Sea region.

3.3. Environmental implication of carbon isotopic composition

Carbon isotope composition has long been used as important proxy for OM origin determination and carbon utilization/circulation in the sediments (Hassan et al., 1997; Liu et al., 2006b). Despite ambiguities in its interpretation caused by multiple influence factors in the context, $\delta^{13}C$ is still widely used in paleoenvironmental reconstruction (Hobson, 1999; Liu et al., 2006b; Emslie and Patterson, 2007).

While guano, algae, and weathered bedrock are the three main constituents of the sediments (profile CC is not influenced by algae according to field observation), the former two account for most of the TOC. The distinctive $\delta^{13}C_{org}$ and C/N values between guano and algae gave us a general view on the material source of the five sediment profiles; however, a means to accurately assess the influence of guano and algae on the sediments is needed. Sun et al. (2005) reported analysis on sediments influenced by the excrements of penguins and seals, and used strontium isotope composition to calculate the percentage of animal excrement in the sediment samples, since the different strontium isotope values from marine source (penguin guano and seal excreta) and weathered bedrock can be used as two end-members to explore the composition of the bulk sediments. Similarly in our study, carbon isotopic composition in MB4, MB6, CL2 and BI is also controlled by two distinctive mixing sources: guano and algae. Under the cold conditions in Antarctica, decomposition of organic carbon (OC) in guano is minor (Orchard and Corderoy, 1983), so the OC from guano should not exert an important influence on algae. As stated above, the penguin guano has average $\delta^{13}C_{org}$ value of $-30‰$, whereas the algae growing in the shallow ponds from the studied area has much higher $\delta^{13}C_{org}$ up to $-10‰$. Thus,

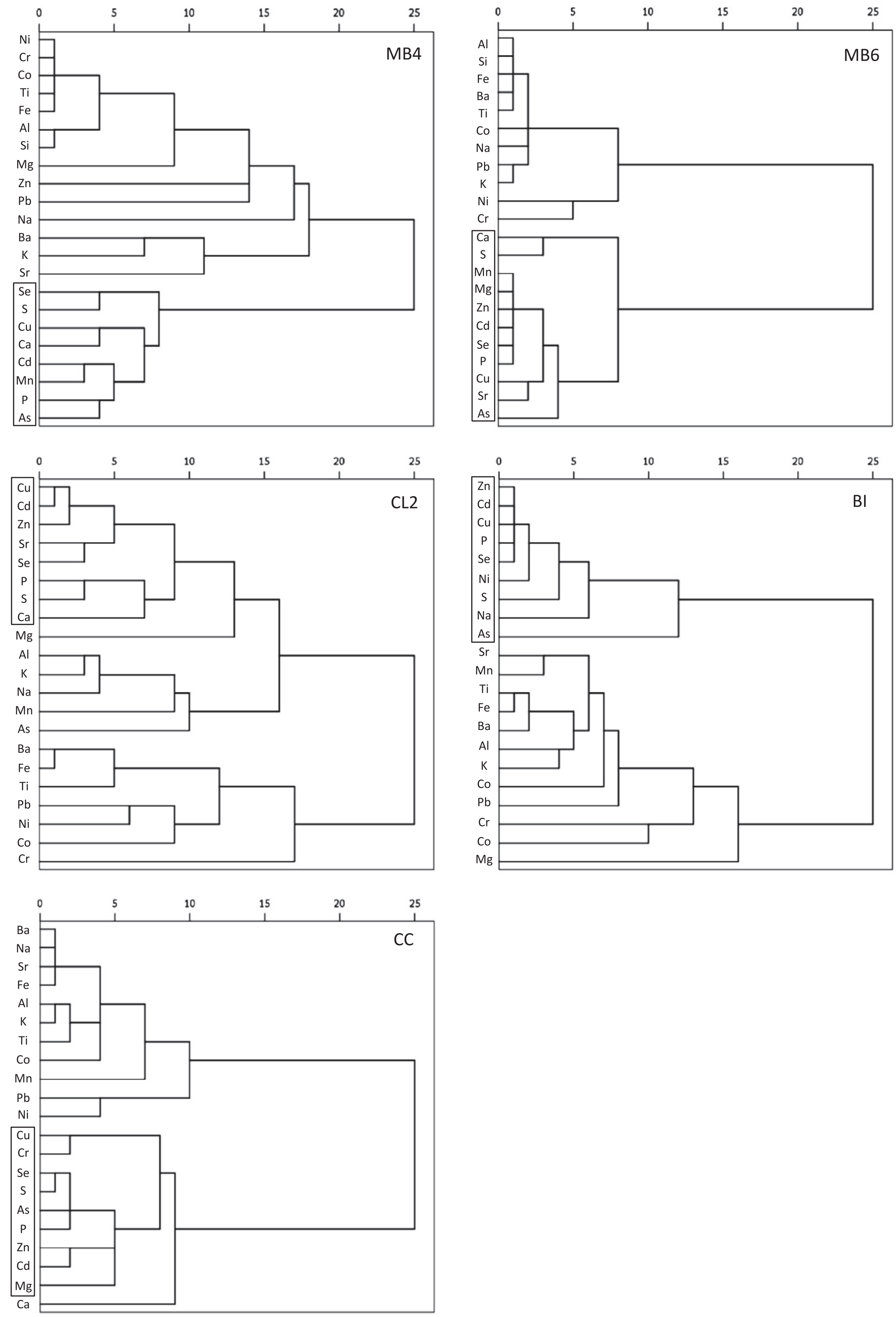

Fig. 6. R clustering results for profile MB4, MB6, CL2, BI and CC using software PASW Statistics 18.

we may employ the $\delta^{13}C$ values of penguin guano and pond algae as two end-members to determine the contribution of the guano in TOC (X_g) with the following isotope mixing equation (Miller et al., 1993; Capo et al., 1998):

$$X_g = [(^{13}C/^{12}C)_s - (^{13}C/^{12}C)_a]/[(^{13}C/^{12}C)_g - (^{13}C/^{12}C)_a]$$

where $(^{13}C/^{12}C)_s$ is the carbon isotope ratio of the bulk sediment samples, while $(^{13}C/^{12}C)_g$ and $(^{13}C/^{12}C)_a$ are average

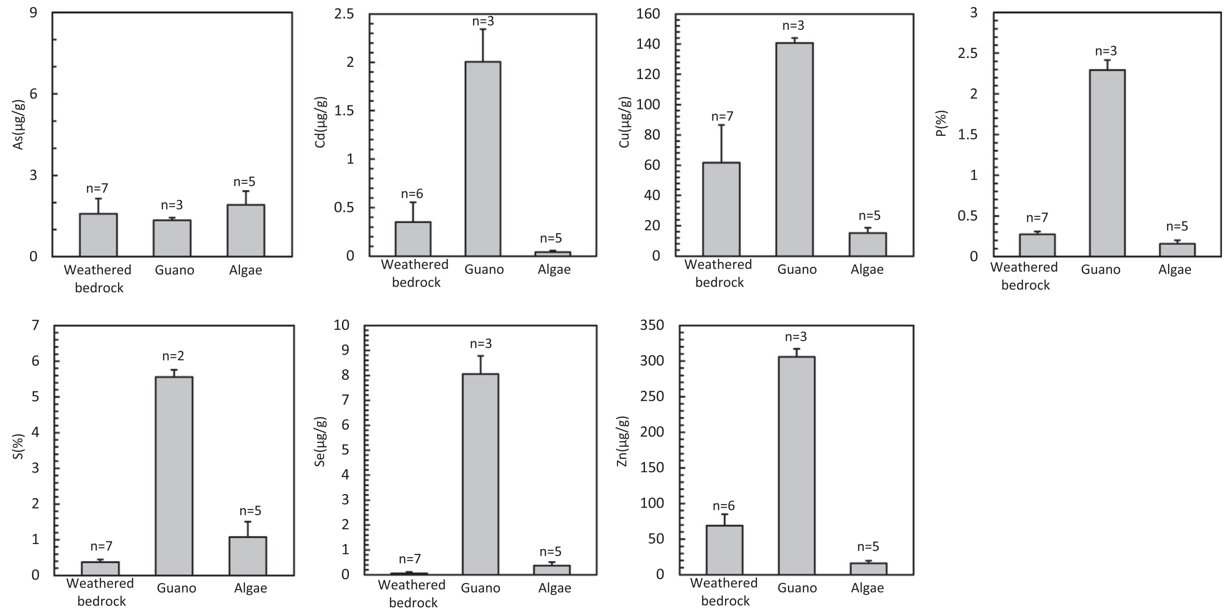

Fig. 7. Concentrations of identified mutual bio-elements in three kinds of environmental media.

Table 1
Bio-elements identified by cluster analysis in each profile and the common bio-elements in the Ross Sea region.

Profile	Identified bio-elements by cluster analysis in each profile													
MB4	P	S	Se	As	Cu		Cd	Ca	Mn					
MB6	P	S	Se	As	Cu	Zn	Cd	Ca	Mn	Mg	Sr			
CL2	P	S	Se		Cu	Zn	Cd	Ca			Sr			
BI	P	S	Se	As	Cu	Zn	Cd						Na	Ni
CC	P	S	Se	As	Cu	Zn	Cd			Mg		Cr		
	Common bio-elements in the Ross Sea region													
	P	S	Se	As	Cu	Zn	Cd							

Table 2
Pearson correlation between the mutual bio-elements and P in the five sediment profiles.

	S	As	Se	Cu	Zn	Cd
MB4 ($n = 38$)	0.56	0.79	0.6	0.8	(0.57[c])	0.72
MB6 ($n = 30$)	0.47 (0.91[a])	0.73	0.94	0.88	0.92	0.95
CL2 ($n = 37$)	0.8	\	0.64	0.7	0.51	0.72
BI ($n = 26$)	0.71	0.39 (0.87[b])	0.96	0.91	0.92	0.94
CC ($n = 12$)	0.88	0.90	0.88	0.83	0.85	0.85

Note: All the correlations are significant at $p < 0.01$; a: profile beneath 2 cm ($n = 28$); b: profile above 16 cm ($n = 21$); c: sediment samples between 15 and 5 cm not included ($n = 32$).

carbon isotope ratios of penguin guano and algae medium samples, respectively.

To avoid the possible influence of TOC fluctuation and facilitate the comparison with other proxies, the calculated contributions of penguin guano in TOC (X_g) of MB4, MB6, CL2 and BI are translated into guano-derived organic carbon (OC_g) and algae-derived organic carbon (OC_a) by the following formulas:

$$OC_g\ (\%) = TOC \times X_g$$

$$OC_a\ (\%) = TOC - OC_g$$

Supposedly, OC_g and OC_a obtained from $\delta^{13}C_{org}$ in the sediments should be effective proxies for guano input and algal biomass, respectively. OC_g and OC_a plotted with the typical bio-element P indicated that, except for the sediment layers with the apparent OM shift (e.g., low-OM sand layer in MB4 and surface algae layer in CL2), generally OC_g and P displayed significantly positive correlations ($R > 0.8$) in all four profiles (Fig. 9), validating our application of the two-end mixture equations on carbon isotope compositions. The levels of OC_g in the four profiles also coincide with the results of guano influencing intensity (Fig. 4):

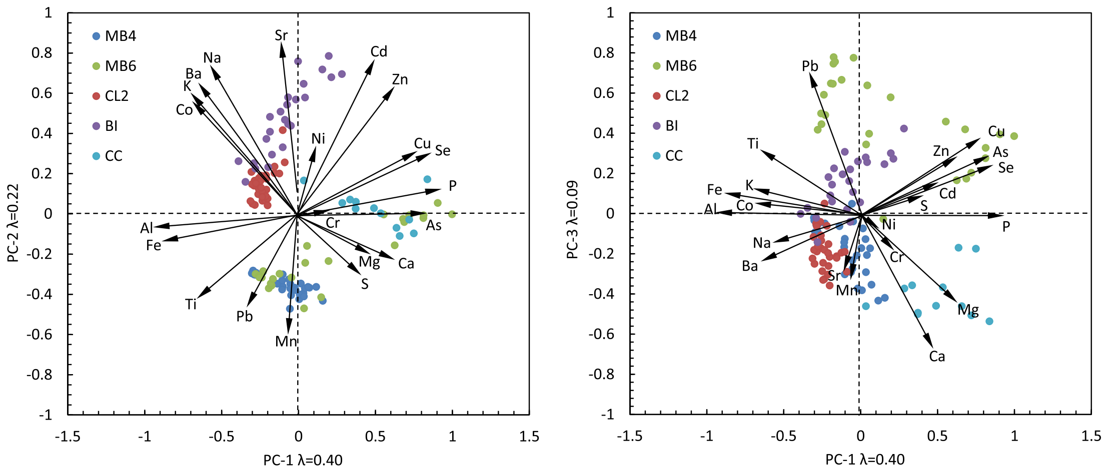

Fig. 8. Bi-plot loadings of PC1–PC2 and PC1–PC3 calculated by PCA, with standardized score of subsamples from the five profiles.

MB6 and BI sediment samples were higher than CL2 and MB4. It is also noted that OC_g and OC_a are closely correlated in MB6, CL2, and BI ($R > 0.78$), though BI has much higher algal biomass than the other two profiles. In the barren world of Antarctica, seabird guano is an important nutrient source in the ponds and catchments where algae grow (Broady, 1989). It is easy to understand algae prosperity in otherwise oligotrophic water bodies is greatly dependent on the nutrients in guano. Thus penguin guano-derived substances play a vital role in ecosystem development by serving as the main nutrient source, and it controls the total OM amount deposited in the sediments due to its influence on algal growth. The correlation between guano (OC_g) and algae (OC_a) in MB4 is weaker with $R = 0.37$ at $p < 0.05$. MB4 is much closer to "algae" end than any other profile (Fig. 4) and its OC_a is on the same level with BI, yet its OC_g inferred from $\delta^{13}C_{org}$ is as low as CL2, suggesting that the growth of algae in the MB4 was likely more sensitive to the input of guano, and the guano-derived nutrients in the MB4 promoted higher algal biomass compared to other sediment sites. As a whole, $\delta^{13}C$ has been shown to be an independent and effective index to reconstruct the input of guano, and to distinguish the influence of guano from algae in the sediments.

3.4. Global comparison of guano-derived bio-elements

Seabirds as an important bio-vector to enrich and transfer marine-derived elements are receiving increasing attention for their geochemical impact on terrestrial ecosystems. Research on ornithogenic sediments at various locations around Antarctica provides insights into the generality of element behavior from the marine environment to land via penguin guano. The Antarctic Peninsula, Vestfold Hills, and Ross Sea regions are the three main ice-free areas where large colonies of Adélie penguins are found today. Sun et al. (2000) reported nine elements including Ba, Ca, Cu, F, P, S, Se, Sr and Zn that are highly enriched in ornithogenic sediments from Ardley Island near the Antarctic Peninsula. Later, Zdanowski et al. (2005) found Ca, F, Fe, Mg, Mn, P and Zn rich in the guano samples from Admiralty Bay, King George Island, while in the Vestfold Hills, As, Cd, Cu, F, Mg, P, S, and Sr were identified as bio-elements in Zolotov Island and Gardner Island, East Antarctica (Huang et al., 2009, 2011). We summarized previous reports and listed the penguin bio-elements around the Antarctic continent by the same selecting standard applied to the Ross Sea region in Fig. 10a, and deemed As, Cd, Cu, F, P, S, Se, Sr and Zn as the common penguin bio-elements (Fig. 10b).

Penguin bio-elements in Antarctica are obtained solely based on one species, and our concern is whether different seabirds living in other parts of the world have similarity in bio-elements with Adélie penguins from Antarctica. To address this issue, we examined various studies on seabirds in Arctic and low-latitude islands of the South China Sea. Together with the data from Antarctica, it is possible to make comparisons of seabird bio-elements on a global scale.

The Arctic holds many important nesting sites for different kinds of migrating seabirds. Studies on multiple species of seabirds such as the northern fulmar (*Fulmarus glacialis*), gulls and terns in the Barents Sea and Arctic Canada show selective enrichment of As, Cd, Cu, P, Se, Sr and Zn in their guano, tissues, and sediments with guano influence (Dietz et al., 1996; Savinov et al., 2003; Brimble et al., 2009a,b; Michelutti et al., 2010). In tropical Xisha Islands of the South China Sea where many red-footed boobies (*Sula sula*) reside, it was found that As, Ba, Cd, Cu, P, Se and Zn are enriched in sediments influenced by these birds (Liu et al., 2006a; Xu et al., 2011).

We compared guano-derived bio-elements of the three different seabird nesting regions across the globe and found that they are surprisingly similar. In particular, As, Cd, Cu, P, Se and Zn are the mutual bio-elements shared by the three groups (Fig. 10b). We believe this overlap is no coincidence with respect to all the differences in the seabirds' physiological features, foraging areas, and resident environment. It is assumed that this phenomenon is ultimately due to a diet in all seabirds that is sourced from the ocean. No matter how different the local circumstances may be, general element composition of the marine environment and

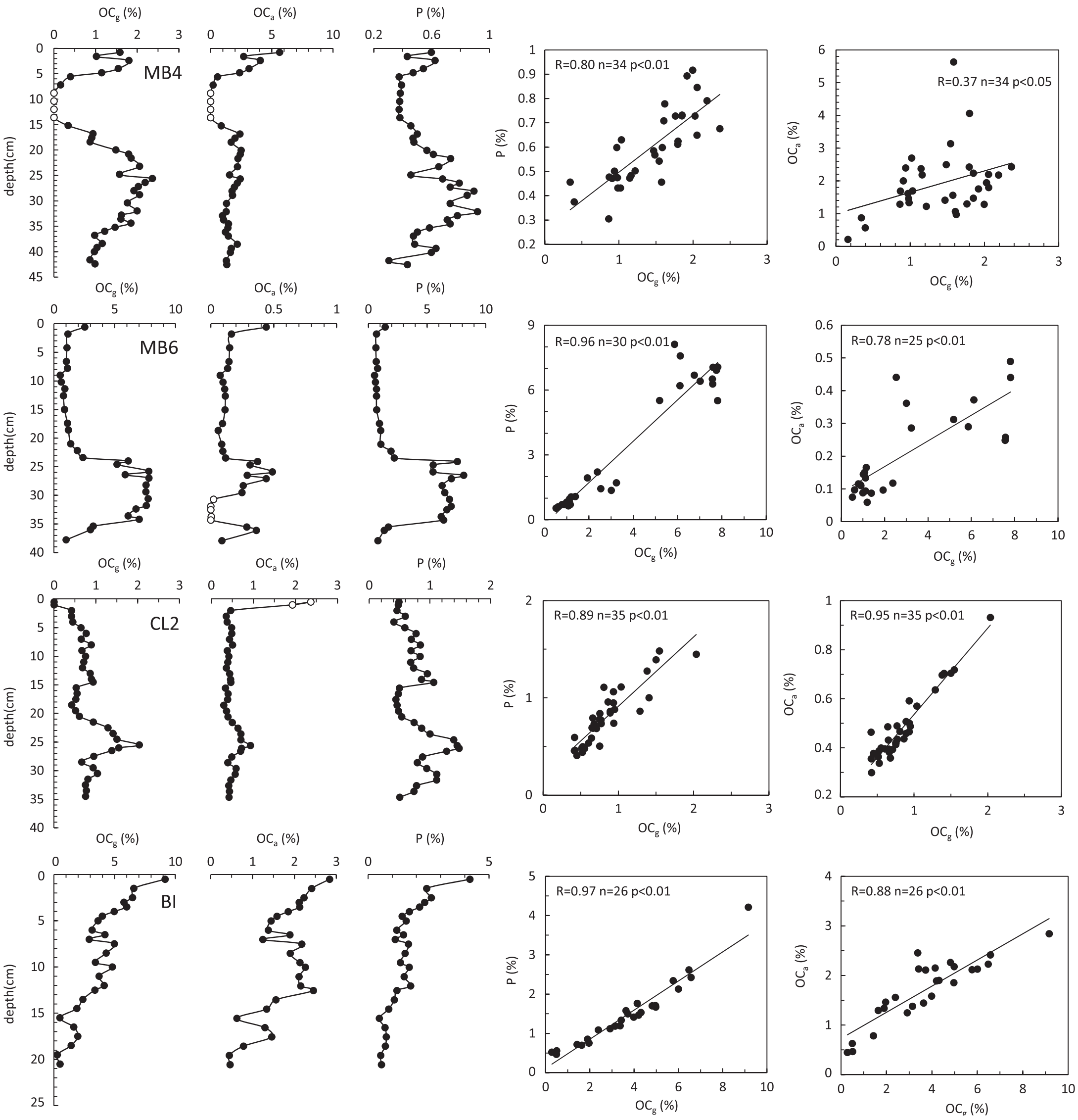

Fig. 9. Calculated OC_g and OC_a and Pearson correlation tests between P and OC_g, OC_a and OC_g in MB4, MB6, CL2 and BI. Several MB6 subsamples (marked by hollow dots) with lower $\delta^{13}C_{org}$ than medium guano are not included in correlation analysis, since this could lead to the proportion of guano in TOC (X_g) higher than 1. Layers with apparent OM shift in MB4 and CL2 (marked by hollow dots) are not included in correlation analysis either.

of seabird prey are relatively stable. It is also noted that the studied seabirds are all piscivorous predators at roughly the same trophic level. According to Ainley et al. (2003), Antarctic silverfish and squid are important food for the Adélie penguins other than krill (*Euphausia* spp.) in Victoria Land, the Ross Sea region, while the red-footed booby in Xisha Islands feeds on flying fish and squid. Michelutti et al. (2010) reported the difference in element enrichment between Arctic terns (*Sterna paradisaea*) and common eiders (*Somateria mollissima*) due to the gap in trophic levels. Terns have similar bio-elements as in penguins and red-footed boobies because they all tend to feed on mid-sized fish for food and eider diet mainly consists of insects, vegetation, and small fish. So overlap on the trophic level of the seabirds will undoubtedly lead to similar bio-elements rich in their guano.

Despite the similarity of the seabird bio-elements on a global scale, each region has its own featured bio-elements. We infer local biomass and geochemical features are responsible for the specific bio-element such as Sr in the polar region, F and S in Antarctic, and Ba in South China Sea (Fig. 10b). F is enriched in the guano of Adélie penguins from Antarctica due to its high content in the penguins' main prey—krill (Emison, 1968; Soszka, 1981). Sr is a typical marine-derived element, but in the Xisha Islands where marine-originated coral sands comprise the bulk of the sediments, Sr from seabirds will be hard to distinguish from the high background value in the coral sand sediments. On the other hand, S turns out to be hard to preserve in the hot and dry tropical climate of the South China Sea compared with the polar region. According to Sun et al. (2000), Ba is a bio-element in the sediments influenced by

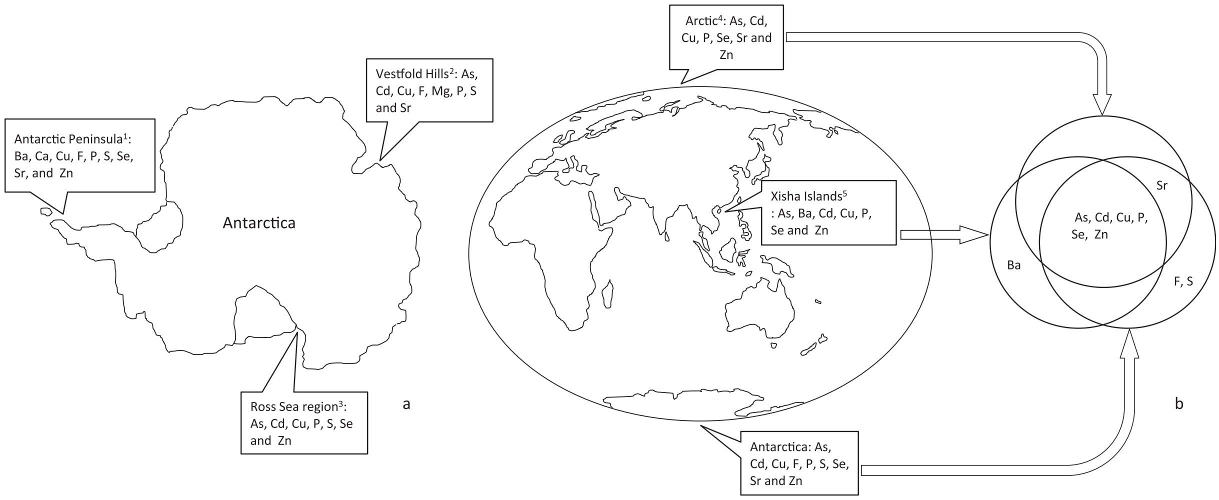

Fig. 10. Comparison of avian bio-elements (a) around Antarctica; (b) on a global scale. (1) Ornithogenic sediments from Ardley Island near the Antarctic Peninsula (Sun et al., 2000); penguin guano from Admiralty Bay, King George Island (Zdanowski et al., 2005). (2) Ornithogenic sediments from Gardner Island, Vestfold Hills (Huang et al., 2009); ornithogenic sediments from Zolotov Island, Vestfold Hills (Huang et al., 2011). (3) Ornithogenic sediments in this study; penguin guano from Seabee Hook area of Cape Hallett in northern Victoria Land (Ancora et al., 2002); penguin guano from Seabee Hook area of Cape Hallett in northern Victoria Land (Hofstee et al., 2006). (4) Seabird tissues from Greenland (Dietz et al., 1996); guano from Cape Vera, Devon Island, Canada (Brimble et al., 2009a,b); sediments from Arctic Canada (Michelutti et al., 2010). (5) Ornithogenic sediments from Dongdao Island, Xisha Islands, South China Sea (Liu et al., 2006a); ornithogenic sediments from Yongle archipelago, Xisha Islands, South China Sea (Xu et al., 2011). The three circles in (b) stands for bio-elements from Arctic, Xisha Islands and Antarctica with the overlapped part showing the common bio-elements among all three locations.

penguins from the Antarctic Peninsula, but in comparison with other bio-elements, it is more likely to subject to post-depositional geochemical effects in complex environment (Xu et al., 2011), resulting in its absence as a common seabird bio-element. Such regional features do not contradict with the similarity of avian bio-elements of different regions as we concluded above.

Although different kinds of seabirds inhabit the Antarctic, Arctic, and South China Sea regions, the identification of As, Cd, Cu, P, Se and Zn as the characteristic bio-elements in the sediments corroborated our hypothesis on the similarity of element behavior transported by the seabird activities on a global scale. This finding facilitates the study of seabird geochemical impact on terrestrial environments owing to the close relationship between the contents of the bio-elements in the ornithogenic sediments and the number of resident seabirds. Thus, it becomes possible to reconstruct the changes of paleoclimatic and historical seabird populations in future studies.

4. CONCLUSIONS

Based on our elemental analysis on the five sediment profiles and corresponding end-member media from the Ross Sea region, we were able to confirm that penguin guano and freshwater algae are the main source of OM. Further comparison of $\delta^{13}C_{org}$ and C/N indicated that the penguin guano exerted stronger influences in the sediment profiles CC, BI and MB6. The accurate amounts of guano input and algal biomass in MB4, MB6, CL2, and BI were determined by a two-member equation using $\delta^{13}C_{org}$ values in the bulk sediments. The calculated index of OC_g was shown to be valid to stand for guano input, and the algal biomass was found to be controlled by nutrients brought by guano. As, Cd, Cu, P, S, Se and Zn were identified as bio-elements in the Ross Sea region through end-member study and multiple statistical methods including cluster analysis, Pearson correlation, and PCA. Our data were compared with avian bio-elements in other parts of Antarctica, the South China Sea and the Arctic, and surprising overlaps were noted. We believe the overlap of avian bio-elements on a global scale is mainly attributed to the notable enrichment through the similar food chain in the ocean, and such findings will facilitate our future work on avian ecology and paleoclimatic reconstruction.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.04.013.

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