Microchemical Journal 114 (2014) 247–260

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

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

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ARTICLE INFO

Article history:
Received 10 January 2014
Accepted 15 January 2014
Available online 24 January 2014

Keywords:
Rare earth elements
Geochemical behavior
Ornithogenic sediments
Ross Sea region
Adélie penguin

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 ΣREE–lithological elements and ΣREE–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 with depth in the sediments. An end-member equation was developed to calculate the proportion 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 paleoecological 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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0026-265X/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.microc.2014.01.010

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 (~2460km^2) 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 (~18km^2), Cape Bird (~15km^2), and Cape Royds (~13km^2). A large number of Adélie penguins (>155,000 pairs, [27]) reside in these areas. Beaufort Island (~18.4km^2) 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 air-dried (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 HNO_3–HF–HCl–$HClO_4$, 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 HNO_3–HCl–$HClO_4$ (As and Se) and H_2O_2–Fe^{3+}oxidant-HNO_3 (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 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 ΣREE in each profile was conducted using the software Matlab 7.1.

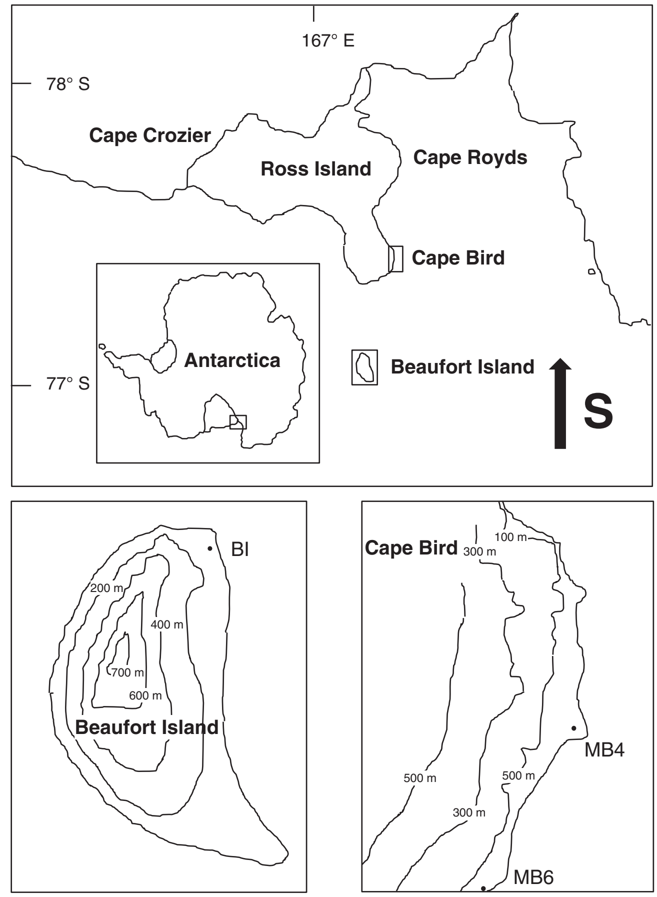

Fig. 1. Sampling sites of the sediment profiles in the Ross Sea region (Ross Island and Beaufort Island).

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

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