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Distribution and sources of rare earth elements in ornithogenic sediments from the Ross Sea region, Antarctica



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ABSTRACT

Concentrations of rare earth elements (REEs) were determined in three ornithogenic sediment profiles excavated at active Adélie penguin (*Pygoscelis adeliae*) colonies in McMurdo Sound, Ross Sea, Antarctica. The distribution of REEs in each profile fluctuated with depth. REEs measured in environmental media (including bedrock, guano, and algae) and analysis on the correlations of Σ REE–lithological elements and Σ REE–bio-elements in the profiles indicated that sedimentary REEs were mainly from weathered bedrock in this area, and the non-crustal biogenetic REEs from guano and algae were minor. Further discussion on the slopes and Ce and Eu anomalies of chondrite-normalized REE patterns indicated that a mixing process of weathered bedrock, guano and algae was the main controlling factor for the fluctuations of REEs from the three constituents in the sediments. The calculation functioned well in estimating bedrock-derived REEs and the magnitude of ornithogenic influence in different profiles. In general, REEs in the ornithogenic sediments showed anti bio-element patterns and thus can be used as an additional proxy to reconstruct historical penguin populations.

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1. Introduction

The accumulation of sediments often requires considerable time, during which various geochemical processes can occur. All environmental changes in the surrounding region during this period could be well preserved in the sedimentary system [1,2]. To decode this information from the past, multiple geochemical proxies have been introduced and systematically studied for decades. Among them, distribution and abundance of elements is the most basic yet most important tool [3-6]. Rare earth elements (REEs) form a group of elements from Lanthanum to Lutetium in the periodic table. With the same layout of valence electrons in the outer shell, REEs tend to possess similar chemical properties [7,8]. For example, they are found to symbioses in the same minerals, and are less susceptible to various fractionations in geochemical processes [9,10]. Thus, REEs in the sediments could record the influence from different factors including parent bedrock properties, redox conditions, content of organic matter, local or long-distance eolian input, and anthropogenic impact during the stages of weathering, transportation, deposition and diagenesis [11–14].

As the most remote region from human influence, Antarctica is also very sensitive to climate change and serves as a natural archive for the paleoenvironment [15]. Considerable research has been conducted in Antarctica using REEs on different carriers to investigate petrology and geochemistry. Lee et al. utilized REEs to study the formation of soils at King George Island, Antarctic Peninsula [16]. Santos et al. reported the origin and geochemical behavior of REEs and other trace elements in the marine sediments from Admiralty Bay, King George Island, and suggested no significant alteration during weathering and transport processes [12]. In the Ross Sea region, more focus has been on REEs in petrology. For example, Sun and Hanson concluded that the mantle source and the processes for magma generation of the Ross Island volcanics were similar to those for ocean island volcanics using Pb isotope ratios and REE abundances of five primary basanitoids from Ross Island [17]. Subsequent research on the differentiation of McMurdo volcanics on Ross Island was conducted by measuring REEs and using a quantitative trace element modeling [18]. Later, REEs were applied in more diverse ways, e.g., they were used in tracing the source of clay in Victoria Land Basin [19]. REEs in the water column of Lake Vanda in the Dry Valleys are considered the highest ever observed at natural oxic/anoxic interfaces due to redox conditions and the scavenging effect of particles [20].

The Ross Sea region has one of the largest concentrations of Adélie penguin (*Pygoscelis adeliae*) colonies in Antarctica. In costal ice-free areas where weathering occurred at a greater extent than continental Antarctica due to the warmer climate, seabird guano is also abundantly deposited, gradually forming ornithogenic sediments [21]. This kind of geo-carrier has been used in numerous studies to interpret paleoecolog-ical and paleoclimatic changes in the Holocene [6]. Sun et al. inferred penguin population change at Ardley Island, Antarctic Peninsula, for the last 3000 years using the distribution patterns of penguin bio-elements [4]. In Vestfold Hills, East Antarctica, long-term seabird

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population dynamics was reconstructed for the last 8000 years [22,23]. Liu et al. investigated REEs in ornithogenic sediments at Ardley Island and calculated the proportion of guano-originated REEs as a new proxy for penguin populations [14]. Hu et al. used the ornithogenic sediments form Cape Bird to reconstruct historical change of the penguin population over the past 700 years [24]. Our previous papers discussed paleoenvironmental implication of elements and isotopes in the ornithogenic sediments from the Ross Sea region [25,26], but geochemistry of REEs has not yet been reported for the sediments and soils in this area. Here, we determined for the first time REEs in ornithogenic sediments from the Ross Sea region. Specifically, we investigated the source and geochemical behavior of REEs, and the controlling factor for their distribution with depth in the profiles. In addition, we attempted to quantify the source of REEs and their connection with penguin population changes over time.

2. Materials and methods

Profile MB4, MB6 and BI used in this study were collected in McMurdo Sound, the Ross Sea region, in January 2010. The sampling sites are located on Ross Island and Beaufort Island. Ross Island (~2460km²) is of volcanic origin on the east side of Victoria Land in McMurdo Sound. Most of Ross Island is covered by ice, leaving three ice-free areas which are Cape Crozier (~18km²), Cape Bird (~15km²), and Cape Royds (~13km²). A large number of Adélie penguins (>155,000 pairs, [27]) reside in these areas. Beaufort Island (~18.4km²) is 21km north of Ross Island with Adélie penguins breeding in its ice-free areas on the eastern and southern parts. Numerous abandoned penguin colonies were also found in the ice-free areas mentioned above, suggesting historical penguin occupations. This region is characterized by harsh environmental conditions and also is sensitive to climate changes, making it an ideal location for paleoclimatic and paleoecological research [24,28,29].

The excavation sites of MB4 and MB6 are located at Cape Bird, while BI was collected from Beaufort Island (Fig. 1). The MB4 profile (42cm) was taken in a small pond between the fourth and fifth beach ridges on the coast at the middle of the penguin colony at Cape Bird (166°22' 25.6"E, 77°14'35.3"S). Abandoned penguin rookeries were found near our sampling site, indicating possible ornithogenic influence in the pond brought by penguin guano. The MB6 profile (38cm) was collected from a currently dried-out catchment on the second terrace above sea level at the northern end of the penguin colony at Cape Bird (166° 26' 44.4" E, 77°12' 47.5" S). Core BI (20.5cm) was excavated from a pond near the active penguin colony on the southwest side of Beaufort Island (166° 58′ 23.6″ E, 76° 58′ 23.6″ S). Details about the sampling, lithology and sectioning of the sediments were documented in our previous study [30]. Environmental media samples including bedrock, fresh algae and fresh guano were also collected in the study region (mainly Cape Bird, Cape Royds and Cape Chocolate). All the samples were kept at -20° C in the laboratory prior to chemical analysis. They were airdried (fresh algae and fresh guano samples were freeze-dried) and homogenized by grinding after the careful removal of large rock fragments and biological remains. The final powder samples were passed through a 74µm mesh sieve.

A chemical volumetric method was employed to measure total organic carbon (TOC) in the sediments. Cd, Cu, P, Ti, Zn were determined by inductively-coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer 2100DV) after digestion with HNO₃–HF–HCl–HClO₄, and Al, Fe and Si were measured by ICP-OES and X-ray fluorescence analyzer (XRF-1800, Shimadzu). As, Hg and Se contents were analyzed by atomic fluorescence spectrometry (AFS-930, Titan Instruments Co., Ltd.) after digestion with HNO₃–HCl–HClO₄ (As and Se) and H₂O₂–Fe³⁺oxidant-HNO₃ (Hg). Analysis of S was conducted on an element analyzer (Vario EL III). These elements were determined for comparison with REEs, and their results have been reported in detail [25,30]. F was measured by ion selective electrode method [22]. Reagent blanks and



Fig. 1. Sampling sites of the sediment profiles in the Ross Sea region (Ross Island and Beaufort Island).

standard sediment reference materials (SRMs) were included in every batch of samples for quality control (data were reported in the references mentioned above). Analysis of REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), Hf and Zr were conducted on an inductively coupled plasma source mass spectrometer (IPC-MS) using a lithium borate fusion method by ALS Chemex (Guangzhou) Co., Ltd. Detailed results for measured REEs and analytical accuracy & precision for SRMs are given in the tables of appendix A. Correlation analysis in this study was performed using the software PASW Statistics 18 and origin 7.5. Calculation of contributions from different constituents to Σ REE in each profile was conducted using the software Matlab 7.1.

3. Results

Distributions of 14 measured REEs (Pm not included) all exhibit considerable fluctuation with depth that is similar in all three profiles (Fig. 2). Range, mean and coefficient of variation (CV) of REEs in the sediments and environmental media (including bedrock, fresh guano and fresh algae; CV of REEs in environmental media was not calculated) are given in Table 1. Apparent fluctuations of individual REE (Fig. 2) are underlined by high CV values (above 10%, especially for MB6 with CV higher than 25%). Range and mean of each REE of the three profiles are generally on the same level for their regional geochemical consistency. Average ΣREE values in the profiles range from 202.34 to 292.17µg/g, similar to that of sediments and shale reported by Haskin et al. [31], but much higher than the sediments from Ardley Island, Antarctic Peninsula, which received heavy influence from penguin activities (37.18–71.21µg/g, [14]). Due to the slight difference in their geochemical properties, REEs are traditionally divided into two groups of light (LREEs, from La to Eu) and heavy rare earth elements (HREEs, from Gd



Fig. 2. Distribution of measured REEs in profile MB4, MB6 and BI.

Table 1

Range, mean and CV (not calculated for the environmental media) of individual REE, SREE, LREE, HREE and L/H in the sediment and environmental media samples.

Element	Range (µg/g)	Average (µg/g)	CV (%)	Element	Range (µg/g)	Average (µg/g)	CV (%)
MB4 (n=39)							
Ce	90-145	114.46	12.26	Pr	9.35-15.25	11.92	13.59
Dy	3.58-6.41	4.85	16.22	Sm	6.07-10.6	7.75	16.02
Er	1.89-3.32	2.55	15.15	Tb	0.67-1.22	0.91	16.44
Eu	1.8-3.21	2.37	16.65	Tm	0.25-0.45	0.35	15.64
Gd	4.49-8.57	6.24	17.02	Yb	1.56-2.65	2.03	15.36
Но	0.65-1.19	0.9	16.42	ΣREE	200.99-326.17	258.54	12.58
La	48.2-73.5	61.27	11.17	LREE	187.62-302.34	240.41	12.37
Lu	0.23-0.39	0.31	13.11	HREE	13.37-23.83	18.13	15.83
Nd	32.2-56.9	42.64	14.95	L/H*	11.85-14.31	13.34	4.63
MB6 (n=30)							
Ce	47.6-127	85.02	26.73	Pr	5.37-14.25	9.61	27.5
Dy	2.37-6.37	4.23	27.63	Sm	3.65-10.5	6.35	29.01
Er	1.21-3.18	2.23	27.12	Tb	0.41-1.2	0.76	28.43
Eu	1.15-3.26	2.01	29.15	Tm	0.16-0.47	0.31	29.21
Gd	2.77-8.07	5.09	28.23	Yb	1-2.58	1.82	27.47
HO	0.44-1.26	0.79	29.02	ZKEE	113.57-306.04	202.34	27.05
La	28.2-72.5	49.12	26.01	LKEE	105.07-282.51	186.85	27
LU	0.14-0.4	0.27	28.19	HKEE	8.3-23.33 11 EE 13 CO	13.49	27.75
INU	19.1-33	54,74	28.00	L/ N	11.55-12.00	12.09	2.29
BI (n=25)							
Ce	83.2-144	122.6	12.87	Pr	9.11-15.5	13.19	12.68
Dy	4.04-6.7	5.59	12.82	Sm	6.43-11.5	9.5	13.61
Er	1.93-3.17	2.7	12.56	Tb	0.71-1.27	1.06	13.14
Eu	2.16-3.78	3.11	13.77	Im	0.28-0.48	0.38	11.67
Gd	4.79-9.08	1.47	14.35	YD	1.57-2.69	2.24	12.09
HO	0.78-1.27	1.07	12.19	ZKEE	199.15-343.83	292.17	13.1
Ld	48.7-85.1	/2.10	13.04	LKEE	184.8-318.89	2/1.35	13.11
Nd	35 2-60 4	0.32 50.78	13.19	I /H*	12 54-13 50	13.03	196
Itta	55.2 00.1	50.70	15,15	L/11	12.51 15.50	15.05	1.50
-	-			-			
Element	Range (µg/g)	Av	/erage (μg/g)	Element	Range (µg/g	g)	Average (µg/g)
Element Bedrocks (n=5)	Range (µg/g)	Av	verage (µg/g)	Element	Range (µg/չ	g)	Average (µg/g)
Element Bedrocks (n=5) Ce	Range (µg/g) 84–204	Av 12	verage (µg/g) 20.2	Element Pr	Range (µg/s 9.65–21.8	g)	Average (µg/g)
Element Bedrocks (n=5) Ce Dy	Range (µg/g) 84–204 5.16–8.92	Av 12 6.2	verage (µg/g) 20.2 26	Element Pr Sm	Range (µg/s 9.65–21.8 8.12–13.15	g)	Average (µg/g) 13.42 9.77
Element Bedrocks (n=5) Ce Dy Er	Range (µg/g) 84–204 5.16–8.92 2.38–5.05	Av 12 6.3	verage (µg/g) 20.2 26 11	Element Pr Sm Tb	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57	g)	Average (µg/g) 13.42 9.77 1.14
Element Bedrocks (n=5) Ce Dy Er Eu Eu	Range (μg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74, 10.2	Av 12 6.3 3.3 	verage (µg/g) 20.2 26 11 27	Element Pr Sm Tb Tm	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71	g)	Average (µg/g) 13.42 9.77 1.14 0.44
Element Bedrocks (n=5) Ce Dy Er Eu Gd	Range (μg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.00, 1.82	Av 12 6. 3. 3. 7. 7.	verage (µg/g) 20.2 26 11 27 27 29 20	Element Pr Sm Tb Tm Yb SPEE	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86	g)	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 201 78
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.2, 127 5	Av 12 6. 3. 3. 7.9 1. 1.	verage (µg/g) 20.2 26 11 27 97 22 22	Element Pr Sm Tb Tm Yb SREE LPFF	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481	g) 1.58	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 269.56
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7	Av 12 6. 3. 3. 7. 1. 65 0.0	verage (µg/g) 20.2 26 11 27 27 27 22 28 8 8	Element Pr Sm Tb Tm Yb SREE LREE LREE HPFE	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77, 23.8	g) 1.58 7.74	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8	Av 12 6. 3. 3. 7. 1. 65 0. 52	verage (μg/g) 20.2 26 11 27 27 27 22 28 8 38 21	Element Pr Sm Tb Tm Yb SREE LREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10 17–13.2	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8	Av 12 6 3.: 7 1.1 65 0.: 52	verage (µg/g) 20.2 26 11 27 27 27 22 8 8 38 2.1	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5)	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8	Av 12 6 3.3 7.9 1.1 65 0.1 52	verage (μg/g) 20.2 26 11 27 97 22 28 8 8 8 8 2.1	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H*	Range (µg/s 9.65-21.8 8.12-13.15 0.94-1.57 0.34-0.71 1.95-4.86 209.61-481 190.84-447 18.77-33.8 10.17-13.2	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.9–2.04	Av 12 6 3. 3. 7. 1. 65 0. 52 52	verage (μg/g) 20.2 26 11 27 27 27 22 28 38 2.1 2.46 5.4	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Scree	Range (µg/s 9.65-21.8 8.12-13.15 0.94-1.57 0.34-0.71 1.95-4.86 209.61-481 190.84-447 18.77-33.8 10.17-13.2	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.10
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1	Av 12 6. 3. 3. 7. 1. 65 0. 52 52 52 2.(verage (μg/g) 20.2 26 11 27 97 22 0.8 38 2.1 2.46 54	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm	Range (µg/s 9.65-21.8 8.12-13.15 0.94-1.57 0.34-0.71 1.95-4.86 209.61-481 190.84-447 18.77-33.8 10.17-13.2 3.91-8.94 2.78-6.22 0.20, 0.60	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.42
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Eu Eu Eu Eu Eu Eu Eu Eu Eu	Range (μg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.07	Av 12 6. 3. 3. 3. 4. 1. 65 0. 52 52 2.0 1.4	verage (μg/g) 20.2 26 11 27 97 22 28 88 88 88 2.1 2.46 54 22	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm	Range (µg/s 9.65-21.8 8.12-13.15 0.94-1.57 0.34-0.71 1.95-4.86 209.61-481 190.84-447 18.77-33.8 10.17-13.2 3.91-8.94 2.78-6.22 0.29-0.09 0.16 0.21	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.22
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Gd	Range (μg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92	Av 12 6. 3. 3. 3. 1. 65 0. 52 52 2.0 1. 4 1. 3	verage (μg/g) 20.2 26 11 27 37 22 28 88 38 2.1 2.46 64 42 3 17	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb	Range (µg/s 9.65-21.8 8.12-13.15 0.94-1.57 0.34-0.71 1.95-4.86 209.61-481 190.84-447 18.77-33.8 10.17-13.2 3.91-8.94 2.78-6.22 0.29-0.69 0.16-0.31 0.88-1.82	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1 23
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho Algae (n=5) Ce Dy Er Eu Gd Ho	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76	Av 12 6. 3. 3. 7.9 1. 65 0. 52 2.0 1. 1. 3. 0. 0. 52 2.0 1. 1. 0. 0. 52 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.	verage (μg/g) 20.2 26 11 27 37 22 28 8 8 8 8 2.1 2.46 64 42 3 17 5	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Tb Tm Yb SRFE	Range (µg/s 9.65-21.8 8.12-13.15 0.94-1.57 0.34-0.71 1.95-4.86 209.61-481 190.84-447 18.77-33.8 10.17-13.2 3.91-8.94 2.78-6.22 0.29-0.69 0.16-0.31 0.88-1.82 81 18-186	g) 1.58 7.74 4 3	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122 1
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Gd Ho La Lu Lu Nd La Lu Lu Lu Lu Lu Lu Lu Lu Lu Lu	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 1.79–41.2	Av 12 6. 3. 3. 7.9 1.1 69 0.1 52 52 2.0 1.4 1.3 3. 0.1 52 2.0 1.4 1.3 3. 0.1 52 52 52 52 52 52 52 52 52 52	verage (μg/g) 20.2 26 11 27 97 22 8.8 38 3.1 2.46 64 42 3 17 5 7	Element Pr Sm Tb Tm Yb SREE LREE LREE HREE L/H* Pr Sm Tb Tm Yb Sm Tb Tm Yb SREE LREE	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172.	g) 1.58 7.74 4 3 88	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 1.23 12.21 112.32
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Gd Ho La Lu Gd Ho La Lu	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31	Av 12 6 3 7 1 65 0 52 52 2 1 1 52 2 1 52 2 1 52 2 1 52 2 0 52 2 0 52 52 52 52 52 52 52 52 52 52	verage (μg/g) 20.2 26 11 27 97 22 88 38 2.1 2.46 64 42 3 17 5 7	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE HREE	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75	g) 1.58 7.74 4 3 88 13	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Ev Eu Gd Ho La Lu Gd Ho La Lu Nd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33	Av 12 6 3 7 1 65 0 52 52 2 1 1 52 2 1 52 2 1 1 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 2 0 52 52 2 0 52 52 2 52 52 52 52 52 52 52 52 52 52	verage (μg/g) 20.2 26 11 27 97 22 88 38 2.1 2.46 64 42 3 3 17 5 7 16 56	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57
Element Bedrocks $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Algae $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Ce Ce Ce Ce Ce Ce Ce Ce Ce Ce	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33	Av 12 6 3 7 1 69 0 52 52 2.0 1.4 1.3 .52 2.0 1.4 1.3 .52 2.0 1.4 1.3 .52 2.0 .52 2.0 .52 2.0 .52 2.0 .52 .52 .52 .52 .52 .52 .52 .52	verage (μg/g) 20.2 26 11 27 97 22 8.8 38 2.1 2.46 64 42 3 17 5 7 16 56	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57
Element Bedrocks $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Algae $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Guano $(n=3)$ Ce	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14	Av 12 6 3 7 1 65 0 52 2 1 1 3 52 2 1 1 3 2 1 3 0 2 1 3 0 2 1 3 0 3 5 5 5 5 5 5 5	verage (μg/g) 20.2 26 11 27 97 22 88 88 88 8.1 2.46 64 42 3 17 5 7 16 56	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE LREE HREE LREE HREE LREE HREE HREA Pr Sm Tb Tm Yb Sm Tb Tm Yb SREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Guano (n=3) Ce Dy	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14 0.29–0.93	Av 12 6 3.3 7.9 1.1 65 0.1 52 2.0 1.4 1.1 3.3 0.9 27 0.1 21 9.1 9.1 9.1 9.1 9.1 9.1 9.1 9.	verage (μg/g) 20.2 26 11 27 97 22 38 38 2.1 2.46 64 42 3 17 5 7 16 56	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Sm	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57 1.07 0.76
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Guano (n=3) Ce Dy Er Cy Dy Er Charles	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14 0.29–0.93 0.13–0.49	Av 12 6 3. 3. 7. 1. 65 0. 52 2. 1. 1. 3.	 verage (μg/g) 20.2 26 11 27 27 22 28 38 2.1 2.46 54 42 3 17 5 7 16 56 73 59 29 	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57 1.07 0.76 0.07
Element Bedrocks (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Algae (n=5) Ce Dy Er Eu Gd Ho La Lu Nd Guano (n=3) Ce Dy Er Eu	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14 0.29–0.93 0.13–0.49 0.12–0.26	Av 12 6 3. 3. 7. 1. 65 0 52 2. 1. 1. 3.	 verage (μg/g) 20.2 26 11 27 22 28 38 2.1 2.46 54 42 3 17 5 7 16 .566 73 59 29 2 	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57 1.07 0.76 0.07 0.057
Element Bedrocks $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Algae $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Guano $(n=3)$ Ce Dy Er Eu Gd Gd Gd Gd Gd Gd Gd Gd Gd Gd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14 0.29–0.93 0.13–0.49 0.12–0.26 0.32–0.98	Av 12 6 3. 3. 7. 1. 65 0 52 2.0 1. 1. 3. 0. 27 0. 21 9 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0	 verage (μg/g) 20.2 26 11 27 37 22 38 2.1 2.46 54 42 3 17 55 16 .56 73 59 29 22 56 	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4 0.66–1.58 0.46–1.04 0.03–0.11 0.05–0.07 0.01–0.18	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.57 1.14 0.44 0.23 1.23 1.23 1.23 1.57 0.78 1.157 1.07 0.76 0.07 0.057 0.14
Element Bedrocks $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Algae $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Guano $(n=3)$ Ce Dy Er Eu Gd Ho La Lu Nd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14 0.29–0.93 0.13–0.49 0.12–0.26 0.32–0.98 0.01–0.16	Av 12 6. 3. 7. 7. 1. 52 52 52 2.0 1. 52 2.0 1. 52 2.0 1. 52 2.0 1. 52 2.0 1. 52 2.0 1. 52 2.0 1. 52 2.0 1. 52 52 52 52 52 52 52 52 52 52	verage (μg/g) 20.2 26 11 27 97 22 38 38 38 38 38 38 38 38 38 38 38 38 38	Element Pr Sm Tb Tm Yb ΣREE LREE HREE L/H* Pr Sm Tb Tm Yb ΣREE LREE HREE L/H* Pr Sm Tb Tm Yb ΣREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4 0.66–1.58 0.46–1.04 0.03–0.11 0.05–0.07 0.01–0.18 14.34–33.0	g) 1.58 7.74 4 3 88 13 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57 1.07 0.76 0.07 0.057 0.14 22.72
Element Bedrocks $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Algae $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Guano $(n=3)$ Ce Dy Er Eu Gd Ho La Lu Nd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 17.9–41.2 0.1–0.31 14.3–33 6.4–14 0.29–0.93 0.13–0.49 0.12–0.26 0.32–0.98 0.01–0.16 3.3–7.2	Av 12 6. 3. 3. 7.9 1. 52 52 52 2.0 1.4 1.1 3. 0.1 52 2.0 1.4 1.1 3. 0.1 52 2.0 1.4 1.1 52 2.0 1.4 52 2.0 1.4 52 52 52 52 52 52 52 52 52 52	verage (μg/g) 20.2 26 11 27 97 22 38 38 38 2.1 2.46 54 42 33 7 7 16 5.56 7 3 59 29 29 20 5 5 7 7	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4 0.66–1.58 0.46–1.04 0.03–0.11 0.05–0.07 0.01–0.18 14.34–33.0 13.44–30.1	g) 1.58 7.74 4 3 88 13 9 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57 1.07 0.76 0.07 0.057 0.14 22.72 20.93
Element Bedrocks $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Algae $(n=5)$ Ce Dy Er Eu Gd Ho La Lu Nd Guano $(n=3)$ Ce Dy Er Eu Gd Ho La Lu Nd	Range (µg/g) 84–204 5.16–8.92 2.38–5.05 2.67–4.49 6.74–10.2 0.99–1.83 46.3–127.5 0.27–0.7 40.1–76.8 34.8–80.8 1.8–3.84 0.95–2.1 0.88–1.97 2.12–4.92 0.31–0.76 1.7.9–41.2 0.1–0.31 1.4.3–33 6.4–14 0.29–0.93 0.13–0.49 0.12–0.26 0.32–0.98 0.01–0.16 3.3–7.2 <0.01	Av 12 6 3 7 1.1 69 0 52 2.0 1.4 1.3 3 52 2.0 1.4 1.3 3 9.2 2.0 0 0 0 0 52 2.0 0 52 2.0 0 52 2.0 0 52 2.0 0 52 2.0 0 52 2.0 0 52 2.0 0 52 52 2.0 0 52 52 2.0 0 52 52 2.0 0 52 52 52 52 52 52 52 52 52 52	 verage (μg/g) 20.2 26 11 27 27 27 28 38 2.1 2.46 54 42 3 17 56 73 59 29 29 29 29 20 50 77 	Element Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE LREE HREE L/H* Pr Sm Tb Tm Yb SREE L/H*	Range (µg/s 9.65–21.8 8.12–13.15 0.94–1.57 0.34–0.71 1.95–4.86 209.61–481 190.84–447 18.77–33.8 10.17–13.2 3.91–8.94 2.78–6.22 0.29–0.69 0.16–0.31 0.88–1.82 81.18–186. 74.57–172. 6.61–14.75 10.52–13.4 0.66–1.58 0.46–1.04 0.03–0.11 0.05–0.07 0.01–0.18 14.34–33.0 13.44–30.1 0.9–2.9	g) 1.58 7.74 4 3 88 13 9 9	Average (µg/g) 13.42 9.77 1.14 0.44 2.7 291.78 268.56 23.22 11.33 5.82 4.19 0.43 0.23 1.23 122.1 112.32 9.78 11.57 1.07 0.76 0.07 0.057 0.14 22.72 20.93 1.79

to Lu) [8,32]. It is quite evident that LREEs are much more abundant than HREEs in our profiles, with the ratio of LREE to HREE (L/H in Table 1) in the analyzed sediments reaching up to 13.34, 12.09 and 13.03 for profile MB4, MB6 and BI respectively. Though individual and total REE values in the sediments are found to be variable, L/H remains

relatively stable in each profile with CV lower than 5%, suggesting no significant change in lithology and REE source. Correlation analysis among individual REE in all measured samples including environmental media showed significant positive correlations among themselves (R>0.84, n=107, p<0.01; Table 2), coinciding with patterns of change

0.858

0 902

0.92

0 922

orrelati	prrelation analysis among REEs in all samples measured.											
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	
La	1											
Ce	0.972	1										
Pr	0.981	0.983	1									
Nd	0.972	0.965	0.986	1								
Sm	0.945	0.943	0.964	0.992	1							
Eu	0.94	0.914	0.947	0.984	0.989	1						
Gd	0.934	0.943	0.96	0.987	0.99	0.982	1					
Tb	0.948	0.95	0.976	0.989	0.983	0.974	0.989	1				
Dy	0.944	0.932	0.973	0.981	0.973	0.969	0.974	0.988	1			
Но	0.947	0.929	0.967	0.983	0.975	0.975	0.974	0.985	0.991	1		
Er	0.933	0.928	0.968	0.947	0.919	0.907	0.923	0.955	0.973	0.965	1	
Tm	0.9	0.888	0.933	0.919	0.893	0.889	0.893	0.926	0.947	0.95	0.964	
Yb	0.93	0.901	0.948	0.929	0.9	0.902	0.893	0.928	0.955	0.956	0.975	

0.841

Table 2 Cor

0 9 0 3

Lu

0 9 07

with depth (Fig. 2). Since the distribution of individual REE is similar to one another, we illustrated the depth profiles of Σ REE, LREE, HREE, L/H with lithological elements (typical Al and Hf) and TOC (Fig. 3). For comparison, bio-elements (typical P and F) indicative of guano amounts in the ornithogenic sediments are also plotted [4,6,25]. As can be seen, REE proxies (Σ REE, LREE and HREE) in MB4 show a quadratic curve from the bottom to 15cm depth, with the lowest values at around 25cm depth. Between 15 and 5cm, REEs experience a plateau in high values and then drop to the level below 15cm in the surface layer. REEs in MB6 have their highest level at the bottom, but immediately go down and form a trough from 35 to 24cm. Above 24cm, the proxies

093

0 894

0.856

remain high and stable, and only decrease gradually from 10cm to the surface. REEs in BI are relatively stable in the layer below 5cm, but begin to drop with fluctuations in the surface layer. The trends of REEs in the profiles are generally the same as the lithological elements, and opposite to that of bio-elements and TOC. Individual REE content, Σ REE, LREE and HREE in the bedrock we collected from this region are similar to that of the sediment profiles, but are much higher than that in algae and guano (Table 1). Also, bedrock samples were found to have slightly lower L/H (on average 11.33) than algae (11.57) and guano (12.52). Comparison of SREE, Al, Hf, P, F and TOC in the different environmental media indicates the dominance of REE, Al and Hf in

0.962



Fig. 3. Distribution of SREE, LREE, HREE, L/H, AI, Hf, P, F and TOC in profile MB4, MB6 and BI.

Lu

1

Tm

1 0.956

0.952

Yb

1

0 9 5 7



Fig. 4. Contents of SREE, Al, Hf, P, F and TOC in environmental media (bedrock, fresh guano and fresh algae).

bedrock samples, and the high values of bio-elements and TOC in guano (Fig. 4).

4. Discussion

The material source of the sediments has been discussed in our previous work. Weathered bedrock, guano and algae are the three main constituents of the ornithogenic sediments from the Ross Sea region, in which weathered bedrock comprises the bulk of the sediments on a mass balance and mainly acts as mineral matrix, while algae and guano are the main sources of organic matter [25]. REE proxies share the same change pattern with depth and resemble those of Al and Hf (Fig. 3). Further, we analyzed the correlations between Σ REE and typical lithological elements Al, Fe, Si (only in MB4 and MB6), Ti, Hf and Zr, and results indicated that they are positively correlated with R≥0.73 at 0.01 level (Fig. 5), strongly indicating a large contribution to REEs from weathered bedrock. It has been reported that REEs, especially LREEs, tend to be adsorbed by organic matter [11], thus affecting their distribution in the sediments. Our results show that TOC, which mainly derives from guano and algae (Fig. 4), and the typically penguin guano-derived elements of P and F display opposite distribution patterns to REE proxies (Fig. 3). Thus, the strong adsorption of REEs by organic matter is unlikely. Instead, the significant negative correlations between TOC and REEs suggest a dilution effect from organic matter on REEs. Considering the absolute concentrations of REEs in the environmental media (Table 1, Fig. 4), we believe weathered bedrock is the main source of REEs in the sediments where non-crustal biogenetic REEs from algae and guano are fairly minor.

Though REEs share similar chemical properties, the subtle differences in their atomic structure would cause fractionation in geological processes, which leads to much higher contents of the even atomicnumbered elements than the adjacent odd-numbered elements, known as the Oddo–Harkins effect [33]. Hence, normalization of REE concentrations becomes a common practice to eliminate that effect and provides insight into their sedimentary characteristics. Here, we employed the most commonly used chondritic standard, which was based on the average value of 22 chondritic meteorites, to normalize our results [34]. Several depths of samples were chosen from each profile and labeled with environmental media (mean values) for comparison (Fig. 6; Lu in the guano samples is not shown because its content is below the detection limit, see appendix A). As can be seen, chondritenormalized REE patterns display highly identical trends within and among profiles, showing a common source and controlling geochemical factor for REEs in this region. Most sediment samples lie above guano and algae, and some are on the same level or slightly higher than bedrock samples, generally illustrating the contribution from the three constituents. Slopes of REE patterns are often used to explore the source and fractionation of REEs in the sediments [35]. As can be seen, the sections corresponding to LREEs show a more obvious slope than the HREE sections in the samples, corroborating the high L/H values mentioned above. Analysis of environmental media samples show that L/H values are the highest in guano, then algae and bedrock by order, but they are all lower than in the sediment profiles (Table 1). Considering that LREEs are also easily adsorbed by fine clay debris other than organic matter [11], we believe the higher L/H in the sediments is caused by the affinity of LREEs to the fine particles. The (La/Yb)_N (ratio of chondrite-normalized La to Yb) value was calculated to address the overall slope of the patterns quantitatively. Mean (La/Yb)_N of MB4, MB6, BI, bedrock, guano and algae are 18.09 ± 1.44 (n=39), $16.14 \pm$ $0.72 (n=30), 19.06\pm0.69 (n=25), 15.26\pm0.70 (n=5), 21.30\pm2.18$ (n=3) and 13.26 ± 1.29 (n=5), respectively. Though it is likely that weathered bedrock is the main REE source, (La/Yb)_N in the sediment profiles are higher than from bedrock, indicating a possible influence from guano. A similar case also was reported that (La/Yb)_N from guano was much higher than in background sediments [14].

Anomalies of REEs, especially Ce and Eu, are important proxies in the patterns which document historical changes in the environment [36]. They are calculated by the formula:

$$\delta Ce = 2Ce_N/(La_N + Pr_N)$$
 $\delta Eu = 2Eu_N/(Sm_N + Gd_N)$



Fig. 5. Correlation analysis between SREE and lithological elements (AI, Fe, Si (only in MB4 and MB6) Ti, Hf and Zr) in profile MB4, MB6 and BI.

where Ce_N , La_N , Pr_N , Eu_N , Sm_N and Gd_N , are chondrite-normalized values. Slight Ce negative anomalies are observed in all analyzed sediment samples and environmental media, and Eu positive anomalies are found in all samples but fresh guano. Though drastic Ce and Eu

anomalies could be introduced by a change of redox conditions and weathering processes, the limited magnitudes of δ Ce and δ Eu in this study are more likely caused by the property of their material sources. δ Ce in guano is 0.85 (n=3) in the Ross Sea region, with more negative



Fig. 6. Chondrite-normalized REE patterns for profile MB4, MB6 and BI and environmental media samples. The chondrite values are cited from Herrmann (1971).

 δ Ce (0.67) in guano reported in West Antarctica [14]. Ce in guano has a strong marine signature, which is due to the source of the food supply of the penguins. Negative Ce anomaly is common in seawater, but the magnitude varies with location and water depth [37,38], and thus accounts for different guano δ Ce between regions. Bedrock and algae are also found to have negative Ce anomalies (δ Ce=0.78 and 0.84, respectively) on the same level as guano. Unlike guano, freshwater algae were developed in the coastal catchments in this region, and REEs in algae mainly originated from weathered bedrock brought to the sampling sites. Thus, in general we can see the patterns of bedrock and algae display differences only on a content level, but not on individual REE anomalies. According to the research of Mittlefehldt and Lindstrom

[39], positive Eu anomalies are common in basaltic clast samples from Antarctica, which corroborates our results (δEu =1.20 and 1.15 for bedrock and algae, respectively). Absence of positive Eu anomalies in guano samples indicate that Eu in the sediments mainly receives influence from bedrock and algae, while the imprint of guano was undetectable. Different from bedrock, algae and any sediment sample, the REE pattern in guano displays more positive anomalies in Dy, Er and Tm, demonstrating its unique origin from the marine environment. None of these anomalies were documented in the sediments, which, on the other hand, indicated that the contribution on REEs from guano is minor. In summary, the chondrite-normalized REE patterns showed that sediments fall between bedrock and algae. In-depth analysis of slope data and Ce and Eu anomalies went one step further to indicate that the mixing process of weathered bedrock, algae and guano is the main controlling factor for the REE distributions and patterns in the profiles.

The most profound characteristic of ornithogenic sediments is that they receive heavy influence from seabird activities, and thus contain abundant information relating to paleoecology and the paleoenvironment [23,40]. Penguin bio-elements are concentrated and accumulated in ornithogenic sediments and they share the same distribution pattern with depth due to a common controlling factor: the input of penguin guano [4]. The assemblage of bio-elements is a powerful tool to reconstruct historical penguin populations [22,41]. Our previous study has identified As, Cd, Cu, P, S, Se and Z as the common penguin bio-elements in the Ross Sea region [25]. In addition, Hg was found to originate mainly from guano as a result of the bioaccumulation effect [30]. Additional measurement of F, which is enriched in the guano of Adélie penguins due to its high content in the penguins' main prey-krill [42,43], shows that it is also a typical bio-element sharing the same pattern with the elements mentioned above in the sediments. We analyzed correlations between these bioelements and Σ REE, and significant negative correlations (R \leq -0.59, p<0.01 the values for Hg indicated by open circles in MB6 below 35cm were not used in these correlation analyses; As trend in BI was a bit deviated from other bio-elements due to some certain geochemical factors, rendering an R=-0.44, p<0.05, Fig.7) were observed. As previously discussed, REEs in the sediments are positively correlated with lithological elements free from guano influence (Fig. 5). The strong associations between REEs, bio-elements and lithological elements corroborated our conclusion that mixing processes of guano, algae and weathered bedrock form the main controlling factor for the REE distributions in the sediments.

Since the REEs in the sediments derive from weathered bedrock, guano and algae, it may be applicable to use the normalized patterns of environmental media to calculate the contribution of the three constituents to total REE. We anticipate that the REE pattern for each sediment sample is a combination of the three constituents, and the ratio of each end-member could be calculated using software Matlab 7.1 from the equation below:

$\text{REE}_{\text{N}} = \text{XREE}_{\text{Nguano}} + \text{YREE}_{\text{Nalgae}} + \text{ZREE}_{\text{Nbedrock}}$

where REE_{Nguano}, REE_{Nalgae} and REE_{Nbedrock} are REE patterns of guano, algae and bedrock, and X, Y and Z are the estimated ratios of each constituent, under the condition that X+Y+Z=1. We assigned different values with increments of 0.01 to X, Y and Z, plotting the guano, algae and bedrock proportion from 0 to 1. For each sediment sample, we hypothesize that X, Y and Z are the estimated ratios of guano, algae and weathered bedrock in the ornithogenic sediments when the calculated REE_N best fits the sample (tested by least square method). The content of pigments in the layer above 24cm in profile MB6 was extremely low, suggesting an almost dry environment, and the algal biomass might be minor [44]. Thus, Y for the algae ratio in this section was set to 0 to better fit the fact.

Using the method described above, we calculated the contributions of the three constituents to Σ REE in each subsample of the MB4 and



Fig. 7. Correlation between SREE and bio-elements As, Cd, Cu, F, Hg, P, S, Se and Zn (absent in MB4) in profile MB4, MB6 and BI.



MB6 profiles and displayed them in Fig. 8. BI from Beaufort Island was not included because many of its subsamples have Σ REE higher than the bedrock constituent (Fig. 6; bedrock samples were collected mainly

in Ross Island, indicating difference between the two islands), making the calculated result always showing all REEs in this profile are from bedrock, which apparently is not the case. In general, the calculated



Fig. 8. Calculated contributions of guano, algae and bedrock to SREE in profile MB4 and MB6, and the correlation between bedrock ratio and SREE.

bedrock proportions display the same trends as ΣREE (R=0.92, 0.99, p<0.01 for profile MB4 and MB6, respectively, Fig. 8), coinciding with our conclusion that REEs in the sediments mainly derive from weathered bedrock. Fractions calculated for guano and algae show some interesting results, for collectively they share the same patterns with TOC with depth, accounting well for the bio-genetic REEs. Guano-derived REEs in MB4 are generally low compared to those in algae. In the layer below 15cm, the appearance of peaks for guano fraction is prior to algae. It is observed that P and F (representing guano) and TOC (representing guano+algae) in Fig. 3 also show this pattern. In the surface layer where an algae mat was present according to field records, algae-derived REEs reached their maximum. Similarly, TOC in the surface layer of MB4 was a lot higher than the trends of P and F, showing the dominance of algae at this depth. Guano-derived REEs in MB6, however, are much more abundant than in MB4 (Fig. 8). In the section below 24cm, the increasing guano input visually reduced the algae fraction to a minor proportion. According to our previous study on material source of the sediments using nitrogen isotopes. MB4 was formed with less ornithogenic input, but more algal influence than MB6 [26]. This conclusion is corroborated by the calculation conducted above. Thus, this method can distinguish the ratio of the three constituents to an extent, and offers an alternative way to analyze the magnitude of penguin influence on the sediments. Moreover, REEs in the ornithogenic sediments showed anti bio-element distributions with depth due to the dominance of bedrock-derived REEs and the relatively simple mineral-organic matter mixing structure of the sediments in the Ross Sea region(See Fig. 7). Since guano is the main nutrient source and limiting factor for algal growth in the otherwise oligotrophic environment [45,46], the two constituents should share the same patterns of change in the sedimentary history, which was

Appendix A

Table 1

Results of REE analysis in the sediment profiles and environmental media.

also verified by previous carbon isotope research in the sediments [25]. Thus, REEs can also be used as an additional proxy to reconstruct historical penguin population.

5. Conclusions

We reported contents and other basic geochemical properties of REEs in three ornithogenic sediment profiles from the Ross Sea region for the first time. Weathered bedrock was deemed to be the main REE source for the sediments in this area, and the proportional contributions from algae and guano were minor according to the correlation analysis between REEs and lithological elements and penguin bio-elements. Chondrite-normalized REE patterns indicated that mixing processes of weathered bedrock, algae and guano are the main controlling factors for the distribution of REEs with depth. An end-member equation was devised to detect the ratio of the lithological and bio-genetic REEs, and the magnitude of guano influence on different profiles using the REE patterns. The REE trends with depth could be used as a potential proxy for the amount of guano input into sediments, indicative of relative change of historical penguin populations.

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	Depth (cm)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (μg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (μg/g)	Yb (µg/g)	Lu (µg/g)
MB4	0.8	50.7	97.6	9.71	34.8	6.62	2	5.02	0.77	4.02	0.74	2.09	0.31	1.74	0.27
	1.6	57.4	111	11.15	40.5	7.52	2.24	5.78	0.92	4.55	0.83	2.32	0.32	1.85	0.3
	2.4	50.4	97.7	9.43	33.7	6.29	1.83	4.96	0.67	3.73	0.68	2.04	0.26	1.56	0.26
	4	55.1	107.5	10.8	39.6	7.34	2.16	5.8	0.84	4.58	0.82	2.22	0.3	1.81	0.3
	4.8	62.2	120.5	12.1	43.9	8.39	2.47	6.61	0.96	5.08	0.96	2.59	0.35	2.02	0.31
	5.6	69.7	136.5	14.05	50.5	9.41	2.89	7.97	1.1	6.1	1.1	2.96	0.41	2.3	0.38
	7.2	71.5	141.5	14.4	52.3	9.76	3.07	7.98	1.15	6.08	1.14	3.11	0.45	2.34	0.39
	8.8	72.3	143	14.95	55.4	10.6	3.18	8.32	1.17	6.41	1.19	3.32	0.42	2.52	0.37
	10.4	73.5	145	15.2	55.2	10.3	3.14	8.43	1.22	6.3	1.14	3.27	0.43	2.65	0.39
	12	68.1	136.5	14.65	54.7	10.15	3.04	8.39	1.21	6.05	1.18	3.27	0.43	2.53	0.38
	13.6	72.7	143.5	15.25	56.9	10.45	3.21	8.57	1.19	6.23	1.18	3.2	0.44	2.59	0.35
	15.2	65.1	126	13.35	49.1	8.9	2.9	7.79	1.15	6.04	1.13	3.08	0.42	2.42	0.36
	16	65.3	124.5	12.7	47.2	8.79	2.59	6.92	1.01	5.28	0.97	2.65	0.38	2.17	0.35
	16.8	61	117.5	11.75	42.5	7.78	2.38	6.46	0.93	4.86	0.91	2.44	0.34	2.17	0.29
	17.6	57.3	110	11.4	42.2	7.7	2.34	6.39	0.92	4.7	0.93	2.59	0.33	2.06	0.29
	18.4	60.4	115	11.9	41.6	7.76	2.37	6.15	0.86	4.69	0.89	2.4	0.33	1.98	0.31
	20	53.9	103.5	10.6	37.6	6.87	2.09	5.92	0.84	4.35	0.78	2.36	0.31	1.69	0.27
	20.8	57.7	110	11.3	40.4	7.27	2.12	6	0.83	4.44	0.86	2.26	0.36	1.81	0.29
	21.6	59.3	113	11.7	42.5	7.75	2.3	5.92	0.85	4.5	0.84	2.48	0.33	1.92	0.29
	23.2	54.9	104	10.55	37.4	6.61	2.09	5.43	0.8	4.14	0.78	2.19	0.29	1.79	0.28
	24.8	58.1	110	10.95	38.9	6.76	2.04	5.72	0.84	4.21	0.82	2.36	0.3	1.81	0.27
	25.6	48.2	90	9.35	32.2	6.07	1.8	4.49	0.69	3.58	0.65	1.89	0.25	1.59	0.23
	26.4	51.9	97.3	9.89	34.6	6.31	1.87	4.99	0.71	3.93	0.71	2	0.27	1.59	0.27
	27.2	54	101.5	10.15	35.2	6.32	1.9	5.27	0.73	3.77	0.76	2.13	0.27	1.6	0.28
	28	55.4	103.5	10.35	36.9	6.47	2.02	5.58	0.79	4.19	0.76	2.2	0.35	1.71	0.28
	28.8	52.2	98.3	9.8	34.8	6.24	1.93	5.07	0.71	3.82	0.69	2.16	0.28	1.62	0.25
	30.4	60.2	112	11.35	39.8	7.38	2.1	5.77	0.82	4.51	0.84	2.42	0.32	1.85	0.27
	32	60.4	112	11.2	39.7	7.12	2.18	5.78	0.85	4.37	0.81	2.26	0.33	1.76	0.3
	32.8	63.6	121	11.95	42.4	7.61	2.28	6	0.89	4.56	0.87	2.47	0.33	1.96	0.31
	33.6	65.4	121.5	12.05	41.9	7.52	2.37	6.14	0.88	4.67	0.85	2.4	0.33	2.02	0.29
	34.4	57.9	108.5	10.6	37.3	6.71	1.98	5.39	0.75	4.12	0.77	2.26	0.29	1.73	0.28
	35.2	59.3	99.4	11.5	40.1	7.02	2.24	5.49	0.84	4.77	0.86	2.55	0.39	2.08	0.31
	36	62.8	107	12.05	42	7.5	2.39	5.91	0.9	5.03	0.92	2.68	0.37	2.17	0.33
	36.8	69.5	117.5	13.35	46.8	8.25	2.69	6.47	0.97	5.38	1	2.95	0.39	2.36	0.35

(continued on next page)

Table 1 (continued)

`	Depth (cm)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (μg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (μg/g)	Yb (µg/g)	Lu (µg/g)
MB4	38.4	64.9	109.5	12.05	41.8	6.97	2.28	5.79	0.89	4.91	0.89	2.68	0.35	2.11	0.33
	39.2	63.2	106	12.25	43.4	7.69	2.44	5.94	0.91	5.17	0.93	2.79	0.37	2.19	0.32
	40	68.8	116	12.95	45.8	8.01	2.46	6.3	0.99	5.46	0.99	2.95	0.4	2.22	0.34
	41.6	69.8	118	13.35	47	8.3	2.63	6.44	0.99	5.42	1	2.79	0.42	2.42	0.34
MDC	42.4	65.6	111	12.75	44.4	7.82	2.47	5.86	0.92	5.04	0.93	2.67	0.38	2.29	0.33
IVIBO	0.0	30.2 46.3	02.8 81.3	0.29	20.2	4.96 6.1	1,54	3.73 488	0.59	3.22	0.58	1.79	0.25	1.42	0.2
	42	40.J 54 7	957	11 15	40	7.22	2.34	4.00 5.87	0.75	4.05	0.74	2.15	0.25	2.15	0.20
	6.6	57.2	101.5	11.7	41.7	7.65	2.46	5.96	0.88	5.13	0.93	2.71	0.39	2.2	0.31
	7.8	57.9	101.5	11.95	42	8.04	2.44	5.98	0.88	5.27	0.95	2.76	0.38	2.2	0.31
	9	61.7	108	12.5	44.9	8.07	2.64	6.78	0.99	5.48	1	2.96	0.41	2.33	0.34
	10.2	61.3	106.5	12.3	43.7	8.27	2.52	6.28	0.98	5.59	0.99	2.88	0.4	2.5	0.35
	11.4	60.2	103.5	11.95	42.6	7.7	2.53	6.34	0.94	5.26	0.96	2.71	0.39	2.33	0.33
	12.6	60.4	104	12.05	42.8	7.68	2.5	6.33	0.96	5.44	0.97	2.95	0.37	2.33	0.34
	15	62.6 60.0	109	12.25	43.6 13.8	7.76 8.03	2.5	6.22	0.95	5.27	0.98	2.74	0.37	2.31	0.33
	18.6	59.9	103.5	12.1	43.8	7.45	2.33	5.96	0.97	5.04	0.98	2.82	0.34	2.24	0.34
	21	58.4	101.5	11.3	41.2	7.3	2.24	5.93	0.9	5.04	0.93	2.67	0.35	2.13	0.32
	22.2	53.4	93.6	10.5	37	7.15	2.21	5.32	0.79	4.41	0.82	2.36	0.35	1.93	0.28
	23.4	49.5	86	9.44	33.6	5.9	1.91	5.01	0.74	4.01	0.75	2.17	0.31	1.82	0.26
	24	41.4	71.3	8.03	29.1	5.15	1.65	4.35	0.63	3.52	0.65	1.79	0.25	1.51	0.22
	24.6	39.2	67.4	7.48	27.2	4.96	1.54	4.06	0.6	3.3	0.6	1.79	0.24	1.41	0.21
	25.8	36.1	61.3	6.77	24.5	4.75	1.5	3.62	0.51	3	0.56	1.53	0.23	1.36	0.19
	26.4	37.9	65.2	7.25	26	4.66	1.51	3.85	0.56	3.16	0.58	1.67	0.22	1.37	0.2
	27	36	61.4	6.91	24.3	4.43	1.42	3.69	0.54	2.99	0.53	1.59	0.21	1.3	0.2
	28.2	32.3 28.2	22.0 47.6	0.20 5.37	22.2 10.1	4.11	1.25	3.29	0.49	2.73	0.5	1.48	0.18	1.21	0.18
	30.6	31.1	527	5.91	21.1	3.85	1.15	3.15	0.41	2.57	0.44	1.21	0.10	1 09	0.14
	31.8	34.7	58.2	6.35	22	3.99	1.26	3.32	0.5	2.75	0.51	1.48	0.19	1.13	0.16
	32.4	38.8	66.2	7.24	25.7	4.46	1.4	3.81	0.57	3.22	0.57	1.7	0.22	1.37	0.2
	33.6	35.1	60	6.52	23.6	4.06	1.34	3.44	0.5	2.8	0.51	1.5	0.22	1.23	0.18
	34.2	40.5	69.7	7.8	29.8	5.52	1.71	4.28	0.68	3.72	0.76	1.9	0.32	1.47	0.29
	35.4	63.7	110.5	12.15	46.6	8.49	2.66	6.94	1.02	5.35	1.09	2.85	0.45	2.24	0.38
	36	65.6	113	12.6	48.6	8.63	2.84	7.02	1.04	5.49	1.11	2.84	0.42	2.37	0.37
DI	36.6	/2.5	12/	14.25	55 25 2	10.5	3.26	8.07	1.2	6.37	1.26	3.18	0.47	2.58	0.4
DI	0.5	40.7 58.4	05.Z 98.7	9.11	35.2 41.6	0.45 7.75	2.10	4.79	0.71	4.04	0.78	2.16	0.3	1.57	0.25
	2.5	68 1	114 5	12.45	47.7	9.16	2.55	7.02	0.00	5.42	1.04	2.10	0.39	2.11	0.32
	3	51.9	88.7	9.49	36.4	6.88	2.21	5.36	0.77	4.12	0.81	2.03	0.28	1.68	0.24
	3.5	55.7	107	11.5	40.8	7.42	2.53	6.01	0.89	4.33	0.86	2.19	0.33	1.81	0.24
	4.5	70	119	12.75	50.5	9.31	3.05	7.15	1.04	5.62	1.04	2.65	0.35	2.23	0.31
	5	75.1	127	13.6	52.8	9.44	3.23	8.01	1.14	5.96	1.14	2.98	0.48	2.35	0.36
	6	77.3	131	14.2	54.2	10.2	3.35	7.86	1.11	5.89	1.14	2.91	0.4	2.43	0.34
	6.5 7	76.2	128.5	13.9	52.4	9.59	3.14	/.8	1.12	5.79	1.13	2.91	0.41	2.29	0.34
	7	76.9 67.5	131	14.15	54.9 47.5	10.25 8.80	3.32	8.02 7.08	1.14	5.93	1.15	2.94	0.4	2.33	0.33
	85	73.2	123.5	13.15	50	9.42	3.02	7.00	1.05	5.44	1 06	2.47	0.34	2.10	0.25
	9.5	75.8	127.5	13.75	53	9.87	3.13	7.55	1.06	5.69	1.00	2.72	0.38	2.36	0.32
	10	67.9	115.5	12.4	47.4	8.94	2.86	7.09	1.01	5.34	1.04	2.69	0.36	2.07	0.32
	11	72.1	120.5	13	50.5	9.47	3.07	7.16	1.01	5.35	1.05	2.7	0.37	2.19	0.3
	12	67.4	114	12.25	47.6	8.85	2.98	7.02	1	5.23	1.02	2.46	0.36	2.21	0.3
	12.5	71.2	120.5	13	50.4	9.52	3.1	7.37	1.04	5.45	1.04	2.61	0.36	2.17	0.3
	13.5	/8./	132	14.1	55.5	10.4	3.38	8.11	1.12	5.93	1.14	2.88	0.38	2.3	0.32
	14.5	83.8 82.0	141	14.8	57.2 60.4	10.0	3.52	8.49	1.19	6.08	1.18	2.97	0.39	2.42	0.35
	16.5	83.9 79.6	145.5	14.2	54.6	10.35	3.70	9.04 7.9	1.27	6.09	1.24	2.15	0.42	2.50	0.30
	17.5	77.1	129.5	14	53.6	10.5	3.4	8.07	1.14	6.2	1.15	2.9	0.41	2.42	0.34
	18.5	79.7	134.5	14.65	56.7	10.7	3.55	8.63	1.16	6.28	1.19	2.96	0.4	2.56	0.34
	19.5	85.1	144	15.5	59.5	11.05	3.74	9.08	1.25	6.7	1.27	3.17	0.42	2.69	0.36
	20.5	82.6	141	15.15	59.2	11.05	3.68	8.72	1.24	6.56	1.24	3.1	0.42	2.55	0.34
Bedrocks	R-1	59.8	107.5	12.1	49.2	9.35	3.11	7.77	1.08	5.81	1.11	2.72	0.39	2.31	0.3
	R-2	61	108.5	12.5	50.1	9.47	3.1	7.87	1.06	5.79	1.13	2.85	0.39	2.27	0.31
	R-3	46.3	84	9.65	40.1	8.12	2.67	6.74	0.94	5.16	0.99	2.38	0.34	1.95	0.27
	K-4	127.5	204	21.8	/6.8	13.15	4.49	10.2	1.57	8.92	1.83	5.05	0.71	4.86	0.7
Fresh algae	K-5 CC-1	04.4 /1 0	97 97	11.05 8 Q/	44.5 33	6.75	2.96	1.25	0.69	3.05	0.76	2.57	0.35	2.11	0.5
r i con digac	((-2	24.6	463	4 98	18.2	3 32	1.07	2.43	0.32	1.87	0.76	1.04	0.51	0.98	0.12
	CC-3	17.9	34.8	3.91	14.3	2.78	0.88	2.12	0.29	1.8	0.31	0.95	0.16	0.88	0.12
	CC-4	25.5	50.1	5.57	21.1	4.27	1.31	3.21	0.45	2.78	0.52	1.44	0.23	1.14	0.14
	CC-5	25.8	50.3	5.68	21.2	4.34	1.27	3.17	0.42	2.9	0.54	1.57	0.25	1.32	0.15
Fresh guano	G-1	4.5	8.8	0.98	3.9	0.78	0.22	0.5	0.03	0.54	0.06	0.24	0.07	0.13	< 0.01
	G-2	7.2	14	1.58	6.1	1.04	0.26	0.98	0.11	0.93	0.16	0.49	0.05	0.18	<0.01
	G-3	3.3	6.4	0.66	2.5	0.46	0.12	0.32	<0.01	0.29	0.01	0.13	0.05	0.1	<0.01

		La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Hf (µg/g)
OREAS	Certified value	18.5~23.7	41.2~51.4	4.48~5.54	17.1~21.1	3.34~4.14	0.90~1.16	2.78~3.50	5.2~6.8
	Observed value	22.3	43.2	4.88	17.4	3.41	1	2.94	6.7
		23.4	49.1	5.43	20.5	4.08	1.11	3.48	6.2
		22.2	49.1	5.51	20.4	3.77	1.13	3.35	6.6
		20.4	46	4.7	17.3	3.44	0.94	2.82	6.2
STSD-1	Certified value	24.6~31.2	42.7~53.3	6.63~8.17	26.6~32.8	5.77~7.11	1.41~1.79	5.80~7.20	5.3~6.9
	Observed value	30.4	49.9	8.1	32.1	7	1.74	6.68	6.3
		25.1	44.7	6.96	28.4	6.33	1.6	5.84	5.6
		26.5	47.9	7.73	30.4	6.8	1.62	6.64	5.4
		26.4	47.8	7.24	30.4	7.09	1.58	6.47	6
SY-4	Certified value	51.7~64.3	109.5~134.5	13.45~16.55	51.2~62.8	11.40~14.00	1.77~2.23	12.55~15.45	9.3~11.9
	Observed value	62.9	120	14.6	57.6	13.7	2.22	14.25	10.9
TRHB	Certified value	411~503	962~1175	110.0~134.0	414~506	111.5~136.5	7.44~9.16	120.5~147.5	385~471
	Observed value	458	981	113	429	119.5	8.57	130	415
		Tb(µg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)	Zr (µg/g)
OREAS	Certified value	0.39~0.49	2.11~2.69	0.42~0.54	1.24~1.58	0.17~0.23	1.18~1.50	0.18~0.24	228~283
	Observed value	0.44	2.4	0.45	1.4	0.17	1.23	0.19	278
		0.47	2.79	0.53	1.6	0.23	1.35	0.18	272
		0.48	2.55	0.53	1.57	0.22	1.34	0.18	273
								0.0	200
		0.4	2.27	0.44	1.26	0.19	1.19	0.2	289
STSD-1	Certified value	0.4 0.89~1.11	2.27 5.36~6.66	0.44 1.12~1.40	1.26 3.51~4.35	0.19 0.49~0.62	1.19 3.25~4.03	0.2 0.49~0.62	289 221~275
STSD-1	Certified value Observed value	0.4 0.89~1.11 1.11	2.27 5.36~6.66 6.58	0.44 1.12~1.40 1.38	1.26 3.51~4.35 4.34	0.19 0.49~0.62 0.61	1.19 3.25~4.03 3.71	0.2 0.49~0.62 0.61	289 221~275 232
STSD-1	Certified value Observed value	0.4 0.89~1.11 1.11 0.9	2.27 5.36~6.66 6.58 5.54	0.44 1.12~1.40 1.38 1.18	1.26 3.51~4.35 4.34 3.53	0.19 0.49~0.62 0.61 0.49	1.19 3.25~4.03 3.71 3.37	0.2 0.49~0.62 0.61 0.49	289 221~275 232 247
STSD-1	Certified value Observed value	0.4 0.89~1.11 1.11 0.9 1.06	2.27 5.36~6.66 6.58 5.54 6.02	0.44 1.12~1.40 1.38 1.18 1.38	1.26 3.51~4.35 4.34 3.53 3.96	0.19 0.49~0.62 0.61 0.49 0.56	1.19 3.25~4.03 3.71 3.37 3.58	0.2 0.49~0.62 0.61 0.49 0.55	289 221~275 232 247 225
STSD-1	Certified value Observed value	0.4 0.89~1.11 1.11 0.9 1.06 1.01	2.27 5.36~6.66 6.58 5.54 6.02 5.91	0.44 1.12~1.40 1.38 1.18 1.38 1.17	1.26 3.51~4.35 4.34 3.53 3.96 3.75	0.19 0.49~0.62 0.61 0.49 0.56 0.52	1.19 3.25~4.03 3.71 3.37 3.58 3.31	0.2 0.49~0.62 0.61 0.49 0.55 0.57	289 221~275 232 247 225 270
STSD-1	Certified value Observed value Certified value	0.4 0.89~1.11 1.11 0.9 1.06 1.01 2.33~2.87	2.27 5.36~6.66 6.58 5.54 6.02 5.91 16.35~20.1	0.44 1.12~1.40 1.38 1.18 1.38 1.17 3.86~4.74	1.26 3.51-4.35 4.34 3.53 3.96 3.75 12.75~15.65	0.19 0.49~0.62 0.61 0.49 0.56 0.52 2.06~2.54	1.19 3.25-4.03 3.71 3.37 3.58 3.31 13.30~16.30	0.2 0.49~0.62 0.61 0.49 0.55 0.57 1.88~2.32	289 221~275 232 247 225 270 481~593
STSD-1 SY-4	Certified value Observed value Certified value Observed value	0.4 0.89~1.11 1.11 0.9 1.06 1.01 2.33~2.87 2.76	2.27 5.36~6.66 6.58 5.54 6.02 5.91 16.35~20.1 19.3	0.44 1.12~1.40 1.38 1.18 1.38 1.17 3.86~4.74 4.7	1.26 3.51~4.35 4.34 3.53 3.96 3.75 12.75~15.65 15.2	0.19 0.49~0.62 0.61 0.49 0.56 0.52 2.06~2.54 2.41	1.19 3.25~4.03 3.71 3.37 3.58 3.31 13.30~16.30 16.1	0.2 0.49~0.62 0.61 0.49 0.55 0.57 1.88~2.32 2.23	289 221~275 232 247 225 270 481~593 532
STSD-1 SY-4 TRHB	Certified value Observed value Certified value Observed value Certified value	0.4 0.89~1.11 1.11 0.9 1.06 1.01 2.33~2.87 2.76 27.0~33.0	2.27 5.36~6.66 6.58 5.54 6.02 5.91 16.35~20.1 19.3 173.0~211	0.44 1.12-1.40 1.38 1.18 1.38 1.17 3.86-4.74 4.7 38.7-47.3	1.26 3.51~4.35 4.34 3.53 3.96 3.75 12.75~15.65 15.2 129.0~157.5	0.19 0.49~0.62 0.61 0.49 0.56 0.52 2.06~2.54 2.41 19.70~24.1	1.19 3.25~4.03 3.71 3.37 3.58 3.31 13.30~16.30 16.1 121.5~148.5	0.2 0.49~0.62 0.61 0.49 0.55 0.57 1.88~2.32 2.23 16.8~20.50	289 221~275 232 247 225 270 481~593 532 >10000~14200
STSD-1 SY-4 TRHB	Certified value Observed value Certified value Observed value Certified value Observed value	0.4 0.89~1.11 1.11 0.9 1.06 1.01 2.33~2.87 2.76 27.0~33.0 27.3	2.27 536-6.66 6.58 5.54 6.02 5.91 16.35-20.1 19.3 173.0-211 189.5	0.44 1.12-1.40 1.38 1.18 1.38 1.17 3.86-4.74 4.7 38.7-47.3 44.6	1.26 3.51~4.35 4.34 3.53 3.96 3.75 12.75~15.65 15.2 129.0~157.5 137	0.19 0.49~0.62 0.61 0.49 0.56 0.52 2.06~2.54 2.41 19.70~24.1 21	1.19 3.25~4.03 3.71 3.37 3.58 3.31 13.30~16.30 16.1 121.5~148.5 135	0.2 0.49-0.62 0.61 0.49 0.55 0.57 1.88-2.32 2.23 16.8-20.50 17.35	289 221~275 232 247 225 270 481~593 532 >10000~14200 >10000

 Table 2

 Analytical accuracy and precision for SRMs of REEs.

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References

- C. Brauer, C. Endres, T. Günter, M. Litt, J.F.W. Stebich, Negendank, High resolution sediment and vegetation responses to Younger Dryas climate change in varved lake sediments from Meerfelder Maar, Germany, Quat. Sci. Rev. 18 (1999) 321–329.
- [2] J.P. Smol, B.F. Cumming, Tracking long-term changes in climate using algal indicators in lake sediments, J. Phycol. 36 (2000) 986–1011.
- [3] S.N. Luoma, D.J.H. Phillips, Distribution, variability, and impacts of trace elements in San Francisco Bay, Mar. Pollut. Bull. 19 (1988) 413–425.
- [4] L.G. Sun, Z.Q. Xie, J.L. Zhao, Palaeoecology: A 3,000-year record of penguin populations, Nature 407 (2000) 858.
- [5] M. Chatterjee, E.V. Silva Filho, S.K. Sarkar, S.M. Sella, A. Bhattacharya, K.K. Satpathy, M.V.R. Prasad, S. Chakraborty, B.D. Bhattacharya, Distribution and possible source of trace elements in the sediment cores of a tropical macrotidal estuary and their ecotoxicological significance, Environ. Int. 33 (2007) 346–356.
- [6] L.G. Sun, S.D. Emslie, T. Huang, J.M. Blais, Z.Q. Xie, X.D. Liu, X.B. Yin, Y.H. Wang, W. Huang, D.A. Hodgson, Vertebrate records in polar sediments: biological responses to past climate change and human activities, Earth Sci. Rev. 126 (2013) 147–155.
- [7] A.J. Fleet, Aqueous and sedimentary geochemistry of the rare earth elements, Geochem. Rare Earth Elem. (1984) 343–369.
- [8] P. Henderson, General geochemical properties and abundances of the rare earth elements, Geochem. Rare Earth Elem. 2 (1984) 1–32.
- [9] S.Y. Yang, H.S. Jung, M.S. Choi, C.X. Li, The rare earth element compositions of the Changjiang (Yangtze) and Huanghe (Yellow) river sediments. Earth Planet. Sci. Lett. 201 (2002) 407–419.
- [10] D.Z. Piper, R.B. Perkins, H.D. Rowe, Rare-earth elements in the Permian Phosphoria Formation: paleo proxies of ocean geochemistry, Deep-Sea Res. II Top. Stud. Oceanogr. 54 (2007) 1396–1413.
- [11] G. Tyler, Rare earth elements in soil and plant systems—A review, Plant Soil 267 (2004) 191–206.
- [12] I.R. Santos, D.I.T. Fávaro, C.E.G.R. Schaefer, E.V. Silva-Filho, Sediment geochemistry in coastal maritime Antarctica (Admiralty Bay, King George Island): evidence from rare earths and other elements, Mar. Chem. 107 (2007) 464–474.
- [13] G.D. Kamenov, M. Brenner, J.L. Tucker, Anthropogenic versus natural control on trace element and Sr-Nd-Pb isotope stratigraphy in peat sediments of southeast Florida (USA), 1500AD to present, Geochim. Cosmochim. Acta 73 (2009) 3549–3567.
- [14] X.D. Liu, L.G. Sun, D. Li, Y.H. Wang, Rare earth elements in the ornithogenic sediments from the Maritime Antarctic: a potential new palaeoecology proxy, Geochem. J. 45 (2011) 15.

- [15] E. Domack, A. Leventer, A. Burnett, R. Bindschadler, P. Convey, M. Kirby, Antarctic Peninsula climate variability: historical and paleoenvironmental perspectives, 79, American Geophysical Union, 2003.
- [16] Y.I. Lee, H.S. Lim, H.I. Yoon, Geochemistry of soils of King George Island, South Shetland Islands, West Antarctica: implications for pedogenesis in cold polar regions, Geochim. Cosmochim. Acta 68 (2004) 4319–4333.
- [17] S.S. Sun, G.N. Hanson, Origin of Ross Island basanitoids and limitations upon the heterogeneity of mantle sources for alkali basalts and nephelinites, Contrib. Mineral. Petrol. 52 (1975) 77–106.
- [18] S.S. Sun, G.N. Hanson, Rare earth element evidence for differentiation of McMurdo volcanics, Ross Island, Antarctica, Contrib. Mineral. Petrol. 54 (1976) 139–155.
- [19] M. Setti, L. Marinoni, A. López-Galindo, Mineralogical and geochemical characteristics (major, minor, trace elements and REE) of detrital and authigenic clay minerals in a Cenozoic sequence from Ross Sea, Antarctica, Clay Miner. 39 (2004) 405–421.
- [20] E.H. de Carlo, W.J. Green, Rare earth elements in the water column of Lake Vanda, McMurdo Dry Valleys, Antarctica, Geochim. Cosmochim. Acta 66 (2002) 1323–1333.
- [21] I.B. Campbell, G.G.C. Claridge, A classification of frigic soils-the zonal soils of the Antarctic continent, Soil Sci. 107 (1969) 75–85.
- [22] T. Huang, L.G. Sun, Y.H. Wang, X.D. Liu, R.B. Zhu, Penguin population dynamics for the past 8500 years at Gardner Island, Vestfold Hills, Antarct. Sci. 21 (2009) 571.
- [23] T. Huang, L.G. Sun, Y.H. Wang, D.M. Kong, Late Holocene Adélie penguin population dynamics at Zolotov Island, Vestfold Hills, Antarctica, J. Paleolimnol. 45 (2011) 273–285.
- [24] Q.H. Hu, L.G. Sun, Z.Q. Xie, S.D. Emslie, X.D. Liu, Increase in penguin populations during the Little Ice Age in the Ross Sea, Antarctica, Scientific reports, 32013.
- [25] X.D. Liu, Y.G. Nie, L.G. Sun, S.D. Emslie, Eco-environmental implications of elemental and carbon isotope distributions in ornithogenic sediments from the Ross Sea region, Antarctica, Geochim. Cosmochim. Acta 117 (2013) 99–114.
- [26] Y.G. Nie, X.D. Liu, T. Wen, L.G. Sun, S.D. Emslie, Environmental implication of nitrogen isotopic composition in ornithogenic sediments from the Ross Sea region, East Antarctica: Δ¹⁵N as a new proxy for avian influence, Chem. Geol. 363 (2013) 91–100.
- [27] D.G. Ainley, The Adélie penguin: bellwether of climate change, Columbia University Press, 2002.
- [28] S.D. Emslie, P.A. Berkman, D.G. Ainley, L. Coats, M. Polito, Late-Holocene initiation of ice-free ecosystems in the southern Ross Sea, Antarctica, Mar. Ecol. Prog. Ser. 262 (2003) 19–25.
- [29] S.D. Emslie, W.P. Patterson, Abrupt recent shift in δ13C and δ15N values in Adélie penguin eggshell in Antarctica, Proc. Natl. Acad. Sci. 104 (2007) 11666–11669.
- [30] Y.G. Nie, X.D. Liu, L.G. Sun, S.D. Emslie, Effect of penguin and seal excrement on mercury distribution in sediments from the Ross Sea region, East Antarctica, Sci. Total Environ. 433 (2012) 132–140.
- [31] L.A. Haskin, T.R. Wildeman, F.A. Frey, K.A. Collins, C.R. Keedy, M.A. Haskin, Rare earths in sediments, J. Geophys. Res. 71 (1966) 6091–6105.
- [32] M. Ravichandran, Distribution of rare earth elements in sediment cores of Sabine– Neches Estuary, Mar. Pollut. Bull. 32 (1996) 719–726.

- [33] W.T. Holser, Evaluation of the application of rare-earth elements to paleoceanography, Palaeogeogr. Palaeoclimatol. Palaeoecol. 132 (1997) 309–323.
- [34] A.G. Herrmann, Yttium and Lanthanides, in: K.H. Wedepohl, C.W. Correns (Eds.), Handbook of geochemistry, Sringer, Berlin-Heidelberg-New York, 1971.
- [35] P. Groment, L.T. Silver, REE variations across the Peninsular Ranges batholith: implications for batholithic petrogenesis and crustal growth in magmatic arcs, J. Petrol. 28 (1987) 75–125.
- [36] B.L. Martín-Puertas, M.P. Valero-Garcés, A. Mata, S. Moreno, F. Giralt, F. Martínez-Ruiz, Jiménez-Espejo, Geochemical processes in a Mediterranean Lake: a high-resolution study of the last 4,000years in Zoñar Lake, southern Spain, J. Paleolimnol. 46 (2011) 405–421.
- [37] J.M. McArthur, J.N. Walsh, Rare-earth geochemistry of phosphorites, Chem. Geol. 47 (1984) 191–220.
- [38] D.S. Alibo, Y. Nozaki, Rare earth elements in seawater: particle association, shale-normalization, and Ce oxidation, Geochim. Cosmochim. Acta 63 (1999) 363-372.
- [39] D.W. Mittlefehldt, M.M. Lindstrom, Generation of abnormal trace element abundances in Antarctic eucrites by weathering processes, Geochim. Cosmochim. Acta 55 (1991) 77–87.

- [40] T.W. Speir, J.C. Cowling, Ornithogenic soils of the cape bird adelie penguin rookeries, Antarctica, Polar Biol. 2 (1984) 199–205.
- [41] LQ, Xu, X.D. Liu, L.G. Sun, H. Yan, Y. Liu, Y.H. Luo, J. Huang, Geochemical evidence for the development of coral island ecosystem in the Xisha Archipelago of South China Sea from four ornithogenic sediment profiles, Chem. Geol. 286 (2011) 135–145.
- [42] W.B. Emison, Feeding preferences of the Adelie penguin at Cape Crozier, Ross Island, Antarct. Res. Ser. 12 (1968) 191–212.
- [43] G. Soszka, M.M. Suplinska, A. Baranski, D. Grzybowska, A. Pietruszewski, Trace metals, fluorine and radionuclides in Antarctic krill Euphausia superba Dana, Polish Polar Res. 2 (1981) 109–117.
- [44] Q.Q. Chen, X.D. Liu, Y.G. Nie, L.G. Sun, Feasibility of using Visible Reflectance Spectroscopy (VRS) to reconstruct historical change of chlorophyll a concentration in East Antarctic lakes, Polar Res. (2013), http://dx.doi.org/10.3402/polar.v32i0.19932.
- [45] J.E. Barrett, R.A. Virginia, D.W. Hopkins, J. Aislabie, R. Bargagli, J.G. Bockheim, I.B. Campbell, W.B. Lyons, D.L. Moorhead, J.N. Nkem, Terrestrial ecosystem processes of Victoria Land, Antarctica, Soil Biol. Biochem. 38 (2006) 3019–3034.
- [46] X.D. Liu, L.G. Sun, Z.Q. Xie, X.B. Yin, R.B. Zhu, Y.H. Wang, A preliminary record of the historical seabird population in the Larsemann Hills, East Antarctica, from geochemical analyses of Mochou Lake sediments, Boreas 36 (2007) 182–197.